Solid Phase Extraction Containing Multi-walled Carbon Nanotubes and Eggshell Membrane as Adsorbent for ICP-OES Determination of Pb(II) and Cd(II) in Various Water and Orange Fruit (Peel and Pulp) Samples

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INTRODUCTION

Transition and non-transition elements with a density of at least five times that of water and a high atomic weight, such as cadmium (Cd) and lead (Pb), are considered heavy metals which are also very toxic to the human body and cause environmental pollutants (1). Therefore, the accurate determination of heavy metals at trace levels in foods and water is very important. Solid phase extraction (SPE) techniques have been used to overcome the problems of determining elements at low levels because it increases the sensitivity and selectivity of the techniques such as ICP-OES, AAS, etc. For SPE, the use of nano-sized sorbents has been proposed to extract the elements onto large surface areas (2-4). In addition, carbon nano-sized materials, such as carbon nanotubes (CNTs), graphene oxide, etc., have been used in SPE but these materials are very expensive (5-9).

For this reason, a novel biopolymer has been investigated, such as eggshell membrane, either alone or mixed with nano-materials (10-12). Some researchers used chelating agents to increase the extraction of the metal ions after formation of a macro-compound (as complex with the chelating agent) (13, 14).

ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) functionalized with soluble eggshell membrane protein (SEP) bio-polymer were prepared as a novel adsorbent for solid phase extraction and ICP-OES determination of Pb(II) and Cd(II). This material was characterized by FTIR, TG-DTA, DSC, and XRD. Also, a new dithiocarbamate chelating agent derived from barbituric acid was prepared and characterized by FTIR, ¹HNMR, and elemental analysis. Various factors influencing the preconcentration of lead and cadmium ions such as pH, sample and eluent flow rates, concentration and type of eluents, sample volume, chelating agent concentration and interfering ions were investigated. The accuracy of the method was confirmed with the standard addition method. The limits of detection (LODs) for this method were found to be 0.10 µg L⁻¹ and 0.073 µg L⁻¹ for Pb(II) and Cd(II), respectively. The relative standard deviation (RSD) was 1.2% for lead and 1.0% for cadmium, with a preconcentration factor of 25. The optimized method was applied to various water and orange fruit (peel and pulp) samples.

In the present research, multi-walled carbon nanotubes (MWCNTs) were oxidized in order to add many functional groups (carboxyl groups) onto the surfaces which then easily react with the protein derived from the soluble eggshell

membrane protein (SEP). Barbituric acid (Bis-sodium barbituric acid dithiocarbamate) (BADTC) was used as the chelating agent to enhance the extraction of cadmium and lead. An optimized method was applied to five water and 10 orange fruit (five peel and five pulp) samples for the ICP-OES determination of cadmium and lead.

EXPERIMENTAL

Instrumentation

The infra-red spectra were recorded with an FTIR-8400S spectrophotometer within the range of 400-4000 cm⁻¹, and the X-ray diffraction measurements by using an XR - 6000 device with a nickel-copper filter for X-ray radiation (Cu Kα, λ = 1.5406 Å) (Shimadzu, Japan). The lead and cadmium ions were determined using the iCAPTM 7000 Series ICP-OES (Thermo Scientific, UK). Thermogravimetric analysis (TG/DTA) was performed using the a PYRIS Diamond TG/DTA apparatus (PerkinElmer, Inc., Shelton, CT, USA), and for differential scanning calorimetry the DSC 131 instrument (Setaram Instrumentation, France) was used.

Reagents and Solutions

The Pb(II) and Cd(II) standard stock solutions (1000 mg/L) were obtained from Sigma-Aldrich Company, USA. Deionized water was used for solution preparation using the Milli-Q[®] system, 18.2 MΩ·cm⁻¹ conductivity (Millipore Corporation, USA). Buffer solutions of

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$\text{KH}_2\text{PO}_4\text{-NaOH}$ (pH 3–8), $\text{NH}_4\text{Cl-NH}_3$ (pH 9–11), and $0.02 \text{ mol L}^{-1} \text{ HNO}_3$ were used for maintaining the pH at less than 3 (Alfa-Aesar, USA). Sulfuric acid, thioglycolic acid, and nitric acid were purchased from (HI-MEDIA, USA). The multi-walled carbon nanotubes (MWCNTs, O.D. $\times$ L 7–15 nm $\times$ 0.5–10 μm) were purchased from Sigma-Aldrich, USA.

Bis-sodium Barbituric Acid Dithiocarbamate (BADTC)

To a solution of barbituric acid (0.8 g, 6 mmol) in 20 mL of DMSO, CS_2 (0.48 g, 6 mmol) was added in the presence of NaOH (0.25 g, 6 mmol). The reaction was maintained at 0–3 °C using a water-ice bath. This mixture was continuously stirred for 3 hours. The obtained pink precipitate was then filtered and washed with benzene. The product was dried in a vacuum oven at 100 °C, m.p. >320. The analytical calculation for $\text{C}_6\text{H}_2\text{N}_2\text{Na}_2\text{O}_3\text{S}_4$ (%): C, 22.22; H, 0.62; N, 8.64; was found at C, 22.32; H, 0.66; N, 8.75, yield 93%. FTIR (KBr): 2922w, 2819w, 1685vs, 1630vs, 1500s, 1412m, 1356m, 911m, 1097m cm^{-1} , $^1\text{H-NMR}(\delta^6\text{-dmsO})$: (δ , 3.25 ppm, 2H).

Synthesis of Soluble Eggshell Membrane Protein (SEP)

Eggshells (250 g) were washed several times with deionized water to remove the albumin. Then they were immersed in 500 mL of 2% acetic acid at 25 °C for 1 hour in order to release the eggshell membrane (ESM). This membrane was washed with deionized water to remove excess acetic acid, dried at 80 °C for 6 hours, and ground. Then, 10 g of ESM powder was immersed in 150 mL of 1.2 N of thioglycolic acid and 10% acetic acid aqueous solution, sonicated for 1 hour at 25 °C to form a suspension, and refluxed for approximately 30 hours until the ESM completely dissolved (11, 15, 16).

Preparation of MWCNTs-SEP Nano-sorbent

The MWCNTs were first oxidized by refluxing 1 g of MWCNTs in 3:1 $\text{H}_2\text{SO}_4\text{:HNO}_3$ at 75 °C for 5 hours (13, 14). The mixture was centrifuged at 8000 rpm and the supernatant dried, then the SEP solution was added to the filtered oxidized MWCNTs powder, sonicated for 2 hours, and refluxed for 8 hours at 80 °C. The greyish powder was filtered, washed with water and ethanol, then dried for 24 hours at 80 °C.

Preparation of Column

An amount of 0.3 g of the prepared nano-material (MWCNTs-SEP) was packed into a glass column (10 $\times$ 100 mm) and both the upper and lower ends were closed with glass wool. The column was connected to a pump with tubing which formed the preconcentration system. A 2 mol L^{-1} amount of HNO_3 aqueous solution and 10 mL of deionized water were passed through the column to clean it, then it was conditioned to the required pH with buffer solution.

Preconcentration Procedure

Amounts of 40–50 mL model solutions containing Pb(II) and Cd(II) ions were buffered to pH 7 with borate buffer solution. Then $3.2 \cdot 10^{-3} \text{ mol L}^{-1}$ BADTC ligand solution was added for metal-chelate formation and passed through the MWCNTs-SEP column at the 5 mL/min flow rate. Control of the flow rate of the sample into the extraction column was performed by gravity. The adsorbed analyte ions were eluted using 2 mol L^{-1} HNO_3 and the eluent solution containing the Pb(II) and Cd(II) ions was analyzed by ICP-OES.

Application to Orange (Peel, Pulp) and Water Samples

The nano-sorbent-containing column was utilized for the precon-

centration and determination of lead and cadmium in 10 orange (peel or pulp) and five water samples (well water, wastewater, tap water, drinking water, and river water) obtained from Kirkuk city, Iraq. The whole orange was washed with deionized water. The orange peel and pulp were separated, and dried in an oven at 100 °C for 48 hours, then crushed, and 1 g of each orange fruit part (peel or pulp) was acidified with HNO_3 (65%) and heated at 120 °C under constant stirring for 4 hours. Then the residue was placed into an automatic shaker for 1 hour, filtered, and diluted up to 50 mL of 1% HNO_3 aqueous solution.

Different water samples were filtered in Fisherbrand™ Grade 601 filter paper. Then 100 mL of these solutions was used for ICP-OES determination of total Pb(II) and Cd(II) concentration using the optimum conditions described earlier.

Characterization of Prepared Materials

FTIR Analysis

The FTIR spectrum of MWCNT-COOH is shown in the bands at 3749 cm^{-1} , 3477 cm^{-1} , 1754 cm^{-1} , 1649 cm^{-1} , and 1510 cm^{-1} . These bands represent the free hydroxyl group, the OH stretching vibration of the carboxylic group, stretching vibration of C=O in the carboxyl group, as well as the bending vibrations of the water and carboxylate anion, respectively (17–20).

The FTIR spectrum of SEP is shown with 9 main bands (3292, 3072, 1658, 1546, and 1396 cm^{-1}). These bands can be attributed to the stretching vibration of NH, C-H of the aromatic ring, amide (I), amide (II), and C-N, respectively. The other peaks at 2962 and 2931 cm^{-1} are due to the stretching vibration of aliphatic C-H, while the two bands at 2634 and 2546 cm^{-1} are attributed to the thiol groups that

formed after the dissolving process with thioglycolic acid (16, 21).

The FTIR spectrum of MWCNTs-SEP shows all characteristic bands of the MWCNTs and SEP, but shifting of the carbonyl group of MWCNTs-COOH from 1745 cm^{-1} towards the lower wavenumber of 1713 cm^{-1} of MWCNTs-SEP. In addition, the disappearance of the NH band at 3292 cm^{-1} of SEP and the OH band at 3477 cm^{-1} of MWCNTs results in the reaction of MWCNTs with SEP from the carboxyl of MWCNT and the amine of the amide group in SEP.

TGA/DTA and DSC Analyses

TG was used to determine the amount of SEP reacting with the MWCNTs by comparing the mass loss found between the MWCNTs and the MWCNTs-SEP during heating (see Figure 1). After functionalization of the SEP, mass loss started at 80°C , which can be attributed to 3.5% of water evaporation. Continuing heating from 120 to 440°C resulted in a 74.0% decomposition of the SEP. The degree of gradual mass loss of the MWCNTs-SEP was expected to be around 74.0%. While the MWCNTs show a single-step decomposition at -637°C and totally oxidize around 700°C (22), therefore the MWCNTs quantity did not exceed 22.5%.

The DSC thermogram for the MWCNTs-SEP showed three main peaks: 168.6°C , 218.7°C , and 433.0°C (Figure 2). The peak observed at 218.7°C was much larger than at the other temperatures. This broad peak due to the heat flow required denaturing of the amino acids in the SEP.

XRD Analyses

The eggshell membrane protein is amorphous material and, therefore, no peak could be detected by XRD analysis. The peaks that appeared are attributed to calcium impurities in the egg shell.

Fig. 1. TG/DTA thermogram of MWCNTs-SEP.

Fig. 2. DSC thermogram of MWCNTs-SEP.

MWCNT-COOH shows two characteristic broad peaks at $2\theta = 26.10$ and $2\theta = 430$ (23). After reaction with the SEP, the first peak shifted towards lower values at $2\theta = 25.890$, while the second peak shifted to higher values at $2\theta = 44.250$ (Figure 3). This indicates that MWCNT-COOH was successfully grafted onto the SEP. The XRD pattern of the MWCNTs-SEP was used to calculate the crystalline size estimated by the Debye-Scherrer equation:

$$d = K \lambda / \beta \cos \theta$$

where λ is the X-ray wavelength (0.1540 nm), K is a constant related

to the crystallite shape mostly equal to 0.9, β is the peak width of the diffraction peak shape at half the maximum height FWHM resulting from the small crystallite size in the radians.

From the Debye-Scherrer equation for the four characteristic peaks of MWCNTs-SEP listed in Table I, the average crystalline size was found to be 26.72 nm . This increase in the size of the MWCNTs from approximately 10 to 26.72 nm proves that MWCNTs have successfully grafted with SEP.

RESULTS AND DISCUSSION

Effect of pH

The quantitative recoveries of Pb(II) and Cd(II) in the SPE process depend on many conditions, the most important being the pH (24, 25). Therefore, the effect of pH ranging from 2 to 11 on the SPE of Pb(II) and Cd(II) using the new sorbent was examined (see Figure 4). Quantitative recovery for Pb(II) was 98% and 96% for Cd(II). Thus, for all subsequent experiments, pH 7 was carried out with borate buffer solution.

Effect of Flow Rates

Sample and eluent flow rates are very important for the quantitative recovery of analytes and were examined in the range of 0.5–5.0 mL/min from the MWCNTs-SEP column. The optimal sample and eluent flow rates for both Cd(II) and Pb(II) were found to be 5 mL/min. The quantitative recoveries based on the eluent flow rates were 96% for Pb(II) and 95% for Cd(II), but the recoveries with the sample flow rates were 97% for Pb(II) and 98% for Cd(II).

Effect of Different Eluents and Their Concentrations

Desorption of Pb(II) and Cd(II) from the MWCNTs-SEP column was studied using three different types of eluent solutions: HNO₃, HCl, and HNO₃ in acetone. The highest recovery of the analyte ions was found with 2 mol L⁻¹ HNO₃ for Cd(II) and Pb(II). The volume of the eluent solution is also very important for obtaining a high pre-concentration factor. For this study, the minimum eluent concentration was found with 4 mL 2 mol L⁻¹ HNO₃ for both Cd(II) and Pb(II).

Effect of Sample Volume

Since sample volume affects the recovery of Pb(II) and Cd(II), this parameter was examined in the range of 5–100 mL with flow rates at 5 mL/min. The optimal sample volume was recorded to be 100 mL for both Cd(II) and Pb(II) and was selected for further work. The recorded quantitative recoveries were 95% for Pb(II) and 96% for Cd(II). The preconcentration factor, defined as the ratio of the highest sample volume (100 mL) to minimum eluent volume (4 mL 2 mol L⁻¹ HNO₃) was calculated as 25.

Effect of Chelating Agent Concentration

BADTC was used as the chelating agent for optimization of the SPE process of Pb(II) and Cd(II).

Fig. 3. XRD of (a) ESM and (b) MWCNTs-SEP in the 2θ range of 10–80 degrees.

Fig. 4. Effect of pH on the recovery of analytes (N=3).

TABLE I
XRD Debye-Scherrer Equation for the Four Characteristic Peaks of MWCNTs-SEP

Peak Position 2θ (deg.)	FWHM (deg.)	Dp (nm)
25.8994	2.72	3.13
19.3149	0.86	9.79
44.2512	1.08	8.30
28.7550	0.10	85.72

This chelating agent plays a main role in the extraction and recovery of the studied analyte ions and is due to the presence of many functional groups which are able to coordinate with the lead and cadmium ions. BADTC ($0-0.008 \text{ mol L}^{-1}$) was added to a model solution containing Pb(II) and Cd(II) for metal-chelate formation, then passed through the column. The results show that quantitative recoveries were obtained with $3.2 \times 10^{-3} \text{ mol L}^{-1}$ BADTC for both Pb(II) and Cd(II).

Effect of Interfering Ions

This parameter was examined by adding different concentrations of interfering ions because it may decrease or increase the recovery of Pb(II) or Cd(II). The results show that the maximum tolerance of the studied cations and anions cause a relative error of not more than 5% (see Table II). The tolerance limits of the matrix ions were very high, which shows that the present method can be applied to high saline and complex matrix media.

Analytical Figures of Merit

The limit of detection (LOD) of the present MWCNTs-SEP column

Table II
Effect of Interfering Ions (N=3)

Ion	Conc. (mg L^{-1})	Recovery%	
		Cd(II)	Pb(II)
Na^+	10,000	96 ± 1	97 ± 1
K^+	13,000	96 ± 2	98 ± 3
Cl^-	20,000	97 ± 1	98 ± 1
Mg^{2+}	5000	96 ± 4	96 ± 1
Cu^{2+}	20	98 ± 3	68 ± 3
Ni^{2+}	25	98 ± 3	96 ± 2
Co^{2+}	20	97 ± 2	96 ± 3
CO_3^{2-}	4500	98 ± 1	98 ± 1
Fe^{3+}	40	96 ± 4	98 ± 2
NO_3^-	4500	95 ± 2	98 ± 3
SO_4^{2-}	4500	98 ± 3	97 ± 1
PO_4^{3-}	4500	96 ± 1	96 ± 3
Zn^{2+}	20	98 ± 3	95 ± 2
Ca^{2+}	5000	99 ± 4	96 ± 3

for the SPE process of Pb(II) and Cd(II) was performed under the optimal conditions after application of the procedure to a blank solution. Based on three times the standard deviation of 10 runs of the reagent blank solution, the LODs were found to be $0.10 \text{ } \mu\text{g L}^{-1}$ and $0.073 \text{ } \mu\text{g L}^{-1}$ for Pb(II) and Cd(II), respectively. The relative standard deviation (RSD %) of this study was 1.2% for Pb(II) and 1.0% for Cd(II), and the preconcentration factor was 25. The accuracy of the present SPE method was confirmed with the standard addition method.

Application to Various Water and Orange Fruit (Peel and Pulp) Samples

The present MWCNTs-SEP column/SPE method was applied to various water samples by using the standard addition method (see Table III). Quantitative recovery values were found in the samples for Pb(II) and Cd(II). The MWCNTs-

SEP column using the SPE method was also applied to 10 orange fruits (five peel and five pulp) samples. The results in Table IV show that the MWCNTs-SEP sorbent can be used as an effective solid phase extraction (SPE) method.

CONCLUSION

In this work, a new nano-sorbent was prepared from soluble eggshell membrane (ESM) on multiwalled carbon nanotubes (MWCNTs). This nano-sorbent is economical and eco-friendly and was used to extract and preconcentrate Pb(II) and Cd(II) for ICP-OES determination in orange fruit (peel or pulp) samples and five water samples. The advantages of this method include simplicity, sensitivity, and require no organic solvents. In addition, by using the newly prepared chelating agent (BADTC), the extraction process was enhanced because of the seven active sites

TABLE III
Determinations of Pb(II) and Cd(II) in Water Samples
After Application of Present Method (N=3)*

Sample	Added ($\mu\text{g L}^{-1}$)	Pb(II)		Added ($\mu\text{g L}^{-1}$)	Cd(II)	
		Found ($\mu\text{g L}^{-1}$)	Recovery (%)		Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Well Water	-	BDL		-	BDL	
	10	9.9 ± 2.3	99	1.0	0.98 ± 0.21	98
	50	49.5 ± 1.4	99	3.0	2.98 ± 0.21	99
Drinking Water	-	—	BDL	-	—	BDL
	20	10.1 ± 1.1	101	1.0	0.98 ± 0.06	98
	20	19.6 ± 2.1	98	3.0	3.04 ± 0.20	101
River Water	—	BDL		—	BDL	
	10	9.7 ± 3.2	97	5.0	4.99 ± 0.01	99
	20	19.8 ± 2.3	99	10	10.0 ± 0.1	100
Tap Water	—	BDL		—	BDL	
	10	10.1 ± 1.3	101	5.0	4.93 ± 1.01	98
	20	19.5 ± 2.0	97	10	9.72 ± 0.24	97
Wastewater	—	BDL		—	BDL	
	10	10.2 ± 3.0	102	5.0	5.01 ± 2.31	100
	20	19.7 ± 2.3	98	10	10.1 ± 0.40	101

*N=3, mean $\pm$ S.D, BDL: below the detection limit.

TABLE IV
Determinations of Pb(II) and Cd(II)
in Orange Fruit (Peel and Pulp) Samples

Sample	Added ($\mu\text{g L}^{-1}$)	Pb(II) Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Added ($\mu\text{g L}^{-1}$)	Cd(II) Found ($\mu\text{g L}^{-1}$)	Recovery (%)
AA	—	BDL		—	BDL	
	1.0	0.98±0.23	98	0.5	0.50±1.13	97
	2.0	1.95±0.31	97	1.0	1.01±1.01	101
aa	—	BDL		—	—	BDL
	1.0	0.99±0.11	99	0.5	0.48±0.31	96
	2.0	2.03±0.22	101	1.0	0.98±0.21	98
BB	—	BDL		—	—	BDL
	1.0	0.98±1.3	98	0.5	0.51±2.21	100
	2.0	1.98±2.03	99	1.0	1.00±0.41	100
bb	—	BDL		—	—	BDL
	1.0	0.96±2.2	96	0.5	0.48±0.21	96
	2.0	1.97±0.3	98	1.0	0.97±0.04	97
CC	—	BDL		—	BDL	
	1.0	0.99±0.41	99	0.5	0.50±1.01	100
	2.0	1.99±1.03	99	1.0	0.98±0.11	98
cc	—	BDL		—	BDL	
	1.0	0.96±1.1	96	0.5	0.49±0.05	98
	2.0	1.98±0.02	99	1.0	1.02±0.21	102
DD	—	BDL		—	BDL	
	1.0	1.01±2.03	102	0.5	0.48±0.04	96
	2.0	2.06±0.15	103	1.0	0.99±0.12	99
dd	—	BDL		—	BDL	
	1.0	1.01±1.03	101	0.5	0.50±2.3	100
	2.0	1.99±0.43	99	1.0	0.99±1.3	99
EE	—	BDL		—	BDL	
	1.0	0.97±2.02	97	0.5	0.48±0.41	96
	2.0	1.99±0.21	99	1.0	0.96±2.31	96
ee	—	BDL		—	BDL	
	1.0	1.00±2.03	100	0.5	0.50±0.15	100
	2.0	1.98±1.21	99	1.0	0.99±2.04	99

*N=3, Mean±SD, BDL: below the detection limit.

AA, BB, CC, DD, EE = Peel

aa, bb, cc, dd, ee = Pulp

available for coordination with the metal ions. The results show that MWCNTs-SEP is a very promising sorbent material for the determination of Pb(II) and Cd(II) in the presence of one of the dithiocarbamate ligands (BADTC). Table V provides a comparison of the present method with literature values and shows that the LOD and RSD values of the present method are lower.

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TABLE V
Comparative Data from Some Recent Studies
Using MWCNTs as Solid Phase Extractor

System	Technique	RSD(%)		LOD ($\mu\text{g L}^{-1}$)		Matrix	Ref.
		Pb	Cd	Pb	Cd		
GO-MCNTs-DETA	ICP-OES	3.0	—	0.24	—	Wastewater	26
MWCNTs/APDC	FAAS	—	>5	0.45	0.6	Food and Environmental	27
MWCNTs	ICP-AES	1.9	1.63	2.1	0.3	Skin	28
MWCNTs-BTAO	FAAS	—	5.0	2.6	0.7	Various Ffoods and Water	14
MWCNTs-Fe ₃ O ₄	ICP-AES	1.23	0.92	0.6	0.3	Water, Milk, Indian Rice, and Red Tea	29
MWCNTs-Tartrazine	FAAS	—	—	6.6	0.8	Food and Natural Water	31
[NMIIM]Br-CSs	FAAS	3.2	—	1.76	—	Waste and Sseawater, Spice, and Street Dust	31
MWCNTs-SEP	ICP- OES	1.2	1.0	0.10	0.073	Water and Oranges	This study

*GO: Graphene oxide; DETA: diethylenetriamine; APDC: Ammonium pyrrolidine dithiocarbamate; [NMIIM]Br-CSs: 1,8-naphthalene monoimide bearing imidazolium salt ([NMIIM]Br) and IL(ion liquid) coated carbon nano spheres.

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