



## Preparation and application of poly(2-amino thiophenol)/MWCNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction

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### ABSTRACT

A new method which utilizes a multiwalled carbon nanotubes/poly(2-amino thiophenol) nanocomposites as an effective sorbents in solid-phase extraction has been developed for separation and preconcentration of Cd(II) and Pb(II) trace levels in environmental samples. The method is based on the adsorption of heavy metals on macromolecular chains due to sharing an electron pair of =N– and –S– groups of conducting polymer with cadmium and lead ions. The results indicate the novel nanocomposite presents a high affinity for heavy metals due to the presence of several good extractive sites (S and N) which are introduced to the synthesized nanocomposite. Some parameters including sample condition such as: pH, flow rate, sample volume, and eluent condition such as: type, volume, and concentration: moreover adsorption capacity of matrix ions was investigated on the recovery of Cd(II) and Pb(II). The maximum adsorption capacity of MWCNTs/P2AT nanocomposite as sorbents at optimum conditions for cadmium and lead ions was found to be 178.7 mg g<sup>-1</sup> and 186.4 mg g<sup>-1</sup>, respectively. The detection limits of this method were 0.3 and 1 ng mL<sup>-1</sup> for Cd(II) and Pb(II), respectively. The validation of the presented procedure was checked by reference material analysis. Finally, the presented procedure was applied for determination of Cd(II) and Pb(II) in some environmental samples.

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### 1. Introduction

The selective extraction and determination of heavy metals especially some toxic metals is still an intensively active research area due to their biological mechanisms [1–3]. The traditional methods for noble metals purification were precipitation and complexation procedures which needed large amount of highly toxic acids and complexation agents; such as potassium or sodium cyanides that have negative impact on environment. Recently, different procedures such as: coprecipitation, liquid–liquid extraction (LLE), and solid phase extraction (SPE) have been developed for preconcentration and separation of heavy metals from natural matrices [4–7]. Among mentioned methods, the most commonly used technique is solid phase extraction for preconcentration of heavy metal ions from environmental samples due to its simplicity, rapidity, minimal cost, and low consumption of reagents [8,9].

The activated carbon has been used as an efficient sorbent with versatility and porous texture in SPE technique for metal ions from aqueous solution [10]. In order to obtain selective sorbents for metal ions, activated carbon is modified utilizing several ligand, e.g. dithiocarbamates, sulfur containing and pyrazolones [11–13]. In recent years, nanomaterials like: mesoporous solids, ion imprinted materials, C<sub>60</sub>–C<sub>70</sub>, and their derivatives have been extensively explored as new adsorbent in SPE technique [14–18].

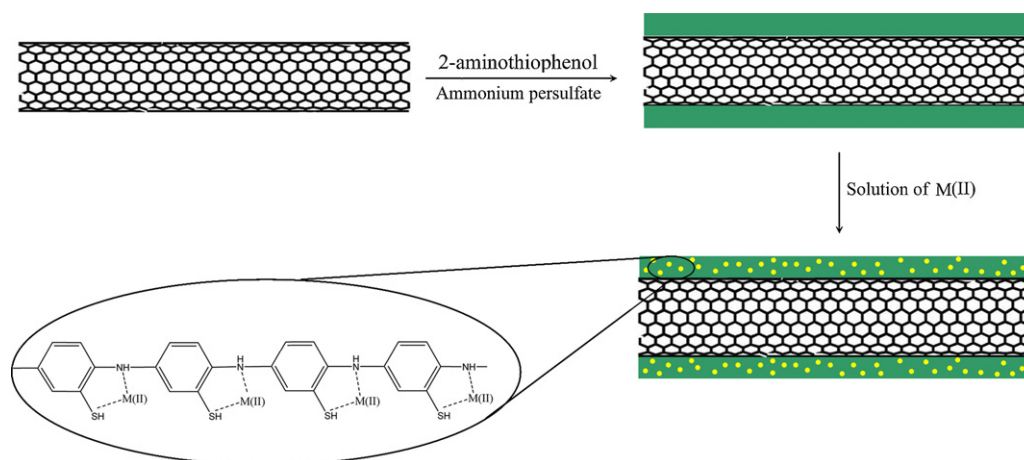
More recently, great attention has been paid to the application of carbon nanotubes (CNTs) in several fields of chemical analysis [19,20] because of their special electronic, metallic and structural properties. These nanotubes are classified into multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the number of layers in the wall of nanotubes. Many applications of MWCNTs for preconcentration of heavy metal ions, organometallic compounds and trace amount of organic materials have been reported [21–24]. However, according to our literature survey, no attempt has been conducted to employ modified MWCNTs using polymers for separation and preconcentration of heavy metals.

In this work modified MWCNTs using conducting poly(2-amino thiophenol) (MWCNTs/P2AT) nanocomposites were synthesized

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**Scheme 1.** The schematic structure of the MWCNTs/P2AT.

and used as a sorbent for separation and preconcentration of trace amounts of Cd and Pb ions in environmental samples prior to its determination by flame atomic absorption spectroscopy (FAAS). All of the factors affecting the preconcentration of heavy metals such as pH of sample, eluent and interfering ions, were studied and optimized. The developed method was validated by the analysis of the Pb and Cd metals in reference and real samples. The final results demonstrate that MWCNTs/P2AT nanocomposites are useful, convenient, and non-expensive materials as adsorbents for Cd and Pb ions, and they can be used for several times because of their recoverability. High capacity for adsorption and selectivity, and small LOD were found using polymeric nanocomposite as sorbent.

## 2. Experimental

### 2.1. Materials

The MWCNTs were synthesized by chemical vapor deposition (CVD) method, with outerwall diameter distribution close to 10–20 nm. MWCNTs were obtained from Research Institute of Petroleum Industry (Iran).

Other reagents were used with analytical grades. Stock solutions of Cu(II), Cd(II), Mn(II), Ni(II), Cr(III), Al(III), Fe(II), Pb(II), Mg(II), Ca(II), Cs(I), Na(I), K(I) were prepared from Titrisol solutions (Merck, Darmstadt, Germany). Working solutions were prepared by dilution of stock solutions ( $1000 \text{ mg L}^{-1}$ ) with deionized water. HCl,  $\text{HNO}_3$ ,  $\text{CH}_3\text{COOH}$  as the eluent solvents were purchased from Merck Company (Whitehouse Station, NJ) and 2-amino thiophenol was purified by distillation in the presence of Zn powder. Soil (NCS DC 73323) and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) from Bulgaria was prepared as the reference material.

### 2.2. Apparatus

A Shimadzu model AA-680 atomic absorption spectrometer equipped with deuterium background correction was used for Cd(II) and Pb(II) determination. Cadmium and lead hollow cathode lamp (HCL) was used as the radiation source with wavelength of 228.8 and 283.3 nm, respectively. An air/acetylene flame was utilized in all measurements. All instrumental parameters were adjusted according to the recommendations of manufacturer. A Metrohm digital pH meter 827 equipped with a glass calomel electrode was employed for adjustment of pH. The Fourier transform infrared (FT-IR) measurements were carried out using a BOMEM MB-Series FT-IR spectrometer in the form of KBr pellets. The morphology of products was also studied by Philips XL-30 scanning

electron microscope. The thermal stability of the nanocomposites was determined using a thermogravimetric analyzer (TGA/DTA BAHR: STA 503) under air and a heating rate of  $10^\circ\text{C min}^{-1}$ .

The Brunauer–Emmett–Teller (BET) of the polymeric nanocomposites was analyzed by nitrogen adsorption in a nitrogen adsorption apparatus (BEL Japan, BELSORP-18 Plus). The BET surface area (SBET) was determined using the adsorption data in the relative pressure ( $P/P_0$ ) range of 0–1 by a multipoint BET method. The samples were degassed at  $150^\circ\text{C}$  prior to the nitrogen adsorption measurements.

### 2.3. Preparation of MWCNTs/P2AT nanocomposite

For preparation of poly(2-amino thiophenol) nanocomposite, 40 mL of HCl solution (1 M) containing 0.5 g MWCNTs was sonicated at room temperature for 10 min. Then  $116 \mu\text{L}$  of 2-aminothiophenol ( $1.15 \text{ mmol}$ ) was added to MWCNTs suspension and stirred for half an hour to disperse 2-aminothiophenol in the reaction medium, then the mixture was cooled below  $5^\circ\text{C}$  by using an ice bath. To initiate the reaction, ammonium persulfate with equimolar amount of monomer in 1 M HCl aqueous solution was added dropwise under vigorous stirring over a period of 1 h. The resulting solution was left in the ice bath for 5 h. The reaction mixture was filtered with sinter-glass, washed with methanol/water solution and finally dried in vacuum oven at  $60^\circ\text{C}$  for 24 h. A fine black powder was obtained. Scheme 1 provides the images of synthesized MWCNTs/P2AT nanocomposite.

### 2.4. Column preparation

100.0 mg of nanocomposite as sorbent was slurred in water and then poured into a glass column ( $120 \text{ mm} \times 20 \text{ mm}$ ) with a porous disk. The columns were used repeatedly after washing with distilled water. It was determined that the columns are stable up to 7 adsorption–elution cycles without any noticeable decrease in the recovery of cadmium and lead. The column was dried in vacuum oven at  $60^\circ\text{C}$  for 3 h.

### 2.5. Real sample pretreatment and analysis

Fish and sediment samples were collected from two different sites in Moosa creek. Moosa creek is located in Northwest of the Persian Gulf ( $21^\circ 30'$  to  $31^\circ 30' \text{N}$ ,  $52^\circ 48' \text{E}$ ), and it has several subsidiary creeks. Among these creeks Jafare as a contaminated site and Behad as a reference site were chosen. Needless to say, Behad as a reference site is located far from petrochemical industries.

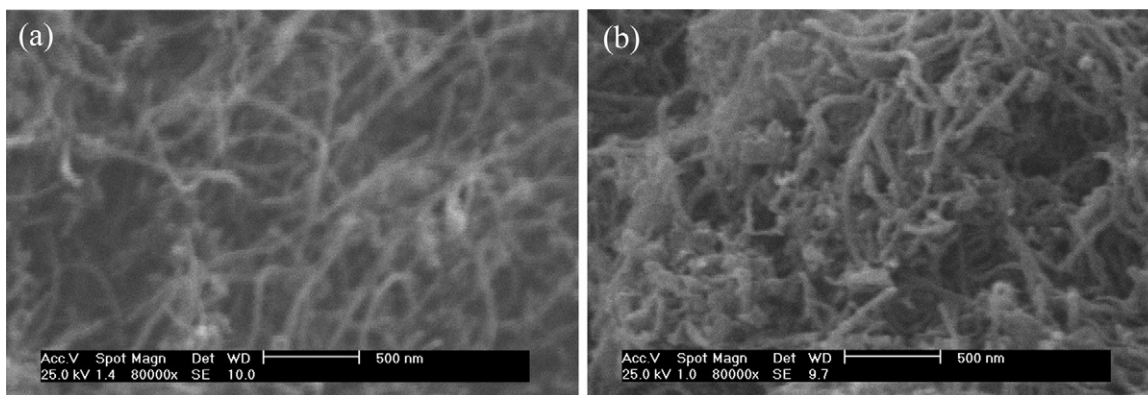


Fig. 1. The SEM images of MWCNTs (a) and MWCNTs/P2AT (b).

The fish samples (*Platycephalus indicus*) were stored in plastic bags on ice and transported back to the laboratory. They were kept at  $-20^{\circ}\text{C}$  before being used. A part of the muscles tissue was taken out quickly and was dried in an oven at  $70^{\circ}\text{C}$  for 48 h [25]. After grinding the dry tissue, 0.5 g of each sample was digested with 5 mL of concentrated  $\text{HNO}_3$  in Teflon beakers for 4 h at  $100^{\circ}\text{C}$ . To deproteinate the sample, resulted mixture was filtered into 100 mL Erlenmeyer flask and then diluted with double distilled water up to 100 mL. Sediment samples were collected from each study site using Peterson grab sampler, stored in plastic bags on ice and transported back to the laboratory and kept at  $-20^{\circ}\text{C}$  until analysis. 1 g of sediment was digested with 6 mL of HCl (37%) and 2 mL of  $\text{HNO}_3$  (65%) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then venting for 8 min [9]. The result solution from digestion was then diluted to 100 mL with deionized water.

The proposed method was applied to the determination of cadmium and lead in different water samples such as distilled, tap, river, lake and waste water samples. The polyethylene bottles filled with the samples were cleaned with detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size  $0.45\ \mu\text{m}$ ), and were acidified to pH 2.0 for storage. Tap water samples were taken from our research laboratory without pretreatment. Before determination, the samples were adjusted to pH 6.0 according to optimized experiment conditions.

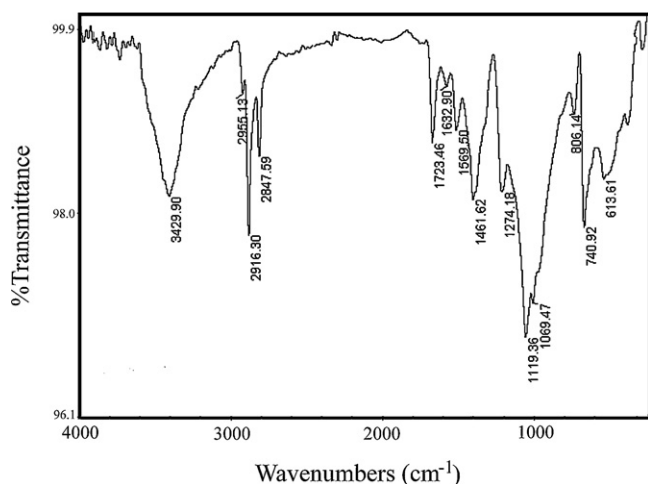


Fig. 2. FT-IR spectrum of the MWCNTs/P2AT.

### 3. Results and discussion

Recently, several researches have indicated the adsorption of organic material using MWCNTs [26,27]. So, we decided to modify MWCNTs surface with a conducting polymer. Cd(II) and Pb(II) ions adsorb on nanocomposites by two possible routes: (1) complexation with the  $=\text{N}-$  and  $-\text{S}-$  atoms and (2) ion exchange between metal ions and  $\text{H}^+$  ions on the  $=\text{NH}^+$  group of the doped polymer chains. High capacity for adsorption and selectivity of ions were achieved by MWCNTs/P2AT as sorbent for trace amounts of cadmium and lead ions.

The extraction and preconcentration of metals on MWCNTs/polymer nanocomposites are highly dependent on several factors. To address this dependence, the SPE procedure was optimized for such various analytical parameters using synthesized nanocomposite. Various ion interference effects were also investigated.

#### 3.1. Characteristic of modified MWCNT with P2AT

SEM images of neat MWCNTs and MWCNT/P2AT nanocomposite prepared by in situ polymerization of 2-aminothiophenol at the presence of MWCNTs presented in Fig. 1. The neat MWCNTs entangled by van der Waals forces form a dense, robust, and network structure (Fig. 1a). The increase in nanotubes diameters in MWCNTs/P2AT nanocomposite (Fig. 1b) was observed comparing to unmodified MWCNTs. The results show the presence of polymer on the surfaces of the MWCNTs synthesized via in situ polymerization of 2-aminothiophenol.

The FT-IR analysis confirmed the modification of MWCNTs and it is shown in Fig. 2. The spectra of MWCNTs/P2AT nanocomposite demonstrate that bands appeared at  $1461\ \text{cm}^{-1}$  and  $1569\ \text{cm}^{-1}$  must be assigned to  $\text{C}=\text{C}$  stretching vibrations of the quinoid and benzenoid rings, respectively, indicating successful preparation of P2AT on MWCNTs [28]. The strong peak at about  $1119\ \text{cm}^{-1}$  is considered to be stemmed from delocalization of electrons in polymer backbone [29].

The thermal stability and the amount of polymers grafted onto the MWCNTs of the nanocomposite were studied by the thermal analysis. In Fig. 3 the thermogram of the MWCNTs/P2AT is presented. The amount of weight loss below  $200^{\circ}\text{C}$  reflects the loss of its humidity and acid. According to Fig. 3 the thermogram of the MWCNTs/P2AT demonstrates that polymer is decomposed below  $600^{\circ}\text{C}$ . The amount of P2AT on the surface of nanotubes is approximately 50%. Consequently, the above results of the experimental analysis suggest the MWCNTs are successfully modified by the P2AT.

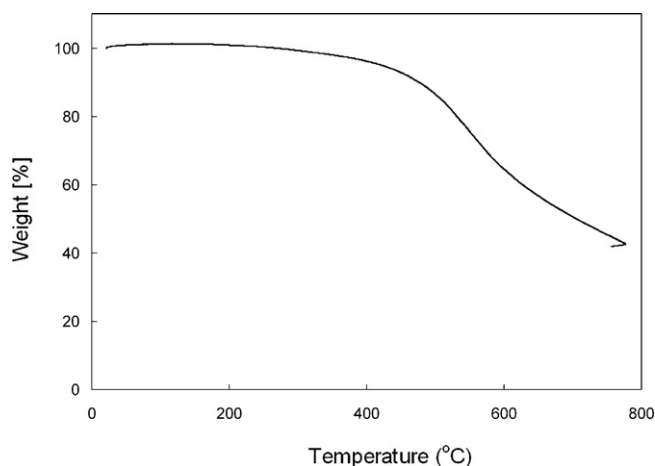


Fig. 3. Thermogravimetric analysis of MWCNTs/P2AT.

In order to further examine the porous structure of the nanocomposite,  $N_2$  adsorption–desorption isotherms were employed. The surface area and mean pore size of the hierarchical porous sorbent determined by BET method was about  $114 \text{ m}^2 \text{ g}^{-1}$  and  $7.74 \text{ nm}$ , respectively.

### 3.2. Effect of pH

The pH of sample aqueous solutions is an important analytical factor in the solid phase extraction studies of metal ions. The pH of the 25 mL sample solutions containing  $1 \text{ mg L}^{-1}$  of cadmium and lead ions was adjusted to fit in the range of 2–8. Generally, the main adsorption sites in the modified MWCNTs for Cd(II) and Pb(II) are  $=N-$  and  $-S-$  groups in the macromolecular chains since the

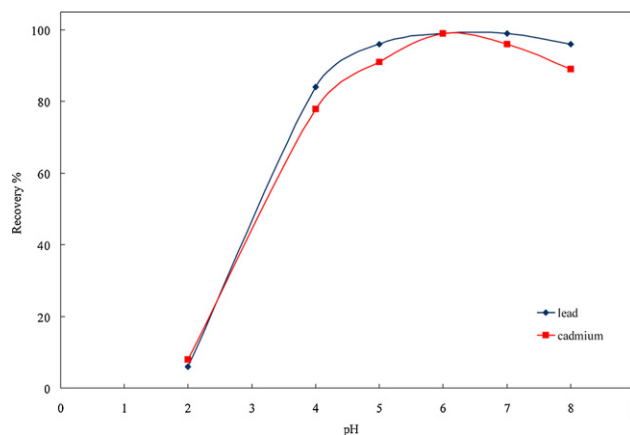


Fig. 4. The effect of solution's pH on sorption (condition:  $1 \text{ mg L}^{-1}$  of cadmium and lead, sample flow rate =  $6 \text{ mL min}^{-1}$ , room temperature).

N and S atoms have an electron lone pair and through sharing an electron pair they can efficiently bind to metal ion and forming a metal complex. In acidic solution protonation of binding sites of the chelating molecules can occur and in basic solution hydroxide ions may form complex with many metals and precipitate them. The recovery percent of analytes are shown in Fig. 4, and as seen at pH 6.0 the two analyte ions were quantitatively ( $>95\%$ ) retained on the sorbent. Therefore further studies were done at pH 6.0.

### 3.3. Effect of type, concentration and volume of eluent

A series of selected eluent solutions, including HCl,  $\text{HNO}_3$  at different concentrations,  $\text{HCl}:\text{CH}_3\text{COOH}$ ,  $\text{HNO}_3:\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOH}$  used for elution of cadmium and lead ions from modified

**Table 1**  
Effect of type and concentration and volume of eluent ( $N=3$ ).

Eluent	Concentration (v/v%)	Volume (mL)	$R^a \% \pm S^b$	
			Cd	Pb
HCl	20	10	$87.0 \pm 1.0$	$79.0 \pm 2.0$
HCl: $\text{CH}_3\text{COOH}$	10:10	10	$67.0 \pm 1.0$	$59.0 \pm 2.0$
$\text{HNO}_3:\text{CH}_3\text{COOH}$	10:10	10	$76.0 \pm 1.0$	$69.0 \pm 2.0$
$\text{CH}_3\text{COOH}$	20	10	$54.0 \pm 1.0$	$52.0 \pm 1.5$
$\text{HNO}_3$	20	10	$99.0 \pm 2.0$	$99.0 \pm 2.0$
$\text{HNO}_3$	10	10	$99.0 \pm 1.0$	$99.0 \pm 1.0$
$\text{HNO}_3$	5	10	$92.0 \pm 1.0$	$87.0 \pm 1.5$
$\text{HNO}_3$	2.5	10	$64.0 \pm 1.5$	$54.0 \pm 1.0$
$\text{HNO}_3$	10	7.5	$99.0 \pm 2.0$	$99.0 \pm 1.0$
$\text{HNO}_3$	10	5	$89.0 \pm 1.0$	$78.0 \pm 1.0$
$\text{HNO}_3$	10	2.5	$62.0 \pm 2.0$	$53.0 \pm 2.0$

<sup>a</sup> Recovery.

<sup>b</sup> Standard deviation.

**Table 2**  
Effect of sample and eluent flow rate ( $N=3$ ).

Sample flow rate ( $\text{mL min}^{-1}$ )	$R^a \% \pm S^b$		Eluent flow rate ( $\text{mL min}^{-1}$ )	$R^a \% \pm S^b$	
	Cd	Pb		Cd	Pb
1	$99.0 \pm 2.0$	$99.0 \pm 1.0$	0.5	$99.0 \pm 1.0$	$99.0 \pm 1.0$
2	$99.0 \pm 1.0$	$99.0 \pm 2.0$	1	$99.0 \pm 1.0$	$99.0 \pm 1.0$
4	$99.0 \pm 1.0$	$99.0 \pm 1.0$	1.5	$99.0 \pm 1.0$	$99.0 \pm 1.0$
6	$99.0 \pm 1.5$	$99.0 \pm 1.5$	2	$99.0 \pm 1.0$	$99.0 \pm 2.0$
8	$99.0 \pm 1.0$	$99.0 \pm 1.0$	2.5	$91.0 \pm 1.0$	$87.0 \pm 1.0$
10	$91.0 \pm 1.0$	$93.0 \pm 1.0$	3	$84.0 \pm 2.0$	$78.0 \pm 2.0$
12	$84.0 \pm 1.0$	$89.0 \pm 2.0$	3.5	$72.0 \pm 1.0$	$64.0 \pm 1.0$
14	$71.0 \pm 2.0$	$76.0 \pm 2.0$	4	$54.0 \pm 2.0$	$48.0 \pm 1.0$
16	$52.0 \pm 1.0$	$55.0 \pm 1.0$	–	–	–

<sup>a</sup> Recovery.

<sup>b</sup> Standard deviation.



MWCNTs. As shown in Table 1, it is found that HNO<sub>3</sub> (10% (v/v)) provided effective elution of cadmium and lead ions from modified MWCNTs.

The effect of eluent volume on the recovery of cadmium and lead ions was also studied. As Table 1 shows, quantitative recovery could be obtained with 7.5 mL of HNO<sub>3</sub> (10% (v/v)). Therefore, volumes of 7.5 mL of eluent for desorption of cadmium and lead ions were used in the next experiments.

### 3.4. Effect of sample and eluent flow rate

The retention of an element on an adsorbent also depends on the flow rate of the sample solution. To optimize the sample flow rate, 25 mL solutions of 1 mg L<sup>-1</sup> cadmium and lead ions were adjusted to pH of 6.0, and then passed through the column at flow rates in the range of 1–12 mL min<sup>-1</sup> with a peristaltic pump. The column was then washed with 10 mL of water to remove free metal ions. Subsequently, 7.5 mL of eluent was passed to desorb the bounded cadmium and lead ions from modified MWCNTs. The results in Table 2 demonstrate that the sample flow rate variation in the ranges of 1–8 mL min<sup>-1</sup> had no effect on the recovery of cadmium and lead ions from modified MWCNTs. On the other hand, quantitative recoveries for cadmium and lead ions were obtained at a flow rate range of 0.5–2.0 mL min<sup>-1</sup> for modified MWCNTs with HNO<sub>3</sub> (10% (v/v)).

### 3.5. Effect of the volume of sample solutions

A higher pre-concentration factor can be obtained by increasing the sample to eluent volume ratio by either decreasing the eluent volume and/or increasing the sample volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution with a constant amount of ions (0.1 mg of cadmium and lead). Samples solution volumes of 50, 100, 500, 1000, 1500, 2000, 2100, 2200, 2300, 2400 and 2500 mL containing cadmium and lead were passed through the column. As shown in Fig. 5, the recovery was found to be stable until 2200 and 2400 mL for cadmium and lead ions, respectively. As the elution volume was 7.5 mL for cadmium and lead, pre-concentration factors of 282 for cadmium and 304 for lead were obtained by assuming a greater than 96% recovery for cadmium and 95% recovery for lead.

### 3.6. Effect of interfering ions

Because of the presence of other elements in real samples, the determination and preconcentration of cadmium and lead ions are difficult. Therefore, the effects of common coexisting cations and anions on the adsorption of cadmium and lead ions on the modified MWCNTs were investigated.

**Table 4**

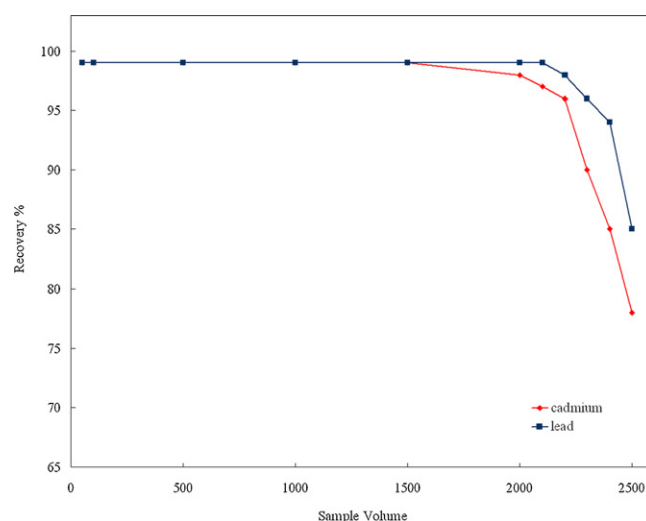
Statistical and calibration parameters.

Analyte	Regression equation	r <sup>2</sup>	LOD (ng mL <sup>-1</sup> )	DLR (ng mL <sup>-1</sup> )	PF	Recovery (%)	RSD (%)	Maximum sorption capacity (mg g <sup>-1</sup> )
Cadmium ion	Y=0.015X+0.032	0.996	0.3	1–100	282	96	2.4	178.7
Lead ion	Y=0.01X+0.022	0.997	1	3–110	304	95	3.2	186.4

**Table 5**

Comparison between modified MWCNT and unmodified MWCNT.

System	Adsorption capacity (mg g <sup>-1</sup> )		Sample volume (mL)		Sample flow rate (mL)	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)
MWCNTs/P2AT	178.7	186.4	2200	2400	10	10
Neat MWCNTs	50	63	500	700	2	3



**Fig. 5.** The effect of volume of sample solution (condition: 1 mg of cadmium and lead, pH 6.0, sample flow rate = 6 mL min<sup>-1</sup>, eluent = 7.5 mL of HNO<sub>3</sub> (10% (v/v)), eluent flow rate = 1.5 mL min<sup>-1</sup>).

**Table 3**

Influence of interfering ion (N=3).

Foreign ion	Tolerable concentration ratio X/Cd and Pb	R <sup>a</sup> % ± S <sup>b</sup>	
		Cd	Pb
K <sup>+</sup>	10000	99.0 ± 2.0	99.0 ± 2.0
Na <sup>+</sup>	10000	99.0 ± 2.0	99.0 ± 2.0
Cs <sup>+</sup>	1000	99.0 ± 1.0	99.0 ± 2.0
Ca <sup>2+</sup>	100	98.0 ± 1.0	99.0 ± 1.0
Mg <sup>2+</sup>	100	96.8 ± 2.0	97.0 ± 1.0
Al <sup>3+</sup>	100	95.0 ± 1.0	97.0 ± 1.0
Cr <sup>3+</sup>	100	98.0 ± 1.0	98.0 ± 1.0
Cu <sup>2+</sup>	100	97.0 ± 1.0	93.0 ± 1.0
Fe <sup>2+</sup>	100	96.0 ± 1.0	97.0 ± 1.0
Ni <sup>2+</sup>	100	90.0 ± 1.0	90.0 ± 2.0
Mn <sup>2+</sup>	100	96.0 ± 1.0	96.0 ± 2.0
Cl <sup>-</sup>	100	98.0 ± 2.0	97.0 ± 1.0
NO <sub>3</sub> <sup>-</sup>	100	97.0 ± 2.0	97.0 ± 2.0
SO <sub>4</sub> <sup>2-</sup>	500	96.0 ± 1.5	98.0 ± 1.0
PO <sub>4</sub> <sup>3-</sup>	500	95.0 ± 2.0	93.0 ± 3.0
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	500	93.0 ± 2.0	95.0 ± 1.0

<sup>a</sup> Recovery.

<sup>b</sup> Standard deviation.

In these experiments, 100 mL of solution containing 0.01 mg cadmium and lead ions was added to interfering ions and treated according to the recommended procedure. The results in Table 3 show that the vast majority of transition, alkaline, and earth

**Table 6**  
Determination of cadmium and lead ions recovery in certified reference materials.

Sample	Element	Concentration (mg kg <sup>-1</sup> )		Relative error (%)
		Certified	Found	
Ore polymetallic gold Zidarovo-PMZrZ (206 BG 326)	Pb	5.47	5.25	-4.0
Soil (NCS DC 73323)	Cd	0.45	0.44	-2.22

**Table 7**  
Analysis of cadmium in different real samples.

Sample	C <sub>added</sub> (μg kg <sup>-1</sup> )	C <sub>found</sub> (μg kg <sup>-1</sup> )	Recovery %	RSD %
Fish sample in Behad creek	-	4.4	-	3.6
	10	14.3	99.3	
Fish sample in Jafare creek	-	19	-	3.5
	10	28.2	97.2	
Sediment sample in Behad creek	-	20	-	3.1
	10	29.8	99.4	
Sediment sample in Jafare creek	-	42	-	3.8
	10	52.2	100.3	
Water sample	C <sub>added</sub> (μg L <sup>-1</sup> )	C <sub>found</sub> (μg L <sup>-1</sup> )	Recovery %	RSD %
Pure water	-	-	-	3.2
	10	9.8	98	
Tap water	-	-	-	3.9
	10	10.05	100.5	
River water	-	-	-	2.8
	10	10.1	101	
Lake water	-	-	-	3.7
	10	9.92	99.2	
Waste water	-	2.8	-	3.1
	10	12.7	99.2	

**Table 8**  
Analysis of lead in different real samples.

Sample	C <sub>added</sub> (μg kg <sup>-1</sup> )	C <sub>found</sub> (μg kg <sup>-1</sup> )	Recovery %	RSD %
Fish sample in Behad creek	-	44	-	3.4
	10	53.2	98.5	
Fish sample in Jafare creek	-	88	-	3.5
	10	97.4	99.3	
Sediment sample in Behad creek	-	241	-	2.9
	50	287	98.6	
Sediment sample in Jafare creek	-	597	-	3.9
	50	646.1	99.8	
Water sample	C <sub>added</sub> (μg L <sup>-1</sup> )	C <sub>found</sub> (μg L <sup>-1</sup> )	Recovery %	RSD %
Pure water	-	-	-	2.1
	10	9.8	98	
Tap water	-	6.4	-	3.2
	10	16.5	100.6	
River water	-	1.4	-	2.5
	10	11.5	100.9	
Lake water	-	-	-	3.1
	10	10.05	100.5	
Waste water	-	5.3	-	3.8
	10	15.15	99.01	

alkaline metals do not interfere at environmentally relevant concentrations. This is due to the low capacity or rates of adsorption for interfering ions under optimum condition. Thus, these results confirm that the procedure using modified nanomaterial is independent from matrix interferences.

### 3.7. Adsorption capacity

In order to study the adsorption capacity of modified MWCNTs, 100 mL of sample solution containing 10 mg of cadmium and lead was adjusted to the optimum pH, and the flow rate

**Table 9**  
Comparison between this method and literature.

System	Preconcentration factor	Detection limit ( $\mu\text{g L}^{-1}$ )		Ref.
		Cd	Pb	
Chelating resin	75	4.2	16.0	[30]
Sulfur adsorbent	250	0.2	3.2	[31]
Modified silica gel	27	1.1	22.5	[32]
Cloud point extraction	43	0.74	4.6	[33]
MWCNTs/P2AT	280	0.3	1.0	This work

was passed through sorbent columns. This procedure followed by determination of cadmium and lead ions in the effluent and elution using flame atomic absorption spectroscopy. The capacities of the modified MWCNTs nanocomposites for cadmium and lead are  $178.7 \text{ mg g}^{-1}$  and  $186.4 \text{ mg g}^{-1}$ , respectively.

### 3.8. Analytical performance

Under the optimized conditions, calibration curves were drawn for the determination of cadmium and lead, according to the general procedure. Linearity was maintained in the range of  $1\text{--}100 \text{ ng mL}^{-1}$  for cadmium and  $3\text{--}110 \text{ ng mL}^{-1}$  for lead in initial solution. The correlation of determination ( $r^2$ ) was 0.996 for cadmium and 0.997 for lead ions. The limits of detection, defined as  $C_{\text{LOD}} = 3S_b/m$ , where  $S_b$  is standard deviation of 10 replicate blank signals and  $m$  is slope of the calibration curve after preconcentration, for a sample volume of 500 mL, were found to be 0.3 and  $1 \text{ ng mL}^{-1}$  for cadmium and lead ions, respectively. The relative standard deviations for 10 separate column experiments for the determination of  $5.0 \mu\text{g Cd}^{2+}$  and  $\text{Pb}^{2+}$  in 100 mL water were 2.4% and 3.2%, respectively.

The results in Table 4 show that the mentioned method using conducting polymers modified carbon nanotubes as sorbents, produced relatively high preconcentration factors and low detection limits. Table 5 demonstrates a comparison between modified MWCNT and unmodified MWCNT, and data in this table prove the advantages of modified MWCNT in comparison with unmodified MWCNT.

### 3.9. Applications

The accuracy of the method results was verified by analyzing the standard reference sample (soil, NCS DC 73323) with the certified content of cadmium and ore polymetallic gold Zidarovo-PMZrZ (206 BG 326) with the certified content of lead. The results are shown in Table 6. The obtained results for the standard material are in remarkable agreement with the certified values in the optimum condition. To demonstrate that this procedure is quantitative for cadmium and lead determination in distilled, tap, river, lake and waste water and also fish and sediment in the Persian Gulf, the standard addition method was used. It is observed that the SPE technique using nanocomposites as sorbents has a high potential for extraction. As seen in Tables 7 and 8, results show that the matrixes of tap water, river water, lake water, waste water, and environmental samples had little effect on cadmium and lead extraction by nanocomposites of MWCNTs. These results indicate the suitability of the MWCNTs/P2AT nanocomposites for selective SPE and determination of trace amounts of cadmium and lead ions in environmental samples.

## 4. Conclusions

To the best of the authors knowledge, this is the first time that the modified MWCNTs using synthesis of conducting polymers on the surface have been used as adsorbent for cadmium and lead. This

SPE technique was successfully applied for separation, determination and preconcentration of cadmium and lead in environmental samples. This method is simple, rapid and reliable and it is known as a selective and sensitive method for determination of trace levels of Cd(II) and Pb(II). One of the most important characteristics of the MWCNTs/P2AT is the excellent selectivity towards Cd(II) and Pb(II) over other ions. Convenient data was found for detection limit and enrichment factor in determination of Cd(II) and Pb(II), and it confirmed this fact that the proposed method using modified MWCNTs has sufficient potential in extraction. As a result, the LOD and preconcentration factor of this method is comparable or better than some of the previously reported preconcentration methods (Table 9).

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