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A new sorbent based on MWCNTs modification for separation/preconcentration of trace amounts of Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II) and their determination by flame atomic absorption spectrometry

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Abstract

Background: A new solid phase extraction (SPE) method has been developed for the separation/preconcentration and determination of lead, cadmium, chromium, nickel, and copper ions using a new sorbent.

Methods: The method is based on the application of multiwalled carbon nanotubes modified with ethylenediamine-*N,N*-diacetic acid (MWCNTs-EDDA) as a selective sorbent in SPE for the separation and preconcentration of Pb(II), Ni(II), Cd(II), Cu(II), and Cr(III). The determination of these heavy metals was followed by flame atomic absorption spectrometry (FAAS).

Results: All quantitative determinations were performed by FAAS, and surface modification of synthesized adsorbents has been confirmed on the basis of characterization with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The parameters such as pH, amount of adsorbent, shaking time, eluent type and its concentration, and matrix effect have been investigated and optimized. The maximum adsorption capacity of the adsorbent at optimum conditions was found to be 51.7, 67.6, 49.9, 57.8, and 62.3 mg g⁻¹ for Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II), respectively.

Conclusions: In the presented study, MWCNTs were functionalized by EDDA and it was applied as an adsorbent for the separation and preconcentration of trace level of Pb, Ni, Cd, Cu, and Cr ions. This method is effective, selective, rapid, and simple for the determination of trace amounts of Pb, Ni, Cd, Cu, and Cr ions and can be successfully applied to analyze the trace amounts of mentioned ions in wastewater and herbal samples without evident interference from the complex matrix. Furthermore, the sorption has high capacity, and the precision and accuracy of the method are also satisfactory.

Keywords: Solid phase extraction; Multiwalled carbon nanotubes; Ethylenediamine-*N,N*-diacetic acid; Heavy metals; Flame atomic absorption spectrometry

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Background

Heavy metal pollution on the planet is increasing day by day and has become an environmental problem throughout the world. Heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, have high solubility in the aquatic environments and can be absorbed by living organisms, enter the food chain, and accumulate in the human body. Therefore, heavy metals are considered as hazardous materials for ecosystems, animals, plants, and human beings. Heavy metals that can be found in vegetables, ground water, and wastewaters are mostly toxic even at a very low concentration, and the determination of heavy metals is one of the targets of analytical chemists (Babel and Kurniawan 2004; Barakiewicz et al. 2010; Eskandari et al. 2006; Peker 1999; Turkoglu and Soylak 2005). However, direct determination of heavy metals is often not sensitive enough to determine heavy metal ions in environmental samples because of their low concentrations, which are near or below the detection limit of the instrument, and matrix interferences. Therefore, a preconcentration and/or separation of analytes is frequently necessary to improve the analytical detection limit, increasing the sensitivity, facilitating the calibration, enhancing the accuracy of the results, and simplifying the matrix of the sample (Baghban et al. 2012; Das et al. 2006; Hu et al. 2002a; 2002b; Palanivelu et al. 1992; Prasad et al. 2006; Rajesh and Manikandan 2008; Soylak et al. 2003).

Various separation-preconcentration techniques have been used for the separation and enrichment of trace amounts of heavy metal ions from environmental sample solutions, such as solvent (Lajunen and Kubin 1986) and cloud point (Giokas et al. 2001; Khader and Varghese 2005) extraction, ion-exchange (Möller et al. 1992), and membrane filtration (Karatepe et al. 2002). Despite many benefits, these techniques have significant disadvantages that many researchers prefer solid phase extraction (SPE) because of its notable advantages including higher preconcentration factor, rapid phase separation, short analysis time, cost saving, and low consumption of organic solvents (Absalan and Aghaei Goudi 2004; Liang et al. 2001; Pourreza and Behpour 1999). One of the

main factors in SPE procedure is suitable sorbent selection because of its effect on enrichment factor and recovery (Poole 2003). Various adsorbents are used for solid phase extraction of heavy metals, for example, chitosan (Martins et al. 2005), activated carbon (de Peña et al. 1995), resins (Tuzen et al. 2004), and chromosorb 108 (Tuzen et al. 2005). Since carbon nanotubes (CNTs) were discovered by Iijima (Iijima and Ichihashi 1993), because of the large surface area, the excellent chemical and thermal stabilities, and strong adsorption ability, they have attracted great attention as SPE adsorbents for various organic pollutants and metal ions. Due to low dispersion of CNTs into solvents and limited selectivity of CNTs and oxidized CNTs for SPE, a common technique is chemical functionalization which is used relatively often to generate functional groups on the surface of CNTs (Liu et al. 2008).

In this paper, we report a new method using multiwalled carbon nanotubes modified with ethylenediamine-*N,N*-diacetic acid (MWCNTs-EDDA) as a selective sorbent in SPE for separation and preconcentration of Pb(II), Ni(II), Cd(II), Cu(II), and Cr(III) prior to their determination by flame atomic absorption spectrometry (FAAS). Characterization of synthesized adsorbent has been done using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The effects of variables such as pH, matrix, amount of adsorbents, shaking time, eluent type, and its concentration were studied. Then, the method was applied to the analysis of wastewater and herbal samples with satisfactory results.

Methods

Materials and reagents

Multiwalled carbon nanotubes (MWCNTs) of 95 % purity and a length of 1–10 μm , outer and inner diameter of 5–20 and 2–6 nm, respectively, and 3–15 number of walls were purchased from PlasmaChem GmbH (Germany, www.plasmachem.com). All other reagents such as *N,N*-dicyclohexylcarbodiimide (DCC), ethyl acetate, bromo-acetic acid, ethylenediamine, sodium hydroxide, concentrated H_2SO_4

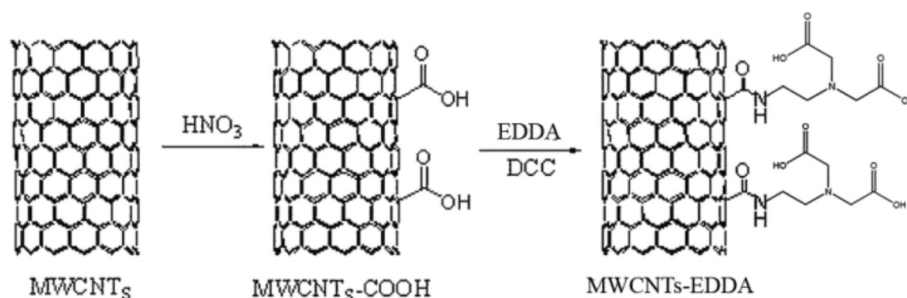


Fig. 1 Schematic of MWCNTs-EDDA synthesis

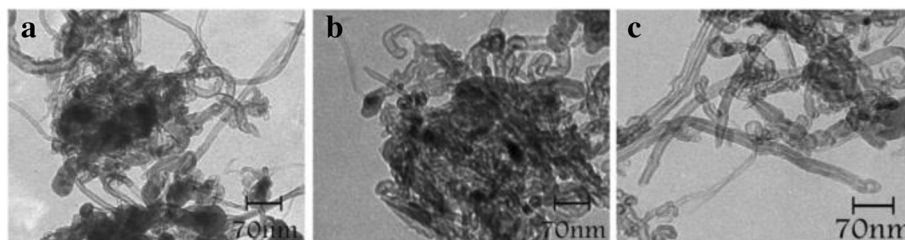


Fig. 2 TEM images of raw MWCNTs (a), oxidized MWCNTs (b), and functionalized MWCNTs by EDDA (c)

acid, concentrated HNO_3 acid, and ethanol were of at least analytical grade and obtained from Merck (Darmstadt, Germany). Standard stock solutions of Cd (II), Cr(III), Cu(II), Ni(II), and Pb(II) (1 mg mL^{-1}) were prepared by dissolving analytical or spectral purity grade chemicals $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ (purchased from Merck) in Milli-Q water and further diluted daily prior to use. Standard glassware used were cleaned with HNO_3 and rinsed with Milli-Q water.

Apparatus

All ion determinations were carried out with a flame atomic absorption spectrophotometer (PG Instruments, England) with an air-acetylene flame equipped with PG instrument hollow cathode lamps. A Metrohm pH meter (model 827 pH lab, combined glass-electrode) was employed for the pH adjustment. Fourier transform infrared (FTIR) spectra ($4000\text{--}400 \text{ cm}^{-1}$) in KBr were recorded by a FTIR Prestige-21, Shimadzu. A Philips TEM (EM 280 model) and a SEM (Tescan Vega II model) were conducted to characterize the raw MWCNTs, oxidized MWCNTs (MWCNTs-COOH), and modified MWCNTs. An ultrasonic bath (S60H Elmasonic, Germany) and a Heidolph rotary vacuum evaporator were also used.

Preparation of the solid sorbent

Preparation of oxidized MWCNTs

For elimination of metal ions and other sorbed impurities on MWCNTs (in preparation process), it was purified with HCl (10 %) for 24 h. Then, it was filtered and treated with concentrated HNO_3 and refluxed for 3 h with stirring to introduce oxygen groups onto the MWCNT surface (Pyrzyska 2010). The product (MWCNTs-COOH) was filtered through a $0.05\text{-}\mu\text{m}$ pore size PTFE membrane filter, washed with Milli-Q water until the pH was neutral, and dried under vacuum at 80°C for 8 h.

Synthesis of MWCNTs-EDDA

The requirement ligand (EDDA) was synthesized and purified as reported in the literature (McLendon et al. 1975). The oxidized multiwalled carbon nanotubes (2.0 g) were suspended in 150 mL of water, and the synthesized EDDA (0.5 mol) was added, then 2.0 g of DCC was added into it, and the suspension was refluxed for 48 h in 100°C . The obtained product (MWCNTs-EDDA) was vacuum filtered using a $0.05\text{-}\mu\text{m}$ pore size PTFE membrane filter, washed with excess ethanol, and dried in an oven at 80°C for 8 h. Figure 1 shows the synthesis process of MWCNTs-EDDA schematically.

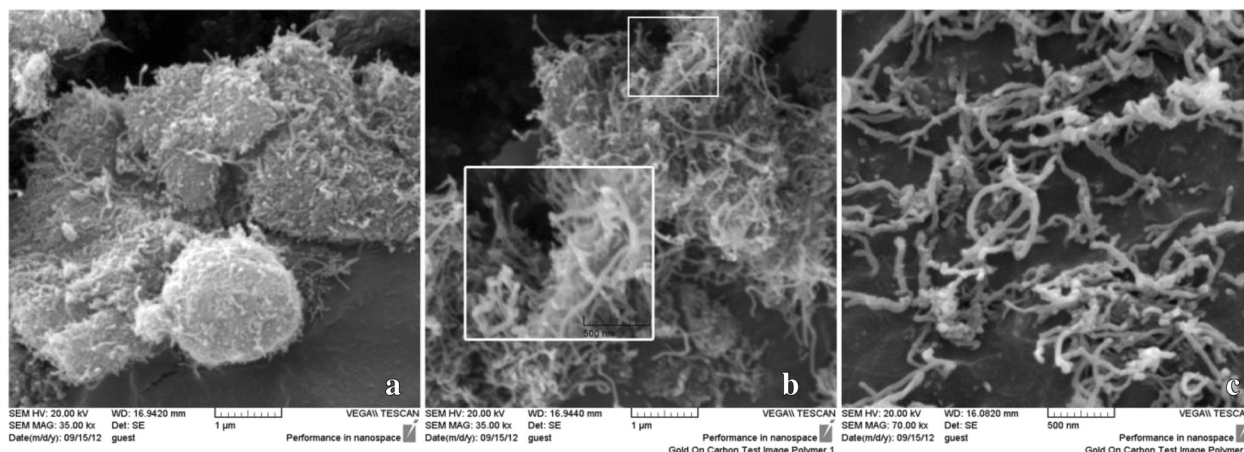


Fig. 3 SEM images of raw MWCNTs (a), oxidized MWCNTs (b), and functionalized MWCNTs by EDDA (c)

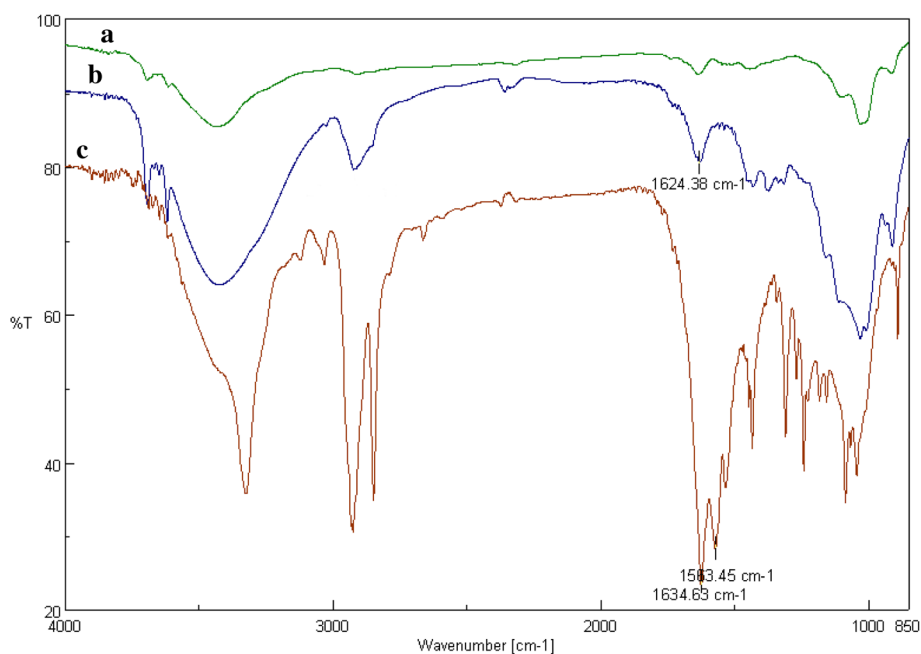


Fig. 4 FTIR spectra of raw MWCNTs (a), oxidized MWCNTs (b), and functionalized MWCNTs by EDDA (c)

General procedure

All adsorption experiments in this work were performed in a batch method. Water samples including four industrial wastewater and herbal samples including mushroom, black tea, and lettuce were prepared as reported in the literature (Manzoori et al. 2012). A portion of standard sample, water sample, or digested herbal sample solutions containing the studied ions were added

into a 50-mL beaker, and the pH of the mixture was adjusted to the desired value with 0.1 mol L⁻¹ HCl and/or 0.1 mol L⁻¹ NH₃.H₂O, and the mixture was diluted to 10 mL with deionized water. Then, 15-mg modified MWCNTs were added to it, and the mixture was shaken for 15 min at room temperature to facilitate adsorption of the cations onto the adsorbents. After vacuum filtering, the concentrations of metal ions were determined

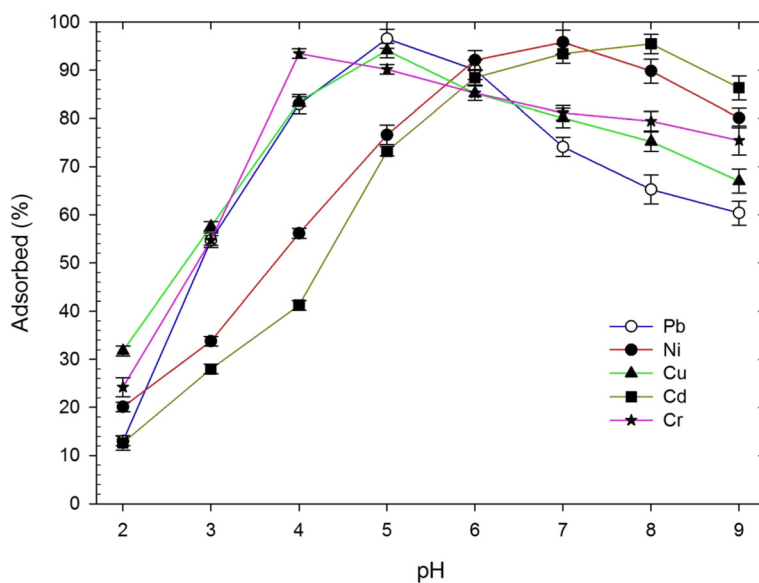


Fig. 5 Effect of pH on adsorption of heavy metal ions. Conditions: 15 mg MWCNTs-EDDA; 10 mL metallic ion solutions of Pb(II), Ni(II), and Cr(III) (10 µg mL⁻¹); 10 mL Cu(II) (5 µg mL⁻¹) and 10 mL Cd(II) (2 µg mL⁻¹) for 15 min

Table 1 Effect of different eluents on the recoveries of heavy metal ions

Eluent	Concentration (mol L ⁻¹)	Recovery (%)				
		Pb(II)	Ni(II)	Cr(III)	Cu(II)	Cd(II)
HNO ₃	0.1	93.3	88.5	88.7	89.9	92.5
	0.3	96.7	95.7	94.1	95.7	97.8
	0.5	98.4	99.6	97.7	98.1	99.7
H ₂ SO ₄	0.1	78.5	83.4	86.7	92.4	87.5
	0.3	80.3	87.1	88.9	96.5	89.4
	0.5	84.2	89.9	91.2	98.7	91.4
HCl	0.1	84.6	80.2	78.6	83.5	88.4
	0.3	86.7	82.4	81.1	88.8	91.2
	0.5	88.2	86.9	84.0	91.2	96.3

by FAAS. Finally, 5 mL of 0.5 mol L⁻¹ nitric acid was added as eluent, and the eluted ions were determined by FAAS.

Results and discussion

Characterization of MWCNTs-EDDA

TEM and SEM were conducted to characterize the raw MWCNTs, MWCNTs-COOH, and MWCNTs-EDDA. The representative TEM and SEM images are shown in Figs. 2 and 3, respectively. In contrast, the observed dispersing property of MWCNTs-COOH was better than that of MWCNTs, and the diameter of MWCNTs-EDDA appeared wider than that of MWCNTs and MWCNTs-COOH. These results confirm MWCNTs modified by the EDDA.

Formation of functionalized MWCNTs also was confirmed by IR spectroscopy. The FTIR spectrums of pure, oxidized, and functionalized MWCNTs are compared in

Fig. 4. Comparison of the FTIR spectra of MWCNTs with MWCNTs-COOH shows a new bond at 1624 cm⁻¹ in MWCNTs-COOH spectra which can be attributed to the stretching vibrations C=O of the carboxyl group. When MWCNTs-COOH was modified by EDDA, several new peaks appeared in the spectrum. That can be assigned as follows: the peak at 1634 cm⁻¹ is due to C–O stretching vibration. The peak at 1563 cm⁻¹ is caused by C–N stretching vibration and N–H bending vibration.

Effect of pH on adsorption

The pH of the solution is the first parameter that should be optimized, because of two reasons: firstly, the competition of the hydrogen and metal ions for the binding site of sorbent in acidic solutions and secondly, precipitation of metal ions that complex with hydroxide (Walcarius and Delacôte 2005). The effect of pH on the adsorption of lead(II), nickel(II), cadmium(II), copper(II), and chromium(III) ions onto MWCNTs-EDDA was investigated over the range from 2 to 9 using the batch procedure. It could be seen in Fig. 5 that a quantitative extraction (>95 %) occurred in the pH range of 4.5–5.5 for Pb(II), 6.5–7.5 for Ni(II), 7.0–8.0 for Cd(II), 4.5–5.5 for Cu(II), and 3.5–5.0 for Cr(III). Therefore, pHs of 5.0, 7.0, 7.5, 5.0, and 4.0 were selected for further studies of lead, nickel, cadmium, copper, and chromium ions, respectively.

Effect of the sorbent amount

The effect of MWCNTs-EDDA quantity on pre-concentration of considered ions was studied in the range of 1–25 mg under the optimum pH and 20-min shaking time. The results show that by increasing the

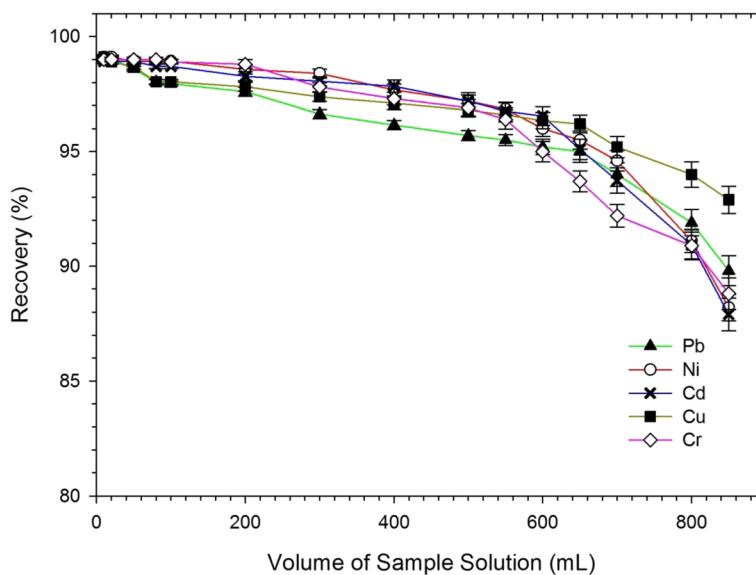


Fig. 6 Effect of sample volume on adsorption of heavy metal ions. Conditions: The conditions are same as Fig. 5 except pH 5.0, 6.0, 9.0, 8.0 and 7.0 for Pb(II), Ni(II), Cd(II), Cu(II) and Cr(III) ions, respectively

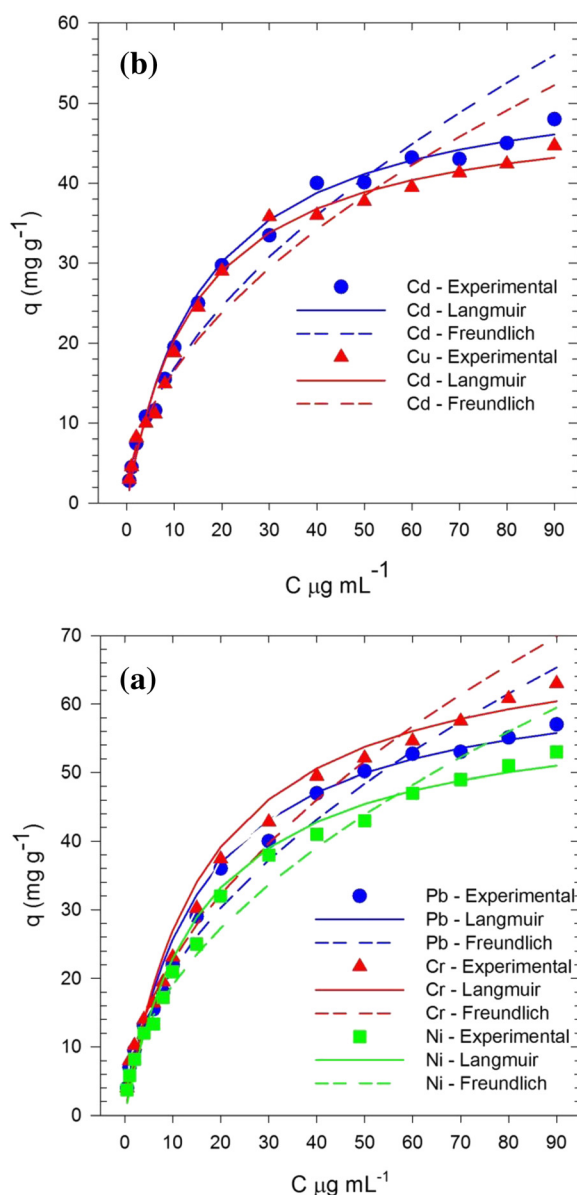


Fig. 7 Adsorption isotherms of **a** Pb(II), Cr(III), and Ni(II) and **b** Cd(II) and Cu(II) by MWCNTs-EDDA at initial metal ions concentration from 0.5 to 90 µg mL⁻¹, pH 5.0, 6.0, 9.0, 8.0, and 7.0 for Pb(II), Ni(II), Cd(II), Cu(II), and Cr(III) ions, respectively, and temperature of 25 ± 0.2 °C for 24 h. The data are fitted by Langmuir model and Freundlich model

amount of the sorbent, the recovery of metal ions increased due to the increasing surface area and accessible sites of the sorbent and finally reached a constant value at 15 mg of the sorbent. Therefore, 15 mg of MWCNTs-EDDA was selected for future studies.

Effect of shaking time

In solid phase extraction, the percentage extraction of metal ions always depends on the contact time of sample with the sorbent. Herein, a different shaking time (ranged from 1 to 30 min) was studied for the percentage extraction of Pb(II), Ni(II), Cr(III) (10 mL,

10 µg mL⁻¹), Cu(II) (10 mL, 5 µg mL⁻¹), and Cd(II) (10 mL, 2 µg mL⁻¹), with 15 mg of the sorbent. The results show that the adsorption of the mentioned ions at first 10 min was higher than 95 %, but 15 min was used for future studies.

Effect of eluent type and concentration

As shown in Fig. 5, the adsorption of metal ions decreases at low pHs, so a series of acidic solutions including HNO₃, HCl, and H₂SO₄ were used for elution of the retained Cd (II), Cr(III), Cu(II), Ni(II), and Pb(II). The obtained results (Table 1) showed that 5 mL of 0.5 mol L⁻¹ HNO₃ solution

Table 2 Langmuir and Freundlich constants for the adsorption of Pb(II), Cu(II), Cr(III), Cd(II), and Ni(II) by MWCNTs-EDDA

Metal ions	Langmuir			Freundlich		
	q_{max} (mg g ⁻¹)	b	R	k_f	n	R
Pb(II)	65.351	0.06468	0.9867	6.5433	0.5114	0.9712
Cr(III)	71.45	0.06063	0.9853	6.9347	0.5132	0.9825
Ni(II)	60.19	0.06155	0.9879	5.7904	0.5177	0.9786
Cd(II)	54.26	0.06267	0.9907	4.8323	0.5445	0.9597
Cu(II)	50.12	0.06905	0.9875	4.9930	0.5217	0.9503

was suitable for complete elution of retained heavy metals.

Effect of sample volume

Due to low concentration of heavy metals in natural samples, it is necessary to obtain the maximum volume in the SPE. For this purpose, various sample volumes in the range of 10–850 mL containing 100 µg of Pb(II), Ni (II), and Cr(III), 50 µg of Cu(II), and 20 µg of Cd(II) were treated according to the general procedure. It was found that quantitative recoveries (>95 %) were obtained for the sample volumes up to 650 mL for Pb(II), Ni(II), Cu(II), and Cd(II) and 600 mL for Cr(III) ions (Fig. 6). The final solution volume was 5.0 mL, and therefore, the preconcentration factors were 120 for Cr(III) and 130 for Pb(II), Ni(II), Cu(II), and Cd(II) ions.

Maximum adsorption capacity

The adsorption capacity of MWCNTs-EDDA investigated using the batch method as reported by Maquieira et al. (1994). A portion of sample solutions of various concentrations (10–100 µg mL⁻¹, 10 mL) of Cd(II), Cr (III), Cu(II), Ni(II), and Pb(II) were adjusted to the appropriate pH, and all processes of separation and preconcentration were applied on it. The maximum adsorption capacities of MWCNTs-EDDA for Cd(II), Cr (III), Cu(II), Ni(II), and Pb(II) were found to be 51.7, 62.6, 49.9, 57.8, and 62.3 mg g⁻¹, respectively. Our

results show that untreated and oxidized MWCNTs have much lower adsorption than new synthesized adsorbent.

Adsorption isotherms

Adsorption isotherms were obtained at 25 °C and pH 5.0, 7.0, 7.5, 5.0, and 4.0 for Pb(II), Ni(II), Cd(II), Cu(II), and Cr(III) ions, respectively, and by varying the initial concentration of these ions (Fig. 7a, b). Langmuir and Freundlich isotherms are two commonly used statistical isotherm models. The Langmuir isotherm demonstrates a monolayer coverage of adsorbate with homogeneous sorption energies, while Freundlich isotherm demonstrates a non-uniform distribution of heat of adsorption over the surface with the possibility of multilayer adsorption (Yu et al. 2007). The adsorption data were correlated with the isotherm models of Langmuir (Eq. 1) and Freundlich (Eq. 2)

$$q = \frac{(bq_{max}C)}{(1 + bC)} \text{ or } \frac{C}{q} = \frac{1}{(bq_{max})} + \frac{C}{q_{max}} \tag{1}$$

$$q = k_f C^n \text{ or } \log q = \log k_f + n \log C \tag{2}$$

where C is the equilibrium concentration of metal ions (µg mL⁻¹), q is the equilibrium amount of metal ion adsorbed per unit weight of adsorbents (mg g⁻¹), q_{max} is the maximum adsorption capacity of the adsorbents for metal ions (mg g⁻¹), b is the Langmuir constant and is a measure of the energy of adsorption (L mg⁻¹), k_f is the

Table 3 Effect of interferences ions on preconcentration and determination of heavy metal ions

Interfering ion	Pb	Cu	Ni	Cd	Cr	Tolerance limit (mg L ⁻¹)
	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , Ni ²⁺	Na ⁺ , K ⁺ , Mn ²⁺ , Ca ²⁺	Na ⁺ , K ⁺ , Ca ²⁺	K ⁺ , Na ⁺ , Fe ³⁺	K ⁺ , Na ⁺ , NH ₄ ⁺	650
	Ni ²⁺ , Mn ²⁺ , Cu ²⁺ , Fe ³⁺	Pb ²⁺ , NO ₃ ⁻ , Mg ²⁺ , NH ₄ ⁺	Mn ²⁺ , Cd ²⁺ , Pb ²⁺ , Fe ³⁺	Mn ²⁺ , NO ₃ ⁻ , NH ₄ ⁺ , Mg ²⁺	Mn ²⁺ , Ni ²⁺ , Cu ²⁺ , NO ₃ ⁻	550
	Cr ³⁺ , Zn ²⁺ , Cd ²⁺	Ni ²⁺ , Hg ²⁺ , Ba ²⁺ , Cr ³⁺ , Zn ²⁺ , CH ₃ COO ⁻	Mg ²⁺ , Cu ²⁺ , NO ₃ ⁻ , NH ₄ ⁺	Ca ²⁺ , Pb ²⁺ , Zn ²⁺ , Hg ²⁺ , Cu ²⁺	Ca ²⁺ , Mg ²⁺ , Fe ³⁺ , Zn ²⁺ , Hg ²⁺	400
	Co ²⁺ , NH ₄ ⁺ , Ba ²⁺	C ₂ O ₄ ²⁻ , SO ₄ ²⁻ , Co ²⁺ , Fe ³⁺	Cr ³⁺ , Zn ²⁺ , Hg ²⁺ , Ba ²⁺ , Co ²⁺	Ni ²⁺ , Co ²⁺ , Br ⁻	Pb ²⁺ , Co ²⁺ , Ba ²⁺ , C ₂ O ₄ ²⁻ , CH ₃ COO ⁻	250
	Hg ²⁺ , NO ₃ ⁻ , CH ₃ COO ⁻	Br ⁻	C ₂ O ₄ ²⁻ , Br ⁻	C ₂ O ₄ ²⁻ , Ba ²⁺	SO ₄ ²⁻ , Br ⁻	150
	SO ₄ ²⁻ , Br ⁻ , C ₂ O ₄ ²⁻		CH ₃ COO ⁻ , SO ₄ ²⁻	SO ₄ ²⁻ , CH ₃ COO ⁻		100

Table 4 Intra-day and inter-day relative standard deviations for three individual experiments and 3 days of analysis in water solution

Days of analysis	Inter-day RSD (%)				
	Pb	Ni	Cd	Cu	Cr
Day 1	3.16	2.19	2.23	1.8	3.1
Day 2	2.83	2.94	2.13	1.88	2.79
Day 3	3.57	1.63	1.87	2.14	2.3
Intra-day RSD (%)	3.12	2.17	2.01	1.82	3.31

The RSDs for three replicate measurements of 10.0 µg mL⁻¹ Cr, Ni, and Pb ions, 2.0 µg mL⁻¹ Cd ions, and 5.0 µg mL⁻¹ Cu ions

Freundlich constant representing the adsorption capacity, and *n* is a constant depicting the adsorption intensity. The Langmuir and Freundlich constants were obtained by fitting the adsorption equilibrium data to the isotherm models; they are listed in Table 2. It can be noticed that the *R* values for the Langmuir model are higher than those of the Freundlich model, thus indicating that the Langmuir model better describes adsorption onto new sorbent.

Effect of interfering ions

Always in real samples, there are many ions and determination of one of them may be influenced by others. Therefore, the effects of interfering ions on the determination of Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II) were examined using 10 µg mL⁻¹ of Pb, Ni, and Cr, 5 µg mL⁻¹ of Cu, and 2 µg mL⁻¹ of Cd containing the added interfering ions. The tolerance limit of the interfering ions, defined as the maximum

concentration of interfering ion causing a relative error of adsorbed Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II), is less than ±5 %. The results listed in Table 3 show that the suggested method had a good selectivity and can be applied in the determination of studied ions in real samples without any interference of other ions.

Analytical performance and method validation

In order to show the validation of the proposed method, the analytical features of the method such as limit of detection (LOD), linear range of the calibration curve, and precision of ions were examined. Under the optimal experimental conditions, eight standard solutions of Cd (II), Cr(III), Cu(II), Ni(II), and Pb(II) were analyzed by the procedure. The LODs were found to be 0.04, 0.15, 0.14, 0.21, and 0.89 µg mL⁻¹ for Cd, Cr, Cu, Ni, and Pb ions, respectively. The linear ranges of calibration curves for Cr(III), Ni(II), and Pb(II) were 0.5–10.0 µg mL⁻¹, 0.5–5.0 µg mL⁻¹ for Cu(II), and 0.2–2.0 µg mL⁻¹ for Cd (II) with correlation coefficients of 0.991, 0.996, 0.997, 0.999, and 0.998, respectively. The regression equations for the lines were $A = 0.014C_{Pb} + 0.001$, $A = 0.059C_{Ni} + 0.034$, $A = 0.008C_{Cr} + 0.010$, $A = 0.261C_{Cd} + 0.006$, and $A = 0.085C_{Cu} + 0.001$, where *A* is the absorbance and *C*_{Pb}, *C*_{Ni}, *C*_{Cr}, *C*_{Cd}, and *C*_{Cu} are the concentrations of Pb(II), Ni(II), Cr(III), Cd(II), and Cu(II) in µg mL⁻¹, respectively. Intra-day and inter-day relative standard deviations for three individual experiments and 3 days of analysis in water solution were 1.82–3.31 % and 1.63–3.57 %, respectively (Table 4).

Table 5 Recovery results of heavy metal ions in wastewater samples

Metallic ion	Wastewater (Copper factory, Sarcheshmeh, Rafsanjan)			Waste water (sewage treatment plant, Yazd)		
	Added	Found	Recovery (%)	Added	Found	Recovery (%)
Pb(II) (µg mL ⁻¹) ^a	0	2.20 (±0.14)	–	0	0.46 (±0.10)	–
	5.0	7.11 (±0.21)	98.2	5.0	5.24 (±0.16)	95.6
	10.0	12.24 (±0.17)	100.4	10.0	10.31 (±0.08)	98.5
Ni(II) (µg mL ⁻¹) ^a	0	1.10 (±0.11)	–	0	0.29 (±0.10)	–
	5.0	6.12 (±0.15)	100.4	5.0	5.37 (±0.12)	101.6
	10.0	11.08 (±0.12)	99.8	10.0	10.36 (±0.14)	100.7
Cd(II) (µg mL ⁻¹) ^a	0	0.50 (±0.09)	–	0	0.42 (±0.13)	–
	5.0	5.44 (±0.14)	98.8	5.0	5.41 (±0.16)	99.8
	10.0	10.52 (±0.19)	100.2	10.0	10.47 (±0.11)	100.5
Cu(II) (µg mL ⁻¹) ^a	0	6.21 (±0.13)	–	0	0.59 (0.10)	–
	5.0	11.13 (±0.15)	98.4	5.0	5.52 (±0.17)	98.6
	10.0	16.10 (±0.18)	98.9	10.0	10.64 (±0.15)	100.5
Cr(III) (µg mL ⁻¹) ^a	0	0.57 (±0.10)	–	0	0.56 (±0.17)	–
	5.0	5.60 (±0.15)	100.6	5.0	5.50 (±0.18)	98.8
	10.0	10.47 (±0.15)	99.0	10.0	10.60 (±0.13)	100.4

^aMean ± standard deviation (n = 5)

Table 6 Recovery results of heavy metal ions in herbal samples

Sample	Cu(II) ^a			Cr(III) ^a		
	Added ^b	Found ^b	Recovery (%)	Added ^b	Found ^b	Recovery (%)
Lettuce	–	–	–	0	0.43 ± 0.08	–
	–	–	–	5.0	5.4 ± 0.11	99.4
	–	–	–	10.0	10.37 ± 0.17	99.4
Mushroom	0	13.71 ± 0.59	–	–	–	–
	5.0	18.58 ± 0.14	97.4	–	–	–
	10.0	23.78 ± 0.23	100.7	–	–	–
Black tea	0	19.68 ± 1.09	–	0	5.39 ± 1.12	–
	5.0	24.46 ± 0.41	95.6	5.0	10.24 ± 1.05	97.0
	10.0	29.75 ± 0.39	103.9	10.0	15.14 ± 0.82	97.5

^aMean ± standard deviation (n = 5)^bUnites by mg kg⁻¹

Analytical applications

In order to establish the validity of the proposed method, it has been applied for the determination of trace amounts of Pb(II), Ni(II), Cd(II), Cu(II), and Cr (III) in wastewaters from Sarcheshmeh Copper factory and Yazd sewage treatment plant and herbal samples (black tea, mushroom, and lettuce). The results are listed in Tables 5 and 6. According to these data, the added ions can be quantitatively recovered from the samples by the proposed procedure. These results indicate that the method is a selective SPE and determination procedure of trace Pb(II), Ni(II), Cd(II), Cu (II), and Cr(III) in environmental samples.

Conclusions

In the presented study, MWCNTs were functionalized by EDDA and it was applied as an adsorbent for the separation and preconcentration of the trace level of Pb, Ni, Cd, Cu, and Cr ions. This method is effective, selective, rapid, and simple for the determination of the trace amounts of Pb, Ni, Cd, Cu, and Cr ions and can be successfully applied to analyze the trace amounts of the mentioned ions in wastewater and herbal samples without evident interference from the complex matrix. Comparison of this method and some of the previously reported preconcentration methods (Table 7) shows that the LOD and preconcentration factor of this method is

Table 7 Comparison of the proposed method with some recent studies using multiwalled carbon nanotubes as solid phase extractor

Analytes	Adsorbent	Detection method	Enrichment factor	RSD (%)	Detection limit (ng mL ⁻¹)	Reference
Pb	MWCNTs	FAAS	20	<2.5	4.9, 8.0	(Ozcan et al. 2010)
Pb, Cu, Cd, Ni	APDC-MWCNTs	FAAS	80	<5	0.3–0.6	(Tuzen et al. 2008)
Pb, Cd	MnO ₂ -CNTs	ETAAS	100	<3.2	4.4, 1.5	(Yang et al. 2011)
Ni	Activated carbon	FAAS	100	2.28	1.72	(Kiran et al. 2007)
Cu, Ni	MWCNT-hexahistidine-tagged protein	FAAS	29.28	2.4	0.3, 0.63	(Liu et al. 2009)
Cr	MWCNT	FAAS	100	<9	0.9	(Tuzen and Soylak 2007)
Cu, Ni	MWCNTs impregnated with D2EHPA	FAAS	25	<10	50	(Vellaichamy and Palanivelu 2011)
Cu, Pb, Ni	MWCNTs	FAAS	100	2.4–3.4	1.0–2.6	(Ghaedi et al. 2012)
Pb				3.16	0.89	
Ni				2.19	0.21	
Cr	MWCNTs-EDDA	FAAS	130	3.34	0.15	This work
Cd				2.23	0.04	
Cu				1.89	0.14	

comparable or better than achieved by other methods described in the literatures. Furthermore, the sorption has high capacity, and the precision and accuracy of the method are also satisfactory.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MAK, AM and SZM conceived of the original idea and design of the work. JY performed the collection of water and herbal samples, preparation of reagents and solutions and execution of experiments. MAK and AHM performed the data interpretation and manuscript writing. All authors read and approved the final manuscript.

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