



Measurement of heavy metals in soil, plants and water samples based on multi-walled carbon nanotube modified with Bis(triethoxysilylpropyl)tetrasulfide by flame atomic absorption spectrophotometry

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ABSTRACT

Heavy metals (HMs) are considered as the major environmental pollutants that accumulated in soil and plant. Consumption of such contaminated plants by humans and animals would ultimately harm the health of communities. This study aims to evaluate the amount of copper(Co), cadmium(Cd), and lead(Pb) in soil and cultivated plants that are irrigated by the city of Zabol's wastewater. Also, the heavy metals determined in 20 mL of Zabol's water based on Bis(triethoxysilylpropyl)tetrasulfide ($S_4[C_3H_6Si(OEt)_3]_2$, TEOSiP-TS) modified on MWCNTs as an adsorbent by the uniform dispersive -micro-solid phase extraction (UD- μ -SPE) at optimized pH. In this study, 52 samples including wheat, corn grain, and wild spinach, as well as agricultural soil were selected randomly from three village stations. The concentrations of heavy metals in plants, soils, and water samples were measured using a flame atomic absorption spectrometer (F-AAS). The one-way ANOVA test was applied to compare the mean value of heavy metals at the three mentioned stations. The results indicate that the amount of lead at all three stations and in all types of plants exceeds the permissible range. The amount of copper in plant species and water is lower than the permitted range, while it is higher in agricultural soil. By optimizing parameters, the linear range (LR) and the detection limit (LOD) of Cu, Cd, and Pb were obtained $1.5\text{-}1000\text{ }\mu\text{g L}^{-1}$, $1\text{-}200\text{ }\mu\text{g L}^{-1}$, $5\text{-}1500\text{ }\mu\text{g L}^{-1}$ and $0.5\text{ }\mu\text{g L}^{-1}$, $0.25\text{ }\mu\text{g L}^{-1}$, $1.5\text{ }\mu\text{g L}^{-1}$, respectively in water samples ($RSD\% < 2$). This study indicates that irrigation of agricultural fields using wastewater causes the accumulation of heavy metals in soil and plants.

1. Introduction

Heavy metals(HMs) as hazardous elements, caused by human activities in different sections of industry, agriculture, and business. It has been discharged for years into the ecosystem and has polluted water, soil, and agricultural farms. Also,

heavy metals have endangered the health of humans and other creatures [1]. Heavy metals enter the environment on a large scale through natural and human-made resources. The releasing amount of heavy metals to the environment is considerable [2]. The first influencing element of metal pollution in an ecosystem is the existence of heavy metals in the biomass of polluted areas which endangers human health. One of the most fundamental issues,

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in terms of heavy metals, is that body does not metabolize them [3]. This would cause several diseases and complications in the body. In general, neurological disorders (Parkinson's, Alzheimer's, depression, schizophrenia), various cancers, nutrient deficiency, and hormones imbalance are the results of heavy metals amass in the human body [4]. Some analytical techniques were used for the measurement of HMs in environmental samples such as atomic absorption spectrophotometry [5,6], laser-induced breakdown spectroscopy [7], X-ray fluorescence spectroscopy [8], and electrochemical methods [9]. Among these techniques, atomic absorption spectrophotometry has a very advantages such as simplicity, effectiveness, reliability, and low detection limit [10]. Zabol's urban wastewater is used in some villages to irrigate agricultural farms at the time of drought. In this study, to evaluate the amount of heavy metals lead, copper, and cadmium in agricultural soil and cultivated plants, such as wheat, corn, and a species of wild spinach, which are irrigated with wastewater, three stations were selected in which the irrigation of agricultural fields with wastewater is common. After wheat sampling and given that most of the planted wheat used to feed livestock in late winter or early spring is immature, the root of the plant was separated and all methods of sample preparation were applied to analyze the plant, without considering other parts of it. A similar approach was applied to grain corn. Wild spinach is a volunteer plant in wheat fields, and as it is used widely in the Sistan region for the purpose of cooking a type of local food during fall and winter, it was sampled from mentioned stations in order to evaluate the heavy metals accumulation. Recently, many adsorbents such as graphene/graphene oxide [11], CNT [12], activated carbon [13], and silica pores [14] were used for extraction HMs in water samples. Also functionalized nanocarbon structures were also reported for extraction heavy metals in water, plant and soil samples [15]. In addition, the different technology such as, liquid-liquid extraction [16], dispersive ionic liquid-liquid extraction [17], dispersive micro solid-phase extraction [18], and

magnetic solid phase extraction were presented for water samples. In this study, the plants and soil samples were analyzed with F-AAS after sample digestion procedure and water samples determined after sample preparation method based on TEOSiP-TS@MWCNTs adsorbent by the UD- μ -SPE procedure.

2. Materials and Methods

2.1. Sampling and reagents

This research is conducted to evaluate the number of heavy metals such as lead, copper, and cadmium in three different types of plants, i.e. wheat, corn, and spinach, as well as in agricultural soil of selected fields. Given that use of wastewater in irrigation is performed in only three stations of Zabol in the east of Iran, and taking the extent of farmland areas, in total 52 samples were selected from all stations. Samples were randomly collected in June 2020 and February 2021. The water sample was prepared from Zabol by a clean glassy tube (100 mL) which was acidified with HNO_3 (2%) and filtered by Whatman filter Sigma, Germany (200 nm) by ASTM method for sampling of waters. The calibration of copper(Co), cadmium(Cd), and lead(Pb) in soil, cultivated plants, and water solution was prepared daily by appropriate Co(II), Cd(II), and Pb(II) stock solution (1000 mg L^{-1}) in Deionized water (DW, Millipore, USA) which was purchased from Sigma, Germany. The acid solutions such as HCl, H_2SO_4 , and HNO_3 were purchased from Sigma, Germany. The bis(triethoxysilylpropyl)tetrasulfide ($\text{S}_4[\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3]_2$, TEOSiP-TS, CAS N:40372-72-3) was purchased from Merck, Germany.

2.2. Synthesis of Adsorbent

The modification of the Bis(triethoxysilylpropyl) tetrasulfide ($\text{S}_4[\text{C}_3\text{H}_6\text{Si}(\text{OEt})_3]_2$, TEOSiP-TS) on the surface of MWCNTs nanostructure has shown in Figure 1. By the acid treatment methods (HNO_3 & H_2SO_4), the carboxylic acid-functionalized MWCNTs (MWCNTs-COOH) were synthesized based on previously reported papers [19]. By reducing the COOH to the OH groups, MWCNTs@

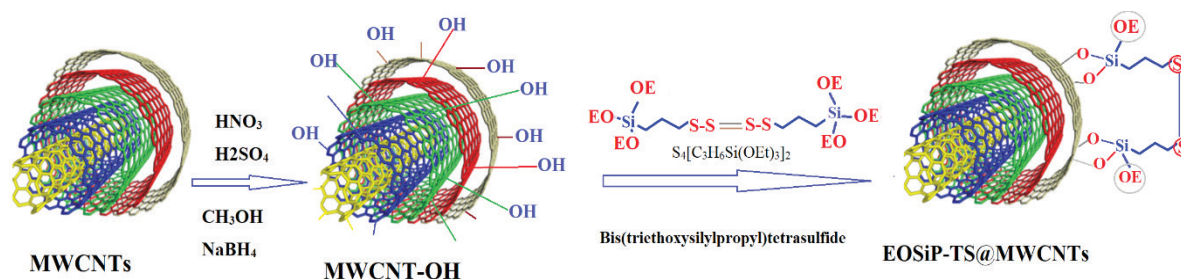


Fig. 1. Synthesis of EOSiP-TS@MWCNTs adsorbent by the Bis(triethoxysilylpropyl)tetrasulfide

OH created. By stirring, 5 g of MWCNTs-COOH mixed with 0.5 g of NaBH_4 and CH_3OH in a 100 mL flask condenser. Then, the mixture was refluxed for 3 h and then it was cooled in room temperature after 2 h. Finally, the MWCNTs-OH nanomaterials were filtered with a Whatman filter and washed many times with the methanol/DW. For the synthesis of the EOSiP-TS@MWCNTs adsorbent, 2 g of MWCNTs-OH were added to a solution of Bis(triethoxysilylpropyl)tetrasulfide (TEOSiP-TS) in presence of toluene in a 100 ml round-bottom flask equipped with magnetic stirring, and then the mixture was heated at 80 °C for 3.5 h by Ar gas. Finally, the TEOSiP-TS @ MWCNTs product was filtered with a Whatman filter.

2.3. Sample preparation

Soil samples were collected from the depth of 2 cm. Polyethylene sampling containers were initially washed with detergent powder and then kept in a container containing 5% nitric acid for a certain period (acid washing). Then, it was rinsed with ionized water. Plant samples were collected inside polyethylene bags, then transferred to the laboratory, and after that completely washed with three-time distilled water to eliminate potential pollutions.

Afterward, the samples were dried up at room temperature. Dried samples were milled and completely crushed and then passed through a sieve with a pore diameter of approximately 0.5 mm. The milled plant samples were placed inside clean glass containers and were dried again at 65°C

for 24 hours. For digestion of plant sample, 2g of milled dried samples were placed inside a round-bottom flask, and then concentrated perchloric acid (4ml), concentrated sulphuric acid (2ml), and concentrated nitric acid (20ml) were added, respectively. The above solution was heated to boil carefully under a hood and over a heater to reduce its volume. In the next step, 20ml water was added to dissolve the sediments, and heated up again to reduce their volume. Afterward, the solution was filtered and its volume was reduced to 250ml. Soil samples were completely oven-dried for 24 hours in the laboratory at 70°C. In the next stage, they were sieved and milled to obtain a completely smooth powder. 0.5 g of the above sample was prepared to be injected into the device, using the complete digestion method [20-22]. After digestion, all samples were analyzed with F-AAS.

2.4. Analytical measurement

Flame atomic absorption spectroscopy (F-AAS, Agilent 55B-AA) was used to measure all elements in the sample. To obtain the required sensitivity in measurements, air/acetylene flame was applied. In order to ensure the accuracy of evaluation, each measurement was performed three times on each sample, and standard deviation and mean of data were obtained. One-way analysis of variance was used to compare the average heavy metals content in various types of selected plants at those three stations. The instrumental conditions for the determination of Cu, Pb, and Cd by F-AAS have explained in Table 1.

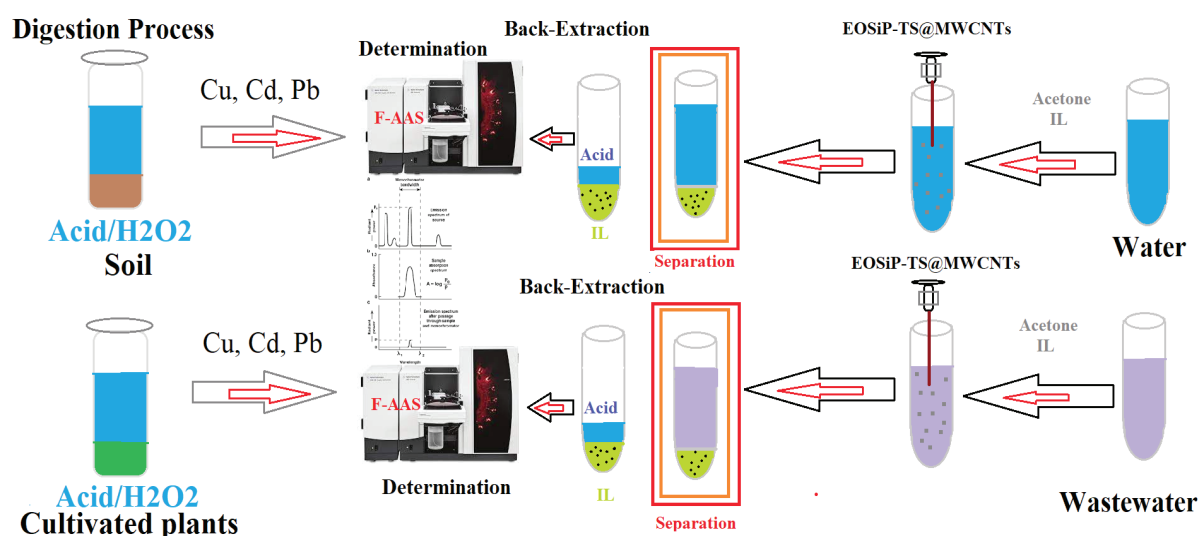
Table 1. The instrument conditions for determination Cu, Pb, and Cd ions by F-AAS

Metal	Lamp current	Fuel	Wavelength (nm)	Slit Width (nm)	Working Range (µg/mL)
Copper	4.0	Air- acetylene	324.7	0.5	0.03-10
			327.4	0.2	0.1-24
			217.9	0.2	0.2-60
Lead	5.0	Air- acetylene	217.0	1.0	0.1–30
			283.3	0.5	0.5–50
			261.4	0.5	5–800
Cadmium	4.0	Air- acetylene	228.8	0.5	0.02–3
			326.1	0.5	20-1000

2.5. General Procedure

The plant and soil samples were digested with acid solutions and after dilution with DW, the Cu, Pb, and Cd ions were determined with F-AAS. On the other hand, by the UD-µ-SPE method, 20 mL of water samples were used for the separation and extraction of the Cu, Pb, and Cd ions at pH 6-6.5. In this procedure, 20 mg of EOSiP-TS@MWCNTs adsorbent dispersed to a mixture of ionic liquid ([HMIM][PF₆], 50 mg) and acetone (250 µL). The mixture was rapidly injected into 20 mL of water and standard solution (5-200 µg L⁻¹) at pH≈6. After ultrasonic for 5.0 min, the Cu, Pb, and Cd ions were chemically adsorbed by four sulfur groups of EOSiP-TS@MWCNTs ([Cu, Cd, Pb]⁺²→[: S-S—

EOSiP]). By procedure, the Cu⁺², Cd²⁺, Pb⁺² ions were extracted by coordination of dative bond of sulfur at pH= 6.5. At high pH of more than 7.5, Cu⁺², Cd²⁺, Pb⁺² ions converted to Cu(OH)₂, Pb(OH)₂, Cd(OH)₂ and precipitated (Recovery of extraction: 65%, 57%, 36%). Finally, the Cu⁺², Cd²⁺, Pb⁺² ions were extracted from waters by a dative bond of S-S and trapped on the IL phase. Then, the IL/ EOSiP-TS@MWCNTs phase was collected by centrifuging for 5 min at 3500 rpm and settled down in the bottom of the conical tube. After back extraction of Cu⁺², Cd²⁺, Pb⁺² ions, the resulting solution was determined by FAAS after dilution up to 1 mL with DW (Fig. 2).

**Fig. 2.** General procedure for determination Ions in the plant, soil, and, water sample

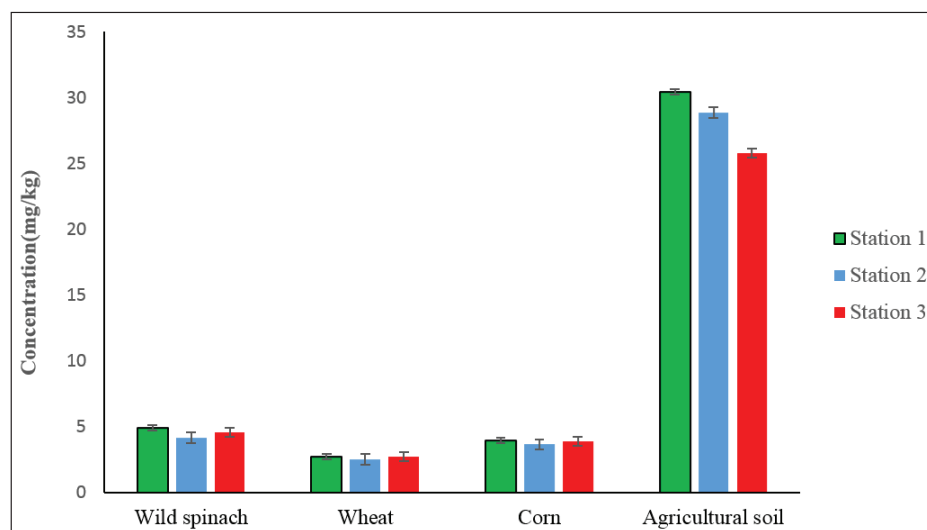


Fig. 3. The concentration of lead in plants and soil in selected stations.

3. Results and Discussion

3.1. Evaluation of Lead in plant and soil

Figure 3 represents that the amount of lead in wild spinach in three stations is above the permissible level for human consumption (2 mg kg^{-1}). While; it is within the normal range for plants ($0.1\text{-}10 \text{ mg kg}^{-1}$). In addition, the concentration of this metal in agricultural soil of all areas is above its permissible range (10 mg kg^{-1}). The statistical analysis was done using SPSS 19 and ANOVA. The findings showed that there is a significant difference between lead concentration in selected areas ($P 7.13 > 4.1$), where the confidence level is 95% and the significance level is less than 0.05.

3.2. Evaluation of Cadmium in plant and soil

Figure 4 indicates that the concentration of cadmium in wild spinach at all three stations is close to the borderline of the permissible range. By increasing in irrigation of wastewater, the cadmium concentration in the plant increased a little. The level of cadmium in wheat and grain corn is lower than the detection limit of the atomic absorption spectrophotometer and therefore not mentioned in Figure 4. The agricultural soil has high level of cadmium. The ANOVA analysis of results indicated that at a confidence level of 95% and a significance level of lower than 0.05, ($P 2.26 > 4.1$), there is a significant difference between mean concentrations of cadmium in the selected regions.

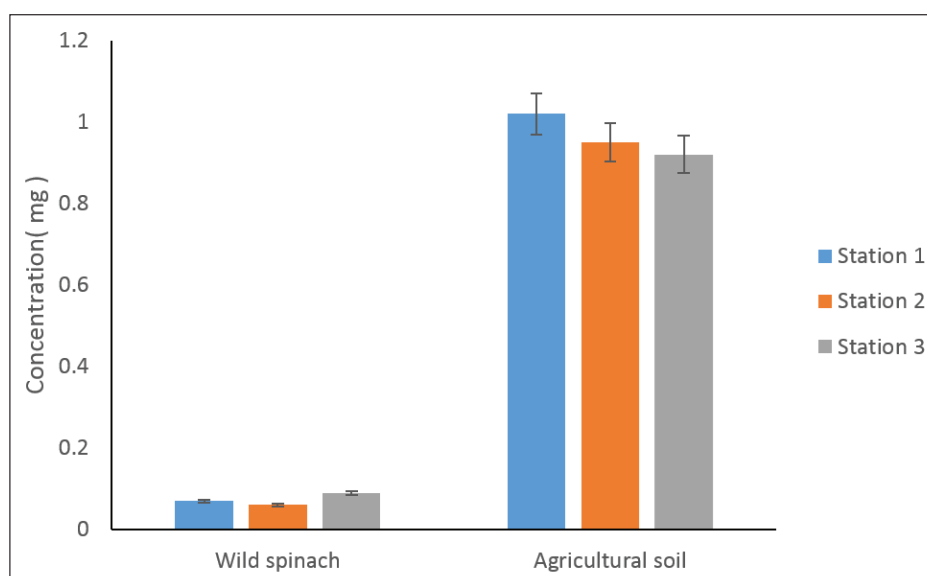


Fig. 4. The amount of cadmium in plant and soil in selected stations

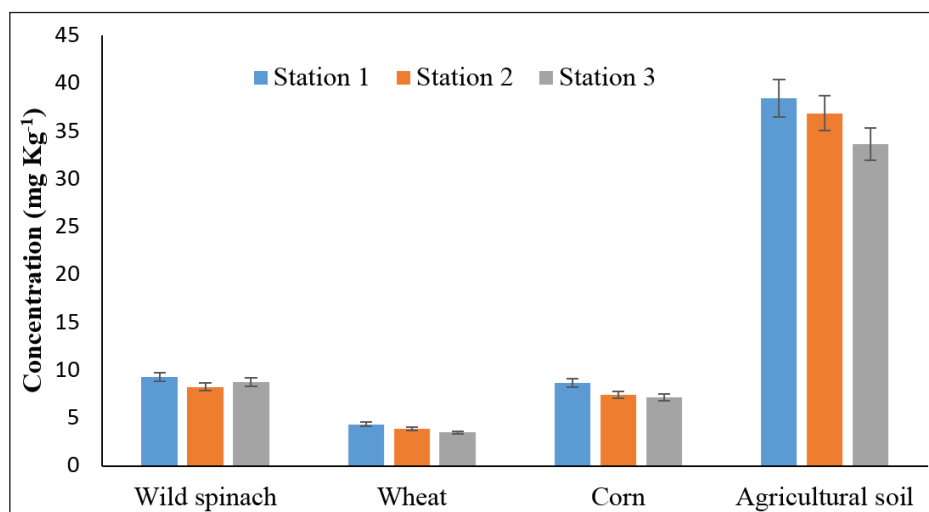


Fig. 5. The amount of copper in plants and soil in selected stations

3.3. Evaluation of copper in plant and soil

Figure 5 showed that the amount of copper in plant samples is lower than its permissible level (20 mg Kg⁻¹) but, in soil samples at all three stations is higher than its permissible range. The findings of ANOVA, at confidence level of 95% and significance level of lower than 0.05 ($P_{12.43} > 4.1$), indicate that the difference of means in copper measured at mentioned stations is significant.

3.4. Optimization process

3.4.1. Digestion reagent and time

1.0 g of plants and soil samples put on the beaker and digested with 10 mL of HNO₃/H₂SO₄ solutions and 2 mL of H₂O₂. The mixture is placed on a heater magnet for 60 min under the hood condition, then 12 mL of extra reagents HNO₃/H₂SO₄/H₂O₂ solutions are added to samples and heated for 60 min at 90°C. The results showed us the favorite time for digestion process is 2 h. The solutions of digested samples (plants and soil) were determined by F-AAS after dilution with DW.

3.4.2. The effect of the amount of adsorbent

The favorite extraction of Cu, Cd, and Pb ions based on the EOSiP-TS@MWCNTs adsorbent was obtained in water samples. By the UD-μ-SPE procedure, the amount of the EOSiP-TS@MWCNTs was studied for 1.5-1000 μg L⁻¹, 1-200 μg L⁻¹, 5-1500 μg L⁻¹ concentrations of Cu, Cd, and

Pb ions, respectively. Therefore, the amount of the EOSiP-TS@MWCNTs adsorbent between 5-50 mg was evaluated for the Cu, Cd, and Pb extraction in 20 mL of water samples before being determined by the F-AAS. The high extraction for the Cu, Cd, and Pb ions was achieved at 20 mg, 18 mg and 15 mg of the EOSiP-TS@MWCNTs adsorbent in standard and water samples. Therefore, 20 mg of the EOSiP-TS@MWCNTs adsorbent was used at pH 6-6.5 (Fig. 6).

3.4.3. The effect of pH

For extraction of Cu, Cd, and Pb ions in water samples, the pH samples were studied from 2 to 11 for 20 mg of adsorbent. So, the different pH sample was evaluated for ions extraction in water and standard samples. The results showed, the high recovery based on the EOSiP-TS@MWCNTs adsorbent for the Cu, Cd, and Pb ions was obtained at pH of 5.5-6.5, 6-7, and 6-6.5, respectively. So, pH 6 was selected for the Cu, Cd, and Pb extraction in water samples (Fig. 7). Also, the recoveries were decreased at less than pH 5.5 and more than pH 7. So, the pH of 6.0 was used as optimum pH for the Cu, Cd, and Pb extraction in water samples (Fig. 7). The mechanism for the Cu, Cd, and Pb extraction based on the EOSiP-TS@MWCNTs adsorbent was obtained by the dative bond of sulfur groups (MWCNTs-S:-S:) at pH 6.0. Also, the Cu, Cd, and Pb ions participated at a pH of more than 8 (M(OH)₂).

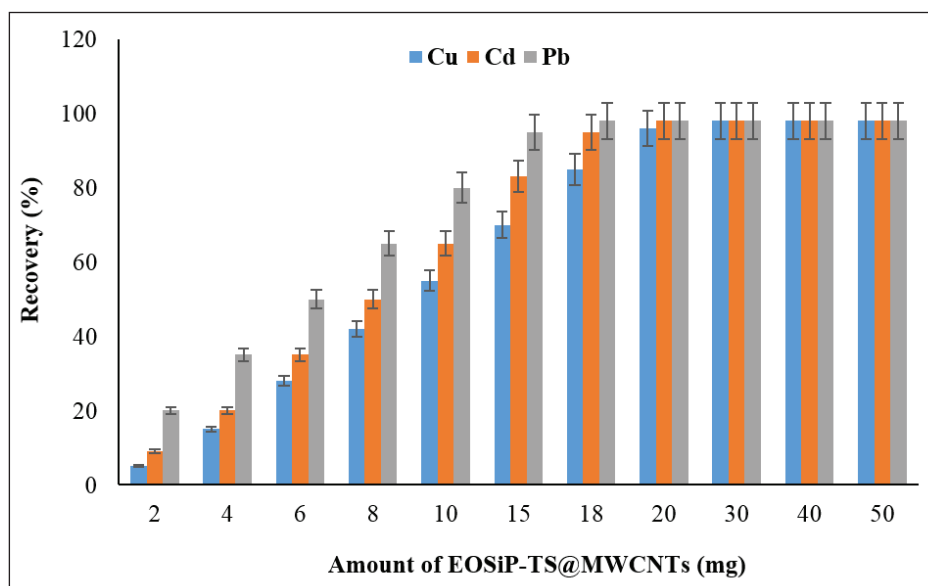


Fig.6. Effect of EOSiP-TS@MWCNTs adsorbent for extraction of Cu, Cd, and Pb ions in water samples by the UD- μ -SPE procedure

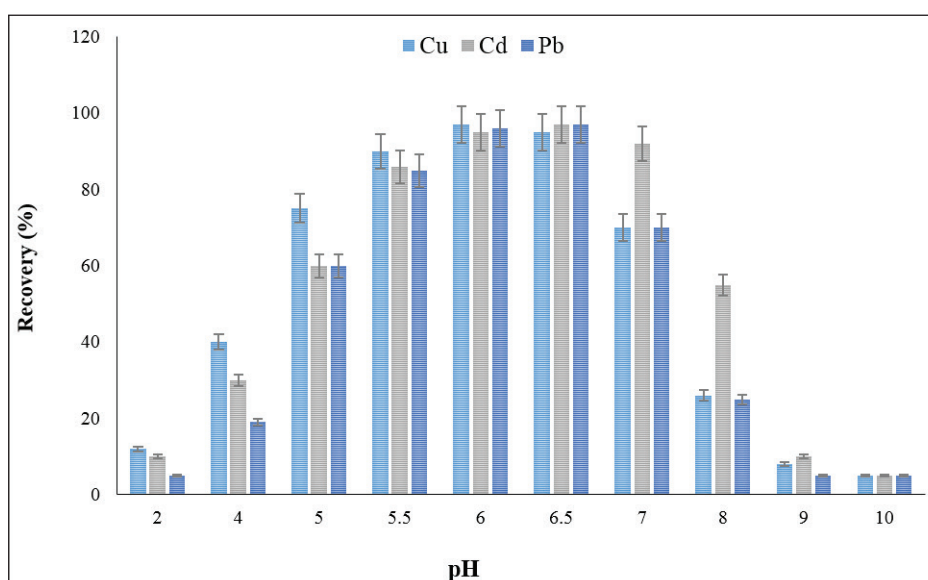


Fig.7. Effect of pH on extraction of Cu, Cd, and Pb ions in water samples by the UD- μ -SPE procedure

3.4.4. The effect of sample volume

Due to the Figure, the extraction of the Cu, Cd, and Pb ions was studied for various volumes of water samples. So, the different volumes between 5-50 mL were evaluated for a concentration of 1.5-1000 $\mu\text{g L}^{-1}$, 1-200 $\mu\text{g L}^{-1}$, 5-1500 $\mu\text{g L}^{-1}$, respectively. The efficient recovery was observed at less than 25 mL, 30 mL and 20 mL for extraction of the Cu, Cd, and Pb ions in water samples, respectively at pH 6.0. So, 20 mL of water samples were used as optimum sample volume for extraction of the Cu,

Cd, and Pb ions in water samples by the EOSiP-TS@MWCNTs adsorbent (Fig. 8).

3.4.5. Interference of ions and absorption capacity

The effect of some ions such as Co^{2+} , Ni^{2+} , Zn^{2+} , V^{3+} , Ag^{+} , Mn^{2+} , Na^{+} , Li^{+} , K^{+} , Mg^{2+} , Ca^{2+} , S^{2-} , CO_3^{2-} , NO_3^{-} , F^{-} , Cl^{-} and I^{-} for extraction of the Cu, Cd, and Pb ions in water samples were evaluated by the UD- μ -SPE procedure. For evaluating, the different interfering ions with various concentrations (2-10

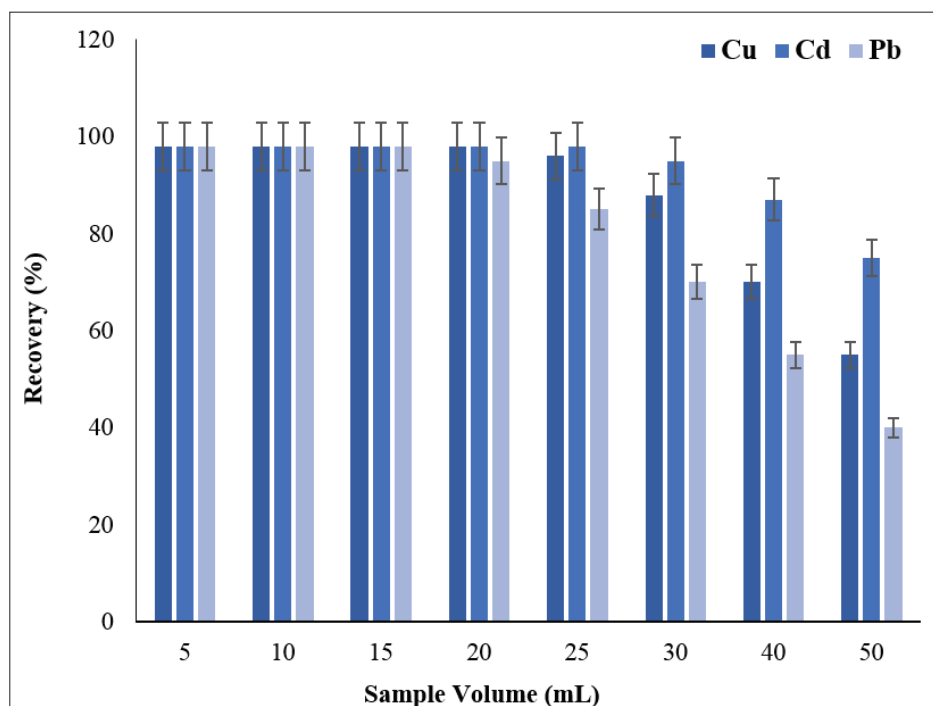


Fig.8. Effect of sample volume on extraction of Cu, Cd, and Pb ions in water samples by the UD- μ -SPE procedure

mg L⁻¹) were examined for 20 mL of water samples. The main concomitant ions in water samples were used and the Cu, Cd, and Pb ions concentrations in the liquid phase were determined by the F-AAS. The results showed that the interference ions cannot decrease the extraction recovery of the Cu, Cd, and Pb ions in water samples by the EOSiP-TS@MWCNTs adsorbent (Table 2).

The absorption capacities of the EOSiP-TS@

MWCNTs adsorbent are related to the size, chemical adsorption, and surface area for the Cu, Cd, and Pb ions extraction in water samples. In a closed tube, 20 mg of the EOSiP-TS@MWCNTs adsorbent were mixed to 100 mg L⁻¹ of the standard solution of the Cu, Cd, and Pb ions in 100 mL of water sample at pH 6.0. After 40 minutes, the Cu, Cd, and Pb ions were chemically adsorbed by the sulfur group of the

Table 2. The effect of the interference of ions for extraction of the Cu, Cd, and Pb ions in water and digested plant/soil samples by the UD- μ -SPE procedure

Interference of Elements	Mean ratio (C _{IE} /C _{Pb,Cd,Cu})	Recovery Pb (%)	Recovery Cd (%)	Recovery Cu (%)
Zn ²⁺	600, 650, 750	97.3	98.4	96.8
V ³⁺	600, 650, 800	97.2	97.9	98.5
Co ²⁺	400, 400, 600	98.3	97.5	98.6
Na ⁺ , K ⁺ , Li ⁺ , Mg ²⁺ , Ca ²⁺	800, 850, 1000	98.7	99.2	98.1
F ⁻ , Cl ⁻ , I ⁻	900, 1000, 1200	98.2	98.6	97.9
Ni ²⁺	400, 500, 500	97.1	98.4	96.9
Mn ²⁺	500, 600, 700	97.9	99.3	96.5
Ag ⁺	200, 200, 250	97.8	98.5	97.1
CO ₃ ²⁻ , NO ₃ ⁻ , S ²⁻	700, 900, 900	98.0	97.5	97.8

EOSiP-TS@MWCNTs adsorbent. Finally, the final concentration of mercury in the liquid phase was determined by F-AAS. Due to the results, the mean of adsorption capacities (AC) of the EOSiP-TS@MWCNTs adsorbent for the Cu, Cd, and Pb ions was achieved at 135.6 mg g⁻¹.

3.4.6. Validation in real samples

By the UD- μ -SPE procedure, the Cu, Cd, and Pb ions were extracted based on the EOSiP-TS@

MWCNTs adsorbent in water samples at a pH of 6.0. The results were validated by spiking to the water samples by the UD- μ -SPE procedure. So, the different concentrations of the Cu, Cd, and Pb ions were spiked by standard solutions (Table 3-5). Also, the Cu, Cd, and Pb ions in plant and soil samples were simply measured by F-AAS after acid digested samples and validated by a microwave digestion system (Table 6).

Table 3. Determination of lead (Pb²⁺) in water samples based on the EOSiP-TS@MWCNTs adsorbent by the UD- μ -SPE procedure

Sample	Added ($\mu\text{g L}^{-1}$)	*Found ($\mu\text{g L}^{-1}$)	Recovery (%)
^a Drinking water	-----	ND	-----
	5.0	4.91 \pm 0.15	98.2
^b Well water	-----	15.75 \pm 0.54	-----
	15	29.94 \pm 0.15	94.6
^c Wastewater	-----	765.76 \pm 28.4	-----
	750	1496.32 \pm 56.33	97.4
^d River water	-----	9.54 \pm 0.43	-----
	10	19.85 \pm 0.88	103.1

* Mean of three determinations \pm confidence interval (P= 0.95, n=5)

†ND: Not Detected

^a drinking water prepared from Zabol city

^b well water prepared from agricultural water of Zabol

^c Wastewater prepared from an industrial chemical in Zabol city

^d River water prepared from Helmand river of Zabol

Table 4. Determination of cadmium (Cd²⁺) in water samples based on the EOSiP-TS@MWCNTs adsorbent by the UD- μ -SPE procedure

Sample	Added ($\mu\text{g L}^{-1}$)	*Found ($\mu\text{g L}^{-1}$)	Recovery (%)
^a Drinking water	-----	ND	-----
	1.0	0.95 \pm 0.15	95.0
^b Well water	-----	6.34 \pm 0.22	-----
	5.0	11.46 \pm 0.46	102.4
^c Wastewater	-----	87.26 \pm 3.72	-----
	100	185.82 \pm 8.34	98.6
^d River water	-----	2.54 \pm 0.11	-----
	2.0	4.47 \pm 0.88	96.5

* Mean of three determinations \pm confidence interval (P= 0.95, n=5)

†ND: Not Detected

^a drinking water prepared from Zabol city

^b well water prepared from agricultural water of Zabol

^c Wastewater prepared from an industrial chemical in Zabol city

^d River water prepared from Helmand river of Zabol

Table 5. Determination of copper (Cu^{2+}) in water samples based on the EOSiP-TS@MWCNTs adsorbent by the UD- μ -SPE procedure

Sample	Added ($\mu\text{g L}^{-1}$)	*Found ($\mu\text{g L}^{-1}$)	Recovery (%)
^a Drinking water	-----	4.65 ± 0.23	-----
	5.0	9.61 ± 0.39	99.2
^b Well water	-----	44.94 ± 2.13	-----
	50	93.96 ± 4.32	98.1
^c Wastewater	-----	523.94 ± 20.73	-----
	500	999.87 ± 43.62	95.2
^d River water	-----	13.65 ± 0.47	-----
	10	23.41 ± 1.08	97.6

* Mean of three determinations \pm confidence interval ($P = 0.95$, $n = 5$)^a drinking water prepared from Zabol city^b well water prepared from agricultural water of Zabol^c Wastewater prepared from an industrial chemical in Zabol city^d River water prepared from Helmand river of Zabol**Table 6.** Validation of acid digested procedure for determination of the Cu, Cd, and Pb ions in plant and soil samples by F-AAS and compared to microwave digestion system coupled to F-AAS

Sample	*Microwave/F-AAS (mg L^{-1})	*Acid digestion/F-AAS (mg L^{-1})	^A Recovery MW (%)
Plant	1.77 ± 0.11	1.82 ± 0.12	102.8
Soil	11.56 ± 0.42	10.96 ± 0.38	94.8
Plant	2.01 ± 0.09	1.93 ± 0.12	96.1
Soil	8.85 ± 0.28	8.66 ± 0.25	97.8

* Mean of three determinations \pm confidence interval ($P = 0.95$, $n = 5$, $\text{RSD} < 2\%$)^A Recovery MW: Recovery Acid digestion/microwave digestion

4. Conclusions

Today, due to potential adverse ecological effects, soil contamination with heavy metals has become a critical concern for the environment. Results obtained in this research showed that amount of heavy metals is accumulated in soil and some plants. Although, the mentioned plants in this study are used to feed livestock and only in a few cases the wheat is used to prepare flour, but lack of suitable grasslands and pastures in Sistan and water shortage would stimulate ranchers to use wastewater increasingly for farmlands. Also, the Cd, Pb, and Cu were determined in digested plant and soil samples by F-AAS. Moreover, the Cd, Pb, and Cu ions in water and wastewater samples based on EOSiP-TS@MWCNTs adsorbent were determined by F-AAS after the UD- μ -SPE

procedure at pH 6-6.5. The RSD% of results was obtained between 1.23-3.11. The mean absorption capacity (AC) of EOSiP-TS@MWCNTs adsorbent for Cd, Pb, and Cu ions was achieved at 144.8 mg g^{-1} , 127.4 mg g^{-1} , and 134.6 mg g^{-1} , respectively in a static system.

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