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Saccharine based carbonyl multi-walled carbon nanotubes: novel modification, characterization and its ability for removing Cd(II) and Cu(II) from soil and environmental water samples

Ahmed Raof Mahmood^{*1}, Mustafa A Alheety², Mohammed M M Asker³, Alarqam Zyaad Tareq⁴ and Ahmet Karadağ⁵

¹Department of Medical Laboratory Technology, Imam Ja'afar Al-Sadiq University, Kirkuk, Iraq

² College of Science, Department of Chemistry, Tikrit University, Tikrit, Iraq

³ College of Education, Tuzkhmatu, Department of Phasic, Tikrit University, Tikrit, Iraq

⁴College of Science, Department of Chemistry, Zakho University, Duhok, Iraq

⁵ College of Science, Department of Biotechnology, Bartin University, Bartin, Turkey

Email ahmedbayatli89@gmail.com

Abstract. This research highlights the chemical modification of one of the carbon nanostructures (multi-walled carbon nanotubes-COOH) with an artificial sweetener (saccharine) to synthesize a highly efficient absorbent material (MWCNTs-CO-Sac). This material was thereafter used to the packing column in solid phase extraction of cadmium and copper divalent ions from real samples. This nano-adsorbent was diagnosed with different techniques: infrared spectroscopy (FTIR), Thermogravimetry (TG), Differential thermal analysis (DTA), powder X-ray diffraction (PXR), energy-dispersive X-ray spectroscopy (EDX), Particle size distribution (PSD) and scanning electron microscopy (SEM). The effect of pH, sample and eluent flow rates, volume, type and concentration of eluent, volume of sample and interfering ions were studied to achieve the optimal conditions for solid phase extraction of Cd(II) and Cu(II) based on the inductively coupled plasma-optical emission spectrometry (ICP-OES). Moreover, the preconcentration factors were calculated to be 75. The results of a limit of detection (LOD) $0.07 \mu\text{gL}^{-1}$ and $0.09 \mu\text{gL}^{-1}$ for Cd(II) and Cu(II) respectively. The relative standard deviation (RSD %) of this study was 0.45% for Cd(II) and 0.51% for Cu(II). The optimized method was applied to soil and environmental water samples.

Keywords. Saccharine; MWCNTs; SPE, cadmium; copper; soil; water.

1. Introduction

In the progression of industrial development, the amount of pollutants has increased in a remarkable way to be the growing problem that must be solved [1]. Among all pollutants in water and soil, heavy elements are considered the most dangerous contaminants of human life. The reason for this is not only due to their ability to accumulate in the tissue of the living cell but also to its non-biodegradation ability [2]. Cadmium, even in low concentrations, is always considered one of the most dangerous elements in humans and animals. Causing damage to the kidney, bronchitis, emphysema and anemia



[3]. According to the reports of the World Health Organization (WHO), its maximum limit for a human is only 0.4-0.5 mg/week, while its concentration in water samples should not exceed 0.005 ppm/litter [4]. Although copper is one of the essential elements in the composition of human and animal, the exposure to this element causes many problems, for example, head pain and increase the heart rate and damage the kidney as well as liver damage [3]. WHO has identified the natural limits of this component and was 1.5 ppm [5]. Particularly, these problems caused by these two elements lead to continued research and design of new materials capable of identifying and removing such elements. In recent years, different techniques such as membrane separation [6], solvent extraction [7] and so on [8, 9] have been used to remove heavy elements from contaminated specimens. These methods have determinants as they can't be considered feasible if the of heavy elements concentration is less than 100 ppm [10]. Among all extraction methods, the technique of solid phase extraction (SPE) is the most suitable technique in terms of (i) adsorbent reusability; (ii) lower cost; (iii) the absence of need for the use of toxic organic solvents; (iv) speed and, most importantly (v) the ability to collect the heavy element from a large volume in no more than 5 ml (preconcentration) [11-15]. In general, this technique is based on the presence of a substance with a high adsorption capacity. Pure or chemically modified carbon nanostructures such as graphene oxide, graphene or carbon nanotubes [10,16-23] were extensively used to extract various elements. Carbon nanotubes have been selected for unique properties such as nanoscale size, tubular nanostructure, high surface area, easy to modify its surface and thermal stability [24]. These properties made this material very famous in the applications of analytical chemistry [25-28]. Interestingly, the MWCNTs has a weak adsorption potential compared to the modified or functionalized one, although it has a larger surface area than its derivatives [4]. These observations are due to the fact that the MWCNT has poor dispersibility and hydrophobic surface in addition to it has no functional groups [3]. Therefore, a covalent modification of the surfaces of MWCNTs is very necessary to promote their adsorption properties [29]. For example, condensation reactions of different amino compounds have been carried out with carbon nanotubes such as 3-aminopyrazole [4], polydopamine [30], indazole [31] and soluble egg shell membrane protein [15]. During the intensive research in published literatures, there is no information on the reaction of saccharine (Figure 1) with carbon nanotubes. By looking at the chemical structure of this poly dentate-heterocyclic amine we can observe that it is rich in the atoms capable of removing heavy metal ions. Thus, in this work, we selected this secondary amine to establish its reactivity with carbon nanotubes.

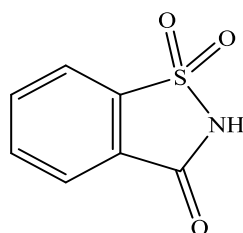


Figure 1 The chemical structure of saccharine

2. Experimental Part

2.1. Materials

The saccharine ($C_7H_5NO_3S$, $\geq 99\%$) and sodium hydroxide ($NaOH$, $\geq 97.0\%$, pellets) are used to prepare sodium saccharinate ($C_7H_4NNaO_3S$). MWCNTs (O.D=7-15 nm, L= 0.5-1.0 μm), nitric acid (HNO_3 , 70%) and sulfuric acid (H_2SO_4 , 99%) are used to prepare carboxylated multiwalled carbon nanotubes (MWCNTs-COOH) which thereafter converted to MWCNTs acyle chloride (MWCNTs-

COCl) by reacting with thionyl chloride (SOCl_2 , 97%) according to the published literature method in [4]. All the previous chemicals are purchased from Sigma-Aldrich, UK. Buffer solutions, ($\text{pH} \leq 3$, 0.02 mol/L HNO_3); ($\text{pH} = 3-8$, $\text{NaOH-NaH}_2\text{PO}_4$); ($\text{pH} = 9-10$, $\text{NH}_3\text{-NH}_4\text{Cl}$) are purchased from Alfa-Aesar, USA. All solvents and the Cd(II) and Cu(II) stock solutions (1000 mg/L) are purchased from Merck, Turkey. Filter papers type (Fisher brandTM Grade 601 filter paper) are supplied from Fisher Scientific, France.

2.2. Instrumentations

The FTIR spectra of the nano materials were measured using (SHIMADZU-FTIR- 8400S) in a range of cm^{-1} (400-4000 cm^{-1}) as KBr discs. Powder XRD patterns were recorded for nano materials by using (Shimadzu – XR – 6000) device. SEM and EDX were measured using (Oxford instruments SEM Tech). PSD measurements were recorded in (Mastersizer, Malvern Instruments Ltd). The Cd(II) and Cu(II) concentrations were determined using (Thermo ScientificTM iCAPTM 7000 Series ICP-OES, Cambridge, UK). TG/DTA analysis was performed using (PerkinElmer, Inc., Shelton, CT, USA).

2.3. Method

2.3.1. Preparation of MWCNTs-CO-Sac

Using an ultrasonic probe device, an amount of 500 mg of MWCNTs-COCl in 50 ml DMSO was sonicated for 30 min. Then 1000 mg of sodium saccharinate (NaSac) in 10 ml DMSO was mixed with suspended MWCNTs-COCl. The mixture was stirred for 24 hours at 100 °C, chilled up to room temperature and then centrifuged for 10 min at 6000 rpm. The solid was collected by decantation and re-dispersed in hot water and ethanol and separated again using a centrifuge. The grayish-black solid was finally dried under a vacuum at 60 °C for 24 hours.

2.3.2. Preparation of Column

In a column of glass (6.40*1cm) filled with a tiny piece of glass wool, a quantity of 0.3982g MWCNTs-CO-Sac was packed and then the upper end was closed with glass wool. The pre-concentration system was designed by connecting the SPE column to a peristaltic pump with tubing.

2.3.3. Preconcentration procedure

A volume of 300 mL standard solutions containing Cd and Cu divalent ions were buffered to pH 7 with phosphate buffer solution and then passed through the column with a flow rate 2 mL/min. The adsorbed ions were eluted using (4ml of 2 mol.L⁻¹ HNO_3) and the eluent solution containing the Cd(II) or Cu(II) was analyzed by ICP-OES.

2.3.4. Digestion of soil samples

The sample was ground in a mill (Glen Mills Inc. type) and sieved with a sieve of 1 mm. 1g of the ground soil sample was digested with 7 ml of concentrated nitric acid at a sand bath, until the dryness, thereafter 25 ml of deionized water was added and then well mixed with stirring for 10 min. The resulting solution was filtered and the volume was completed with water to 50 ml.

2.3.5. Application to soil and water samples

The MWCNTs-CO-Sac packed column was exploited to determine and pre-concentrate of cadmium and copper ions in 3 different water samples and 3 different soil samples obtained from Kirkuk governorate, Iraq. A 100 mL of the digested soil samples and filtered water were used to determine the total concentrations of Cd(II) and Cu(II) in ICP-OES using the optimal conditions.

3. Results and Discussion

3.1. Synthesis and characterization of MWCNTs-COOH, MWCNTs-COCl and MWCNTs-CO-Sac

In the process of preparation of the solid phase material (MWCNTs-CO-Sac) was relied primarily on the conversion of the raw MWCNTs to carboxylic derivative to make the surface interact-able and then we adopted the conversion of this carboxylic modified MWCNTs to the acyl chloride modified MWCNTs. In fact, this is due to the following reasons: (i) the chlorine is a better leaving group than the hydroxyl and (ii) it does not allow the formation of water molecules as a by-product, which forwards the reaction to the starting materials and thus reduces the proportion of the reacted saccharine. In addition, we have converted the saccharine into sodium salts and the reason to prevent the formation of HCl which is able to reverse the reaction rate. Instead, sodium chloride will be formed so the process of purifying the product is easy.

3.1.1. The FTIR measurements

The FTIR spectrum of sodium saccharinate showed the following strong intense absorption peaks: 1641, 1257, 1149, and 1460 cm^{-1} , attribute to $\nu(\text{C}=\text{O})$, $\nu_{\text{asym}}(\text{SO}_2)$, $\nu_{\text{sym}}(\text{SO}_2)$, and $\nu(\text{C}=\text{N})$, respectively [32]. The FTIR spectrum of MWCNT-COOH showed the following relatively strong intense peaks: 3477, 1714, 1649, and 1510 cm^{-1} . These bands represent the $\nu(\text{OH})$, $\nu(\text{C}=\text{O})$ in the carboxyl group, in addition to the bending vibrations of the H_2O and COO^- , respectively [4, 15]. The FTIR spectrum of MWCNT-COCl showed two main peaks at 1668, and 644 cm^{-1} represent the $\nu(\text{C}=\text{O})$, and $\nu(\text{C}-\text{Cl})$ in the acyl chloride group. This spectrum also shows a very weak peak at 3490 cm^{-1} implies the residual group of non-converted carboxylic acid. See Figure 2 (a). In the case of FTIR spectrum of MWCNT-CO-Sac (Figure 2(b)), compared with the FTIR spectrum of MWCNTs-COCl the presence of the new main peak at 1636 cm^{-1} , can be apportioned to the $\nu(\text{O}=\text{C}-\text{NH})$. Furthermore, the presence of the peaks at 3040, 1260 and 1144 cm^{-1} represent the $\nu(\text{C}-\text{H})$, $\nu_{\text{asym}}(\text{SO}_2)$ and $\nu_{\text{sym}}(\text{SO}_2)$ respectively. These assignments confirmed that MWCNTs-COCl was successfully modified by saccharine.

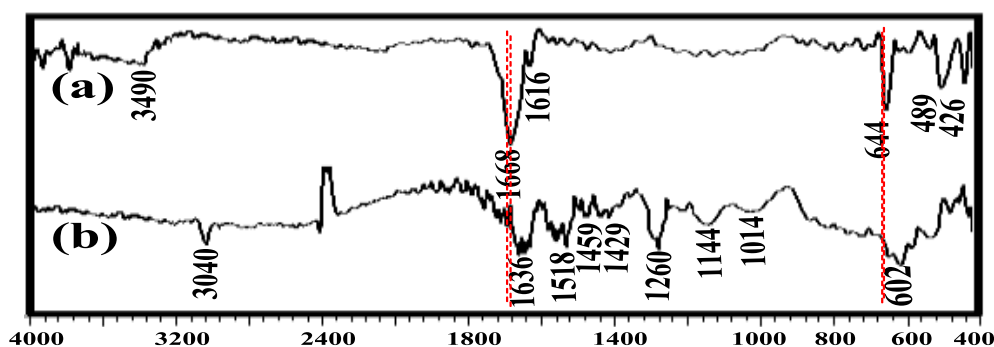


Figure 2 FTIR spectra of (a) MWCNTs-COCl and (b) MWCNTs-CO-Sac

3.1.2. The SEM and EDX measurements

The SEM-cooperated EDX technique provides an excellent platform for both chemical composition and morphology of nanomaterial. The results of the EDX measurements showed the presence of carbon (0.27 KeV) and oxygen (0.52 KeV) in the MWCNTs-COOH as shown in Figure 3 (a). In the case of MWCNTs-COCl, the EDX revealed the presence of chlorine at 2.62 KeV in addition to the carbon and oxygen peaks as shown in Figure 3 (b). While in the MWCNTs-CO-Sac (Figure 3 (c)) the

disappearance of the chlorine peak with appearance of a sulfur peak at 2.30 KeV, which is attributed to the endocyclic sulfur in saccharine, is conclusive evidence of the success of the reaction.

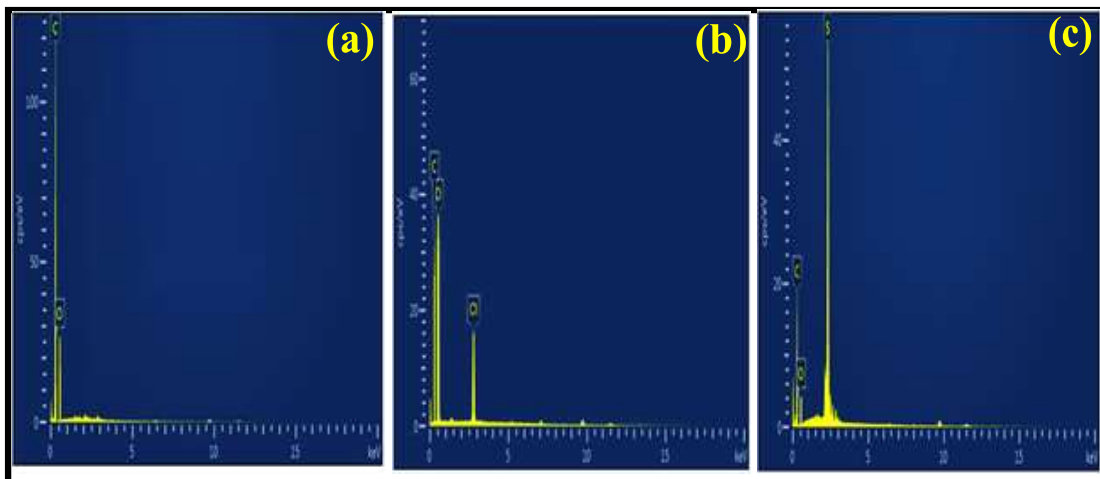


Figure 3 EDX measurements of (a) MWCNTs-COOH, (b) MWCNTs-COCl and (c) MWCNTs-CO-Sac.

The results of SEM measurements showed the tubular structures in all prepared nanomaterials with varying the diameter of the nanotube. Through the attached Figures 4 (a-c) and the diameter calculations of the nanotubes, we observed that the diameter of the carbon nanotubes in the MWCNTs-COOH (Figures 4 (a)) was about 24 nm and the homogeneity was quite high, thus facilitating the reaction on the surface of all the nanotubes. As for the MWCNTs-COCl (Figures 4 (b)), it can be easily observed the increase of the diameter from 24 nm to 30 nm. This may be due to the fact that the interaction here is greater than in the MWCNTs-COOH because, in the case of a carboxylic derivative, it gets more interaction by hydrogen bonds between the surface molecules. It also may be due to the fact that the chlorine size is larger than the hydroxyl group. A significant increase in the diameter of the tubes was observed after the addition of the saccharine (Figures 4 (c)). This is due to the large molecule size of saccharine compared to chlorine, where the diameter of the tube is 41 nm and perfectly homogenous in all the nanotubes. This increase in the diameter is the evidence of the success of the reaction. The maintaining this tubular structure is a challenge in the process of MWCNTs modification because most of such modifications are accompanied by a conglomeration or asymmetry in the addition of molecules on the surfaces of all nanotubes.

3.1.3. The XRD and PSD measurements

The PXRD pattern of the MWCNTs-COCl (Figures 5 (a)) showed that there are only two broad peaks at 26.1° and the other at 43.0° . The peak at 26.1° indicates the graphitic peak resulting from the presence of the cylindrical morphology of the carbon atoms in the MWCNTs with (002) planes [33]. The PXRD peak at 43.0° attributes to the (101) planes of the carbon nanotube structure [34]. The PXRD of MWCNTs-CO-Sac (Figures 5 (b)) exhibited five peaks at 25.29 , 38.10 , 44.28 , 4.42 and 77.39° . These peaks indicating the crystalline feature of MWCNTs-CO-Sac is more than in the MWCNTs-COCl. Besides, the existence of 25.29 and 44.28 proving that the MWCNTs has maintained its cylindrical structure after the modification process and this is concordant with the measurement of SEM. In order to obtain information on how to distribute the particle sizes in the nano samples, a PSD measurement was performed. Furthermore, using this measurement we can obtain the surface area of the prepared nanomaterial. The distribution of the particles in all the samples ranged from 20 nm to 80 nm as broad peaks. The results of surface areas showed that the MWCNTs-COOH

has a higher surface area than the pure and saccharine functionalized species and as follows: MWCNTs-COOH(215 m²/g)>MWCNTs(186 m²/g)>MWCNTs-CO-Sac (75 m²/g). Interestingly, the surface area of the MWCNTs-CO-Sac was substantially lower than that of MWCNTs-COOH and MWCNTs-COCl. Comparable investigations were summarized in the reports [4, 35-37].

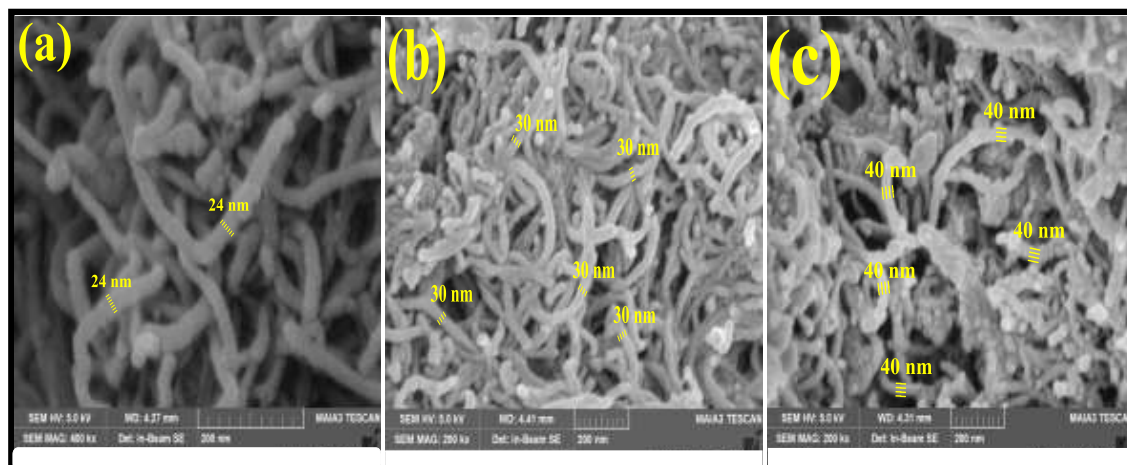


Figure 4 SEM measurements of (a) MWCNTs-COOH, (b) MWCNTs-COCl and (c) MWCNTs-CO-Sac

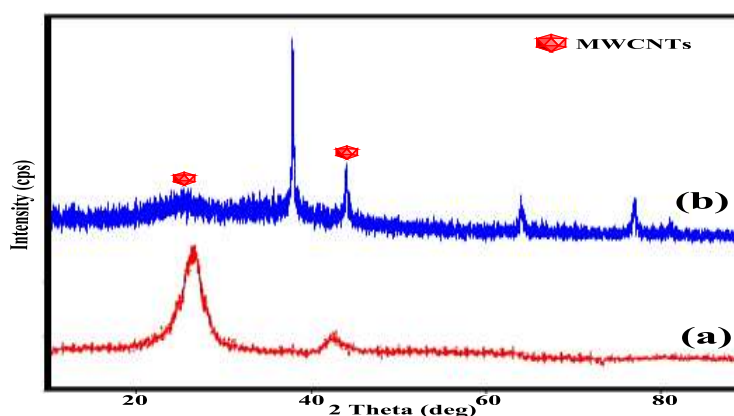


Figure 5 XRD patterns of (a) MWCNTs-COCl and (b) MWCNTs-CO-Sac

3.1.4. Thermal analysis

The majority of functional groups that are grafted on the surface of carbon nanotubes show changes in weight when heated, so the thermal analysis is a significant technique to study the thermal stabilities and changes of the MWCNTs derivatives. All prepared MWCNTs derivatives (Figures 6 (a-c)) showed high thermal stability under approximately 210 °C. All the prepared nano MWCNTs derivatives have decomposed into two stages. The first weight losses were as follows: at 240-450 °C (20%), 225-429 °C (25%), and 210-400 °C (21%) for MWCNTs-COOH, MWCNTs-COCl and MWCNTs-CO-Sac, respectively. The second weight losses were as follows: at 450-740 °C (27%), 430-600 °C (13%), and 400-750 °C (51%) for MWCNTs-COOH, MWCNTs-COCl and MWCNTs-CO-Sac, respectively. In the case of MWCNTs-COOH and MWCNTs-COCl the first and second weight losses can be attributed to the loss of hydroxyl groups in the water between the nanotubes as well as the associated hydroxyl groups or the chlorine, respectively. While in the case of MWCNTs-CO-Sac the first stage can be assigned the dissociation of the amide bonds and the second stage can be attributed to the dissociation of saccharin molecule. All these assignments and their related data are illustrated in Table

1. These changes were more pronounced in the TGA than TG and this is the evidence for the changes in the TG measurement, which were explained in detail.

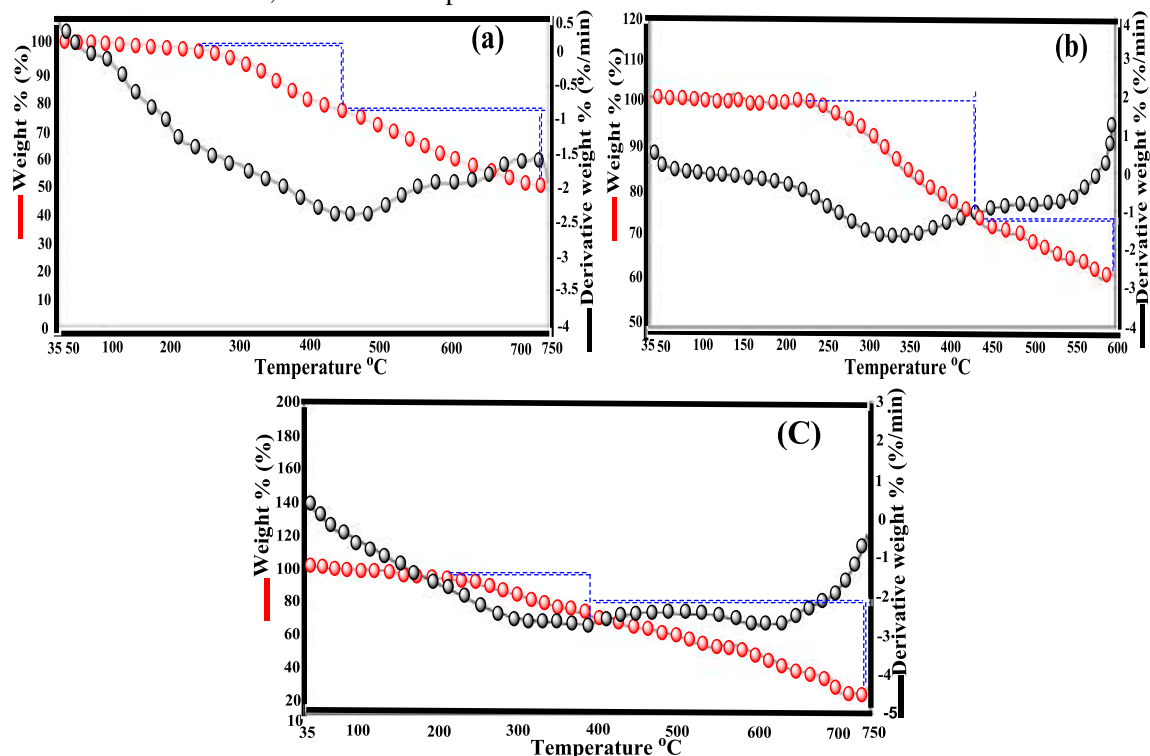


Figure 6 Thermal analysis of (a) MWCNTs-COOH, (b) MWCNTs-COCl and (c) MWCNTs-CO-Sac

Table 1. Thermal analysis data

Comp.	Temp. (°C)	Wt. loss (%)	Assignments
MWCNTs-COOH	240-450	20	Loss H ₂ O, COOH
	450-740	27	
MWCNTs-COCl	225-429	25	Loss H ₂ O, COCl
	430-600	13	
MWCNTs-CO-Sac	210-400	21	Loss H ₂ O, breaking amide bond
	400-750	51	Dissociate of Sac.

3.2. Optimal conditions study

3.2.1. The effect of pH

The recovery results in the different pHs (Figure 7(a)) showed that in a strong acid solution (below 6), the maximum recovery values were 73.88 and 77.10 for Cu and Cd, respectively. It was noted that the increase in recovery was gradual at the trend from the lowest pH to the largest until reach 97.92 and 98.61 for Cu and Cd respectively in pH 7. Then the recovery values gradually declined in basic medium.

3.2.2. The effect of sample and eluent flow rates

When the flow of the sample solution was studied (Figure 7(b)), it was observed that the sample flow rate of 2 ml/min was the best to obtain a higher recovery for both cadmium and

copper ions. The higher flow rates of 2 ml/min were less recoverable and this is a good indication that no adsorption of all ions from the solution at a flow rate of higher than 2 ml/min. The flow rates of less than 2 ml/min are also relatively low, and this explains a very strong correlation between MWCNTs-CO-Sac and the analytes with increasing the time so that it is difficult to remove easily. In the case of eluent flow rates (Figure7(c)), the results showed that 1 ml/min was the best flow rate to recover most ions from the SPE column. As the eluent flow rate increases, the recovery is lower because the saturation of the SPE column with the eluent solution is accompanied by the non-saturation of the SPE column with the eluent solution.

3.2.3. The effect of volume, types and concentration of the eluent solution

In this study, the effect of volume of 2 mol/L of HNO₃ on ions recovery was examined and the results show that the best recovery 98.1 for Cu(II) and 97.7 for Cd(II) was obtained using 4 ml (Figure7(d)). Three eluent types (HNO₃, HCl, CH₃COOH) were examined with different concentrations (0.5, 1.0, 2.0) mol/L (Figure7(e)). The results show that the best recovery was achieved using (2 mol/L of HNO₃). The maximum recoveries were 97.92 and 98.49 for cadmium and copper, respectively.

3.2.4. The effect of sample volume

This effect was examined in the range (50-500) ml with a sample flow rate of 2ml/min (Figure7(f)). The optimal sample volume was recorded to be 300 ml for both copper and cadmium. The recorded quantitative recoveries were 97.7% for copper and 96.3% for cadmium.

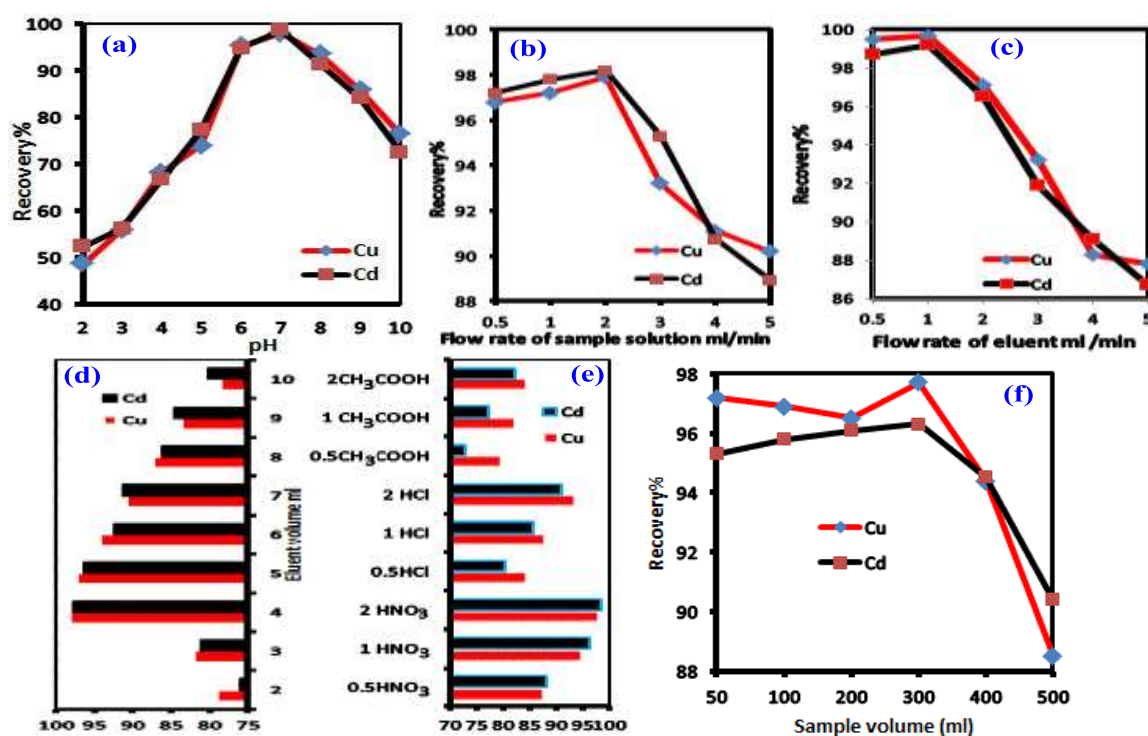


Figure 7 The effect of (a) pH, (b) sample flow rate, (c) eluent flow rate, (d) eluent volume, (e) eluent concentration and (f) sample volume on the recoveries of Cu and Cd.

3.2.5. The effect of existing of interfering ions

In Table 2, anions have very little effect on Cd(II) and Cu(II) recovery, which means that these ions do not compete Cd and Cu on the active sites in MWCNTs-CO-Sac. The same effect was observed when

high concentrations of alkali and alkaline earth metal ions were used. The tolerans limits of the interfering ions were very high, showing that the current method can be applied to high saline and complex matrix media. The maximum concentrations of transition and heavy metals that can be available in solution and does not affect the values of recovery available have been determined in Table 2.

Table 2. The effect of the interfering ions on recovery of the analytes

Ion	Conc. mg.L ⁻¹	Recovery%	
		Cd	Cu
Na ⁺	8000	97±1.3	98±0.3
K ⁺	10000	98±2.1	96±1.2
Cl ⁻	12000	95±1.6	98±1.1
Mg ²⁺ ,Ca ²⁺	5000	97±1.6	96±0.22
Cu ²⁺	20	99±1.4	-
Ni ²⁺	25	99±1.3	97±0.8
Co ²⁺	20	99±1.5	95±1.7
Fe ³⁺ ,Cr ⁺³ ,Al ⁺³	40	98±0.4	98±1.0
NO ₃ ⁻ ,CO ₃ ²⁻ ,SO ₄ ²⁻ ,PO ₄ ³⁻	4500	97±2.2	96±2.1
Cd ²⁺	20	-	99±0.8
Zn ²⁺	20	100±1.1	99±1.5
Pb ²⁺	20	99±1.0	97±0.7

3.3. Analytical figures of merit

The limit of detection (LOD) for the solid phase extraction process of Cd and Cu divalent ions of the present MWCNTs-CO-Sac column was carried out under ideal conditions after application of the procedure to a blank solution. The limits of detection were found to be 0.07 µg L⁻¹ and 0.09 µg L⁻¹ respectively for Cd(II) and Cu(II) based on the 3 standard deviations of 10 reagent blank solution lines. The relative standard deviation (RSD%) in this study was calculated to be 0.45% for Cd(II) and 0.51% for Cu(II) and the preconcentration for both ions was 75. The accuracy of the SPE using MWCNTs-CO-Sac was established with the standard addition method.

3.4. Application to various water and soil samples

The present MWCNTs-CO-Sac column/SPE method was applied to 3 water and 3 soil samples using the standard addition method. Quantitative recovery values were found in the samples for Cd(II) and Cu(II). The results in (Table 3) show that the MWCNTs-CO-Sac sorbent can be used as an effective nano sorbent in a solid phase extraction method.

Table 3. Determinations of Cd(II) and Cu(II) in soil and environmental water samples

Water	Added $\mu\text{g.L}^{-1}$	Cd(II)		Cu(II)		Soil	Added mg.L^{-1}	Cd(II)		Cu(II)	
		Found $\mu\text{g.L}^{-1}$	Rec. %	Found $\mu\text{g.L}^{-1}$	Rec.%			Found $\mu\text{g.g}^{-1}$	Rec.%	Found $\mu\text{g.g}^{-1}$	Rec.%
River	-	<BDL	-	<BDL	-	City Centre	-	0.28±0.1	-	1.21±0.4	-
	5.0	4.89±0.2	97.8	4.97±0.2	99.4		0.5	0.77±0.2	98.2	1.70±0.4	99.6
	10.0	9.98±0.1	99.8	10.1±0.3	100		1.0	1.25±0.4	97.1	2.18±0.1	96.9
Waste	-	<BDL	-	0.61±0.4	-	Senaey street	-	0.15±0.3	-	2.33±0.3	-
	5.0	5.03±0.2	100.6	5.48±0.2	99.4		0.5	0.66±0.1	102	2.82±0.2	98
	10.0	9.85±0.4	98.5	10.4±0.1	99.9		1.0	1.12±0.1	97.4	3.32±0.7	99.4
Tap	-	<BDL	-	<BDL	-	Kirkuk citadel	-	<BDL	-	<BDL	-
	5.0	4.94±0.3	98.8	4.88±0.7	99.6		0.5	0.48±0.8	96.9	0.50±0.5	100.2
	10.0	9.92±0.2	99.2	9.87±0.3	98.7		1.0	0.99±0.1	99.3	0.97±0.3	97.6

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

Conclusion

In this work, the new nanotubular adsorbent (MWCNTs-CO-Sac) was prepared using saccharine sodium salt and carbon nanotubes, which gave the product with a good yield and less reaction time than if saccharine was used in the raw form. We were also able to maintain the tube structure with the possibility of modifying the entire tube surface and this is demonstrated by the SEM and XRD techniques. This nanotubular adsorbent is economically less expensive than raw carbon nanotubes with a much greater ability to remove metals than if used alone. The MWCNTs-CO-Sac provided full adsorption of the studied elements with moderate reaction conditions of pH and at room temperature with no need to use hazardous solvents. We recommend using this material to solve water pollution problems with heavy metals because it involves the use of pH 7 at room temperature with a high re-usability of 10 times without frequent washing. However, after 10 times of use, it can be reactivated by soaking in diluted nitric acid (2 mol.L⁻¹) for only 24 hours and then washed with water to get discarded of the acid.

The use of MWCNTs-CO-Sac was compared with previously prepared nano adsorbents which are illustrated in Table 4. According to the results of previous studies the limit of detection was calculated to be very small in value, which additional demonstrates that, this nano tubular adsorbent is very sensitive and more preferable for removal and determination of cadmium and copper in water and soil samples.

Table 4. A comparison between MWCNTs-CO-Sac and previously prepared nano adsorbents

Ion	System	Technique	pH	eluent Mol L ⁻¹	PF	LOD ng/ml	Ref.
Cu ²⁺ , Cd ²⁺	MWCNTs-APDC	FAAS	7	1HNO ₃ in acetone	100	0.30&0.45	[38]
Cu ²⁺ , Cd ²⁺	Fe ₃ O ₄ @catechol	FI-ICP-OES	9	0.3EDTA	138&9	0.2&0.5	[39]
Cu ²⁺	MWCNTs-violuric acid	FAAS	6	1 HNO ₃	40	0.36	[40]
Cd ²⁺ , Cu ²⁺	MWCNTs-TSC	FAAS	5	1.5 HNO ₃	100	0.13&0.21	[41]
Cd ²⁺ , Cu ²⁺	MWCNTs- α -benzoin oxime	FAAS	6.5	2 HNO ₃	50	1.7&2.3	[42]
Cd ²⁺ , Cu ²⁺	1-Nitro-2-naphthol-3, 6-disulfonic acid disodium salt	FAAS	7	2 HNO ₃ in acetone	15	1.4& 5.8	[43]
Cd ²⁺	MWCNTs -tartrazine	FAAS	7	2 HCl	40	0.8	[44]
Cu ²⁺ , Cd ²⁺	MWCNTs/quinalizarin	FAAS	6	2 HNO ₃	100	0.30&0.65	[45]
Cd ²⁺ , Cu ²⁺	MWCNTs - BTAO	FAAS	7	2HNO ₃	100	0.7&1.2	[46]
Cd ²⁺ , Cu ²⁺	MWCNTs - Sac	ICP-OES	7	2 HNO ₃	75	0.07&0.09	This work

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