



Effect of oxidation and geometrical dimensions of carbon nanotubes on Hg(II) sorption and preconcentration from real waters

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ABSTRACT

This study reports for the first time the use of oxidized and non-oxidized multi-walled carbon nanotubes (MWCNTs) of different geometrical dimensions for Hg(II) adsorption and preconcentration in water samples. The shapes of the Hg isotherms varied from L2, C1 and H2 according to the dimensions and oxidation conditions of the MWCNTs. Analysis of adsorption data by Langmuir, Freundlich and Dubinin–Radushkevich isotherms revealed that Hg(II) removal by L-MWCNT-4060-NA (nitric acid-oxidized MWCNT of external diameter 40–60 nm and length 5–15 μm) has the lowest sorption energy, which reflects the favorable uptake of Hg(II) by this adsorbent. Sorbents showed variable sorption capacities for mercury (0.70–3.83 mg g^{-1}). However, in the preconcentration experiments, L-MWCNT-4060-NA exhibited the highest enrichment efficiency for a preconcentration of 100 $\mu\text{g L}^{-1}$ Hg(II) at pH 7. The limit of quantifications of Hg(II) was 0.0123 $\mu\text{g L}^{-1}$ in water. Analysis of Hg(II) in tap and reservoir waters gave high spike recovery (88–95%, RSD < 3%). Mineral water was used to check interference from foreign ions. The method was validated by determination of mercury in digested phosphate rock samples and certified reference Polish tobacco leaves, in which the method was highly accurate and precise.

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1. Introduction

Mercury is one of the most harmful elements to man and other organisms [1,2]. It is also cumulative and persistent in human body and the environment as well [1]. Mercury may be found in soil and river bed sediments due to direct application of fertilizers and fungicides [3,4]. Howari and Banat [5] studied heavy metal pollution in sediments of Jordan valley and Yarmouk River and they found that they are contaminated with mercury. The presence of mercury in Jordan valley and Yarmouk sediments is probably attributed to anthropogenic sources. Thus its determination in water is very important. The upper limit for total mercury concentration in drinking water set by the European Community is 1.0 $\mu\text{g L}^{-1}$ [6].

Cold vapor atomic absorption spectrometry (CV-AAS) was extensively used for the quantitative determination of mercury in various types of samples due to its high sensitivity and selectivity as well as relatively low operation costs with an extremely low detection limit (<1.0 $\mu\text{g L}^{-1}$) [7–9]. The direct determination of trace concentrations of heavy metal ions has many problems associated with matrix interferences and low sensitivity due to the extremely low concentrations of these metals. For this reason, a preliminary separation and preconcentration of trace elements from the matrix are required. Solid-phase extraction (SPE) is a sample preparation technique that is

employed to clean up or concentrate samples prior to analysis. Compared to other sample preparation techniques, SPE provides cleaner extracts with higher enrichment factor, lower cost and better performance [10].

Many natural adsorbents including multi-walled carbon nanotubes (MWCNTs) were extensively used for sorption of heavy metals. Sorption of divalent metal ions from the aqueous solution by carbon nanotubes (CNTs) was reviewed by Rao et al. [11]. The sorption mechanism was mainly attributed to chemical interactions between the metal ions and the surface functional groups of the CNTs. The sorption capacities of CNTs remarkably increased after oxidation by NaOCl, HNO₃ and KMnO₄ solutions. Some studies reported the use of carbon-based sorbents for adsorption of Hg(II) from the aqueous solution. For example, the removal of Hg(II) ions from contaminated water using MWCNTs was investigated by Tawabini et al. [12]. The sorption properties of CNT and the possibility of their chemical functionalization have attracted the attention of many authors to use the MWCNT for SPE of pollutants from various matrices. Preconcentration of organic compounds using the MWCNT was reviewed by Valcarcel et al. [13], Cserhádi [14] and Pyrzynska [15], while preconcentration of inorganic metals was reviewed by Lemos et al. [16] and Pyrzynska [17]. With a very low detection limit, Shang [18] has reported the novel application of the MWCNT for mercury preconcentration in natural waters and detection by cold vapor atomic fluorescence spectrometric. The results of Shang [18] were promising and more investigations for understanding the behavior of different MWCNTs are necessary.

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In our previous studies, we have shown that dimensions and oxidation of the MWCNT gave various preconcentration and SPE efficiencies for pesticides [19] and metals [20]. In this work, we report for the first time a detailed study for the effect of geometrical dimensions and oxidation of MWCNTs on Hg(II) adsorption and preconcentration. Assessment of Hg(II) adsorption by MWCNTs is carried out by batch adsorption experiments, while SPE/preconcentration studies were performed by column experiments. The method of Hg(II) SPE/preconcentration is optimized and used to quantify Hg(II) in different matrices including real waters and phosphate rocks. The figures of merits were estimated. The effect of interferences from foreign ions was checked by analysis of mineral waters which are known to contain nominal amounts of ions. The validity of the SPE method was checked by analysis of certified reference tobacco leaves.

2. Materials and methods

2.1. Materials and reagents

Mercury(II) ion standard stock solution (1000 mg L⁻¹) was purchased from Scharlau (Spain) and used for preparing other diluted Hg(II) solutions using distilled water. All reagents used were of analytical grade or better. Hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), disodium hydrogen phosphate–sodium dihydrogen phosphate (pH 6–8), and ammonium chloride–ammonia (pH 8–10) were used as buffers. Six multi-walled carbon nanotubes (MWCNTs) of different dimensions (length and external diameters) were purchased from Shenzhen Nanotech port Co. Ltd., Shenzhen, China. The adsorbents were abbreviated according to their dimensions/oxidation as: L-MWCNT-1020 (external diameter range: 10–20 nm, length: 5–15 μm); L-MWCNT-1030 (external diameter range: 10–30 nm, length: 5–15 μm); L-MWCNT-2040 (external diameter range: 20–40 nm, length: 5–15 μm); L-MWCNT-4060 (external diameter range: 40–60 nm, length: 5–15 μm); L-MWCNT-60100 (external diameter range: 60–100 nm, length: 5–15 μm); and S-MWCNT-4060 (external diameter range: 40–60 nm, length: 1–2 μm). Before use, MWCNTs were dried at 70–80 °C for 2 h. Oxidation of L-MWCNT-4060 was performed using three different oxidation conditions: concentrated HNO₃ solution (at 25 °C for 24 h); 1.0 M of (NH₄)₂S₂O₈ (25 °C for 18 h); and 50% by vol. of (H₂O₂ and 1.0 M H₂SO₄) at 50 °C for 1 h. Adsorbents were then washed with water to remove excess oxidizing agent and other water soluble species. The oxidized adsorbents were labelled L-MWCNT-4060-NA, L-MWCNT-4060-HP and L-MWCNT-4060-APS, respectively, where NA, HP and APS refer to nitric acid oxidation, hydrogen peroxide oxidation and ammonium persulphate oxidation, respectively. L-MWCNT-4060 refers to the non-oxidized sorbent. The certified reference material (INCT-PVTL-6 Polish Virginia Tobacco Leaves) was purchased from the Institute of Nuclear Chemistry and Technology (Warszawa, Poland). A phosphate rock (PR) sample was supplied by the Jordan Phosphate Mines Company (JPMC, Jordan). The phosphate rock is mainly made up of P₂O₅ (33%), CaO (48%) and SiO₂ (10%) as indicated from the XRF analysis provided with the sample.

2.2. Hg(II) adsorption by MWCNTs

Adsorption isotherm of Hg(II) at 25 ± 1 °C was measured at different initial concentrations and for all adsorbents according to the following procedure: A 25 mg sorbent was added to 100 mL volumetric flasks containing 50 mL of Hg(II) solution of varying concentration within the range 1–10 mg L⁻¹ at pH 7.0. pH measurements were made by Weilheim type (Germany). The flasks were sealed and placed in a thermostated shaker (GFL 1083, Germany) for one day to attain equilibrium. After equilibrium, the adsorbent was separated from the solution using centrifugation and the remaining concentration was analyzed using A Cary 100Bio UV–VIS spectropho-

tometer and the remaining concentration was determined using a calibration graph constructed at 302 nm.

2.3. Adsorption parameters and models

The measured surface concentration (q_e) was estimated as: $q_e = [C_o - C_e]V/m$, where C_o , C_e , V , and m are initial metal concentration (mg L⁻¹), metal concentration at equilibrium (mg L⁻¹), total volume (L) and mass (g) of the adsorbent, respectively. Three common equations relating q_e with C_e were used to model adsorption data:

$$\text{Langmuir model: } \frac{C_e}{q_e} = \frac{1}{b \cdot Q_{\max}} + \frac{C_e}{Q_{\max}}$$

where Q_{\max} (mg g⁻¹) is the amount of adsorbate at complete monolayer coverage, and b (L mg⁻¹) is a constant that relates to the heat of adsorption [21].

$$\text{Freundlich model: } q_e = K_F C_e^n$$

K_F (mg¹⁻ⁿ g⁻¹ Lⁿ) represents the sorption capacity when metal equilibrium concentration equals to 1, and n represents the degree of dependence of sorption on equilibrium concentration, or it reflects the surface heterogeneity.

$$\text{Dubinin–Radushkevich model: } q_e = q_m e^{(-B/RT \ln(1 + \frac{1}{C_e^2}))}$$

This model was chosen to estimate the porosity characteristics of the MWCNTs and the apparent energy of adsorption [22]. The constant B (kJ² mol⁻²) is related to the free energy of Hg(II) sorption by MWCNTs. The apparent energy E (kJ mol⁻¹) of adsorption is calculated from B using the formula $E = 1/(-2B)^{1/2}$ [23]. The parameters of the models were predicted using non-linear fitting methodology.

2.4. SPE procedure of mercury(II)

Typical SPE cartridge was prepared by placing 200 mg of L-MWCNT-4060-NA in an empty 6 mL polypropylene SPE-tube “filtration tube” (from Supelco). Extractions were carried out using a visiprep-12-port vacuum manifold (Supelco, Germany) connected to a vacuum pump (KNF NEUBERGER D-7800, Germany). The adsorbent was pre-washed with 10 mL of distilled water and finally with 10 mL of the desired buffer solution in preparation to extraction procedure. Typically, 150 mL of water sample containing mercury(II) at pH 7 was passed through the column at a flow rate of 6 mL min⁻¹, and the retained Hg(II) was eluted with 5 mL of 1.0 M HNO₃ solution. Hg(II) was quantified using atomic absorption spectrometer (Thermo S1 atomic absorption spectrometer, Thermo Electron Corporation, Cambridge) equipped with a Hg-hollow cathode lamp and a cold vapor kit model (Thermo VP100). Hg(II) was measured at 253.7 nm.

2.5. Sample preparation

Hg(II) was quantified in different matrices including: tap water, reservoir water, mineral water, phosphate rock, and tobacco leaves. Tobacco leaves were worked as a sample and as a certified material as well. Tap water was obtained from our school and the reservoir water was collected from a local well in the Amman area. The mineral waters were purchased from a local store. The leaves were Polish Virginia Tobacco Leaves (INCT-PVTL-6) and digested prior to extraction using 50% by vol. of the HNO₃–H₂O₂ mixture at 80 °C for 2 h as outlined in the literature [24]. The final mixture was carefully filtered. Local phosphate rock was crushed, ground, passed through 0.30 mm sieve, and then homogenized prior to use in this work. Digestion was carried out by adding 10 mL of 4.0 M HNO₃ to 1.0 g phosphate rock, the mixture was heated for 30 s in a 170 W microwave oven (SAMSUNG, model number

MS83HCE, China). The final mixture was carefully filtered. In preparation for SPE, all solutions were filtered through 0.45 μm micropore membranes, the pH was adjusted to 7.0 and stored in polyethylene bottles at 4 °C.

3. Results and discussion

Our previous investigations have indicated that the geometrical dimensions of the MWCNT provided various SPE efficiencies for pesticides [19] and metals [20]. Additionally, oxidation of the CNT surface may alter the adsorption properties of the CNT and open the caps (tips) of the CNT [25]. Generation of surface oxides by chemical oxidation of the surface was previously reported [26,27]. In this work, the influence of geometrical dimensions and oxidation of MWCNTs on Hg(II) adsorption and preconcentration is investigated.

3.1. Adsorption characteristics of Hg on various dimensions of MWCNTs

Adsorption isotherms of Hg(II) at 25 °C by different MWCNTs are presented in Figs. 1–3. At pH 7, the predominant species of Hg(II) is Hg(OH)₂ as indicated from the constructed distribution curves of mercury (α -pH plot). Based on precipitation calculations, the ion-product value $[\text{OH}] \times [\text{Hg(II)}]$ does not exceed the corresponding K_{sp} value of Hg(OH)₂ and this rules out the formation of the metal hydroxide during adsorption and even in preconcentration studies. The shapes of the Hg isotherms indicate L2 (five isotherms), C1 (two isotherms) and H2 (two isotherms) according to Giles and Smith classification [28]. In L2-type isotherm, adsorption of solute on the adsorbent proceeds until a monolayer is established [28]. The shape of isotherms presented in Fig. 1 is indicative of high affinity between the sorbents' surfaces (L-MWCNT-1020, L-MWCNT-1030, L-MWCNT-2040, S-MWCNT-4060, and L-MWCNT-4060-HP) and the colloidal Hg(OH)₂. Relatively speaking, the Hg(OH)₂ colloids were strongly adsorbed by L-MWCNT-1020 and L-MWCNT-2040 and poorly adsorbed by S-MWCNT-4060. In fact, L2 isotherm is usually reported for ionic solutes (e.g., metal cations) adsorbed on a polar adsorbent with weak competition with the solvent molecules [28]. C1-adsorption isotherm was noted in L-MWCNT-4060 and L-MWCNT-4060-NA. As indicated in Fig. 2, the surface concentration of Hg ions (q_e) was linear with Hg(II) ion concentration in the solution over the studied concentration range (1–10 mg L⁻¹). The third type of isotherms was H2 (Fig. 3) and reported when Hg ions were adsorbed by L-MWCNT-60100 and L-MWCNT-4060-APS. In H2 isotherm, the affinity of Hg(OH)₂ colloids for the surface was very high at lower concentration, due to lack of competition from H₂O and the surface is filled at lower levels of Hg ions. Accordingly, L-MWCNT-60100 and L-MWCNT-4060-APS would have a high extraction power and preconcentration of Hg(II) ions from the solution at pH 7. The adsorption data of all isotherms were represented by Langmuir isotherm to find the saturation value,

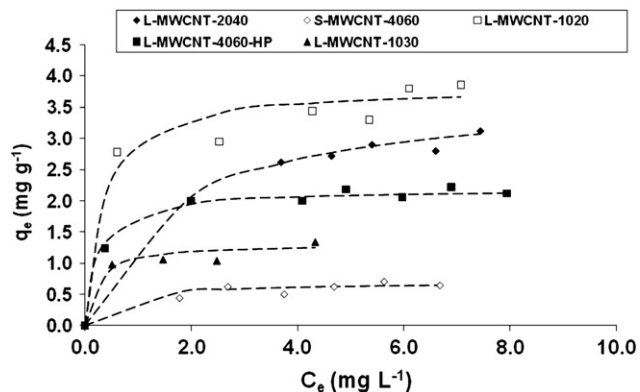


Fig. 1. L2-type adsorption isotherms of Hg(II). Dashed lines represent the Langmuir model.

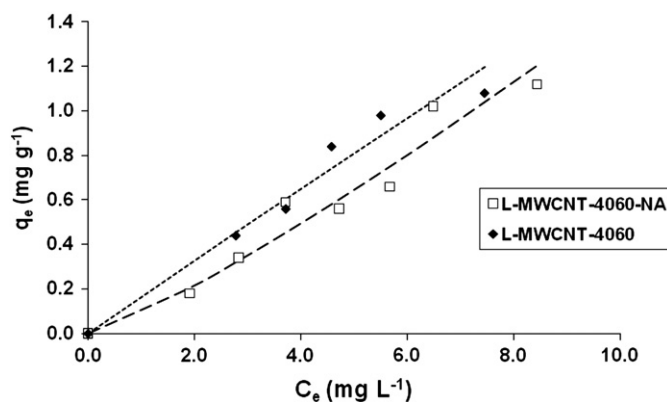


Fig. 2. C1-type of adsorption isotherms of Hg(II). Dashed lines represent the Freundlich model.

Freundlich isotherm to find the “favorability” of adsorption and heterogeneity of adsorbent and finally by Dubinin–Radushkevich isotherm to find the magnitude of adsorption energy and the extent of adsorption. The parameters of the models were summarized in Table 1. The maximum adsorption capacity, Q_m (mg g⁻¹) for Hg(II), showed the following trend: L-MWCNT-1020 > L-MWCNT-2040 > L-MWCNT-4060-HP > L-MWCNT-60100 > L-MWCNT-4060-APS > L-MWCNT-1030 > S-MWCNT-4060. Accordingly, the first two extractants would have a high preconcentration performance compared to others. According to the b value, L-MWCNT-60100 would be the best extractant for Hg(II) from the solution, and a higher b value indicates a favorable adsorption/extraction process. Tawabini et al. [12] reported a higher capacity of MWCNTs for Hg(II) 13 mg g⁻¹. Nonlinear energy distribution active sites and surface heterogeneity of MWCNTs were inferred from Freundlich analysis. As K_F increases, performance increases and this indicates that L-MWCNT-1020 and L-MWCNT-60100 are the best adsorbents/SPE for Hg(II). The n values for almost all systems are less than unity, which reflects the favorable adsorption of Hg(II). The surface of all MWCNTs is highly heterogeneous and contains active sites of variable energies as n is less than unity. The surface of L-MWCNT-4060-NA is more homogenous than other adsorbent as indicated from the n value ($n=1.2$). Finally, the Dubinin–Radushkevich model ($r^2=0.7036-0.9554$) indicated that Hg(II) adsorption followed the order: L-MWCNT-1020 > L-MWCNT-2040 > L-MWCNT-4060-HP > L-MWCNT-60100 > L-MWCNT-4060-NA > L-MWCNT-4060-APS > L-MWCNT-4060 > L-MWCNT-1030 > S-MWCNT-4060. From this trend, the first two adsorbents would be a good choice for extraction/preconcentration of Hg(II) from water. The calculated mean energy values of adsorption of the Hg(II) by MWCNTs were

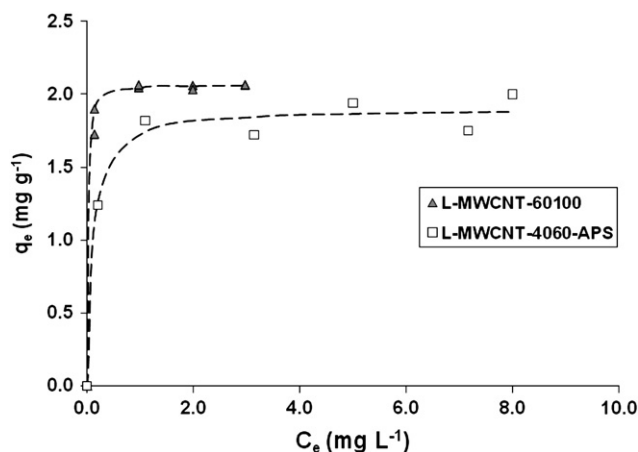


Fig. 3. H2-type adsorption isotherms of Hg(II). Dashed lines represent the Langmuir model.

Table 1
Parameters of isotherms for Hg(II) adsorption.

Adsorbent	L-MWCNT-1020	L-MWCNT-1030	L-MWCNT-2040	L-MWCNT-4060	L-MWCNT-60100	S-MWCNT-4060	L-MWCNT-4060-NA	L-MWCNT-4060-APS	L-MWCNT-4060-HP
<i>Langmuir</i>									
Q_{\max} (mg g ⁻¹)	3.83	1.32	3.75	–	2.06	0.70	–	1.86	2.19
b (L mg ⁻¹)	3.1	4.4	0.61	–	79.44	1.81	–	10.69	4.01
r^2	0.9827	0.9700	0.9449	–	0.9998	0.9343	–	0.9819	0.9901
<i>Freundlich</i>									
K_F	2.85	1.0	1.66	0.17	1.97	0.395	0.095	–	1.51
n	0.13	0.12	0.32	0.98	0.059	0.29	1.2	–	0.187
r^2	0.7811	0.7015	0.8388	0.9275	0.8694	0.6962	0.9454	–	0.9186
<i>Dubinin–Radushkevich</i>									
q_m (mg g ⁻¹)	4.12	1.36	4.05	1.16	2.14	0.85	2.00	1.96	2.24
B (kJ ² mol ⁻²)	-7×10^{-5}	-7×10^{-5}	-35×10^{-5}	-4×10^{-5}	-2×10^{-5}	-30×10^{-5}	-120×10^{-5}	-6×10^{-5}	-90×10^{-5}
r^2	0.7978	0.8135	0.9366	0.9554	0.9405	0.8797	0.9455	0.7036	0.9266
E (kJ mol ⁻¹)	87.0	86.7	37.7	118.1	156.9	40.7	20.7	88.4	73.1

variable and fall in the range (18–157 kJ mol⁻¹) and this implies that the type of adsorption appears to be chemical in some systems and physical in the others [29]. Hg(II) adsorption has a chemical nature in more than half of the studied sorbents (L-MWCNT-1020, L-MWCNT-1030, L-MWCNT-4060, L-MWCNT-60100, and L-MWCNT-4060-APS). In such systems, the complete elution of Hg(II) would be difficult due to the strong interaction. The strongest interaction was recorded for L-MWCNT-60100, thus the sorption was most favored on this sorbent. However, the sorbent L-MWCNT-4060-NA, which gave the highest recovery in the SPE process (as will be shown next), showed the lowest E value (20.7 kJ mol⁻¹). This probably explains the highest recovery achieved with this sorbent in the SPE process, in which the Hg species are easier to elute from this sorbent.

3.2. Assessment of MWCNTs for Hg(II) extraction from water

In this section, the preconcentration power of all adsorbents will be assessed using the column method where the Hg(II) ions will be at the trace level and, at the same time, have short contact time with the extractant. Due to the large variations in experimental procedures of adsorption and preconcentration systems, it is expected that the adsorbents will behave in a different manner. Simply, adsorbent of high equilibrium capacity for Hg(II) does not ensure that it will perfectly function as a solid-phase extractant. The effect of MWCNT dimensions, surface oxidation, pH, mass of the extractant, sample volume, and eluent concentration/volume on Hg(II) preconcentration from water will be optimized. Experimental conditions that achieved the maximum enrichment of Hg(II) will be applied on natural waters, tobacco leaves and phosphate rocks.

3.2.1. Effect of adsorbent oxidation

Oxidation of MWCNTs creates more functional groups on the surface such as carboxylic acid groups, phenolic groups, and lactonic groups as reported in our earlier research [19]. This increases the capability of interaction with analyte either by ion-exchange or polar interaction. This is in addition to opening the caps of the CNTs when they are oxidized with nitric acid [25], and thus more surface area is available for mercury(II) species adsorption either internally or externally, which enhances the uptake of mercury(II) species. Hg(II) preconcentration by different oxidized MWCNTs (L-MWCNT-4060-NA, L-MWCNT-4060-APS, and L-MWCNT-4060-HP) and non-oxidized L-MWCNT-4060 was studied at pH 7 and the results are presented in Table 2. The oxidation by nitric acid gave the best recovery among all treatments. Nitric acid modifies the surface characteristics of the MWCNT by creating a larger surface area, and more acidic surface functional groups, and by opening the caps of the tubes [19], accordingly, this will attract more Hg(II) from

the solution. The other oxidizing agents were not as effective as nitric acid.

3.2.2. Effect of pH

The pH of the water sample is an important factor in the SPE process especially for metal cations due to hydrolysis reactions. The distribution curve of the Hg(II)–water system showed that at pH < 2, free Hg(II) ions are predominant in the solution. Between pH 2 to pH 4, a mixture of Hg(II), Hg(OH)⁺ and Hg(OH)₂ are present in the solution mixture. Between pH 4 and pH 7, Hg(OH)₂ is predominant. At pH > 7, negatively charged species Hg(OH)₃⁻ or Hg(OH)₄²⁻ are predominate. Extraction of 100 µg L⁻¹ Hg(II) at different pH values from water was studied and the best recovery was observed at pH 7 (Table 2). The recovery was modest within pH 1–5 and at pH 9. The low mercury recovery at acidic (pH 1–5) is attributed to the competition between the proton H⁺ and Hg(II) for the surface. The poor recovery at basic conditions may be attributed to repulsion between the negatively charged surface and (Hg(OH)₃⁻, Hg(OH)₄²⁻) species [18]. Mercury was retained quantitatively by L-MWCNT-4060-NA at pH 7 and this favorable interaction back to the low electrostatic competition between neutral Hg(OH)₂ molecule and other ions. The process depends on interaction between colloidal Hg(OH)₂ species with the surface functional groups of MWCNTs. Both the internal and the external surfaces of the MWCNT may play a role in the process. Thus it is expected that MWCNTs of various geometrical dimensions may have various abilities to capture colloidal Hg(OH)₂ at pH 7.

3.2.3. Effect of dimensions of MWCNTs (external diameter and length)

The effect of the external diameter of the MWCNT on the Hg(II) preconcentration was investigated using five types of MWCNT (all oxidized by nitric acid) of various external diameters but of similar length range (5–15) µm. Hg(II) extraction by S-MWCNT-4060-NA (which has a short tube length ranging between 1 and 2 µm) was studied for comparison. The results presented in Table 2 indicate that the order of mercury recovery was as follows: L-MWCNT-4060-NA > L-MWCNT-1020-NA > L-MWCNT-60100-NA > L-MWCNT-2040-NA > L-MWCNT-1030-NA. This order probably reflects the ability of the MWCNTs to retain the colloidal Hg(OH)₂ at pH 7. Of course this depends on the dimensions of the suspended solid mercury species that best fit the dimensions of the MWCNTs. The results in Table 2 show that L-MWCNT-4060-NA is more efficient in mercury removal than the shorter one (S-MWCNT-4060-NA). Thus the sorbent L-MWCNT-4060-NA was selected as the optimum extractant for other experiments. The effect of MWCNT dimensions on toxic metal cations and pesticide preconcentration from natural waters has been explored in our laboratories [19,20]. It was found that HNO₃–

Table 2
Effect of experimental variables on Hg(II) preconcentration at 100 µg L⁻¹.

Parameter	Recovery, % (±%RSD)	Conditions
<i>pH of the water sample</i>		
1.0	43.6±0.0	loading: 25 mL water sample, 4.3 mL min ⁻¹ ; elution: 5 mL of 0.5 M HNO ₃ ; sorbent: 200 mg of L-MWCNT-4060-NA.
3.0	49.4±1.0	
5.0	57.8±0.5	
7.0	95.0±0.0	
9.0	52.4±2.5	
<i>Adsorbent oxidation</i>		
L-MWCNT-4060	93.8±4.1	loading: 25 mL water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 5 mL of 0.5 M HNO ₃ ; sorbent: 200 mg.
L-MWCNT-4060-NA	104.0±0.6	
L-MWCNT-4060-HP	82.6±0.0	
L-MWCNT-4060-APS	77.0±13.0	
<i>MWCNT dimensions</i>		
L-MWCNT-1020-NA	95.4±5.5	loading: 25 mL water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 5 mL of 0.5 M HNO ₃ ; sorbent: 200 mg.
L-MWCNT-1030-NA	62.6±9.7	
L-MWCNT-2040-NA	86.2±3.8	
L-MWCNT-4060-NA	98.0±7.5	
L-MWCNT-60100-NA	88.2±0.6	
S-MWCNT-4060-NA	63.0±0.0	
<i>Mass of L-MWCNT-4060-NA (mg)</i>		
100	93.0±6.5	loading: 25 mL water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 5 mL of 0.5 M HNO ₃ ; sorbent: L-MWCNT-4060-NA.
200	110.0±8.2	
300	94.6±14.4	
400	78.0±1.3	
<i>Eluent concentration (M_{HNO3})</i>		
0.1	71.2±2.1	loading: 25 mL water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 5 mL of HNO ₃ ; sorbent: 200 mg of L-MWCNT-4060-NA.
0.2	81.2±6.1	
0.5	90.0±2.2	
1.0	111.0±7.2	
<i>Volume of 0.5 M HNO₃ (mL)</i>		
2.5	80.0±11.1	loading: 25 mL water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 1.0 M HNO ₃ ; sorbent: 200 mg of L-MWCNT-4060-NA.
5.0	110.0±6.8	
7.0	107.0±0.5	
10.0	116.0±0.5	
<i>Sample volume (mL)</i>		
25	97.6±12.5	loading: water sample (pH 7), 4.3 mL min ⁻¹ ; elution: 5 mL of 1.0 M HNO ₃ ; sorbent: 200 mg of L-MWCNT-4060-NA.
50	97.1±0.9	
100	93.5±1.6	
150	88.0±0.8	
200	59.8±0.6	
250	53.6±1.3	

oxidized and short tubes have better efficiency for pesticide extraction while longer tubes have better extraction for metal extraction.

3.2.4. Optimization of other SPE parameters

Applying suitable/optimized loading volume, flow rate, extractant mass, and eluent volume/type is essential to clean interferences and end up of high enrichment factors.

Extraction of Hg(II) was evaluated at many flow rates within the range (6 and 25 mL min⁻¹) and the results indicated that the retention of Hg(II) is not significantly affected by the sample flow rate (recovery: 105–115%) and the rest of experiments were run at 6.0 mL min⁻¹ to save analysis time. The optimal mass of L-MWCNT-4060-NA for perfect Hg(II) preconcentration pH 7 was 200 mg (Table 2). This amount of the sorbent was sufficient for the quantitative adsorption/desorption process and recovery goes down at higher masses due to incomplete elution. Thus 200 mg of L-MWCNT-4060-NA is the optimum mass for extraction. The results presented in Table 2 indicated that 5.0 mL (1.0 M HNO₃) was optimum for full recovery of Hg(II). For this reason it was selected in future experiments. Studying the breakthrough volume is important in preconcentration processes because it represents the sample volume that can be concentrated without loss of analyte during

Table 3

Chemical composition of some natural mineral water samples and the spike recovery of mercury(II) according to the proposed SPE method; spiking level of Hg(II) is 15.0 µg L⁻¹.

	Mineral water 1 ^a	Mineral water 2 ^b	Mineral water 3 ^c	Mineral water 4 ^d
<i>Chemical composition (mg L⁻¹)</i>				
Ca ²⁺	50	59	1.3	13.6
Mg ²⁺	25	26	19	7.8
Na ⁺	27	–	3.3	46.5
K ⁺	0.79	0.7	0.2	3.9
SO ₄ ²⁻	23	24	80.0	21.6
HCO ₃ ⁻	239	224	10.0	101.3
Cl ⁻	–	–	3.0	38.7
F ⁻	–	–	0.13	0.18
TDS	300	–	110	198
pH	–	7.5	6.6	8.2
<i>Determination of Hg(II)</i>				
Unspiked	ND	ND	ND	ND
Spike recovery, % (±RSD)	84.5±5.7	82.0±5.3	92.1±5.2	88.3%±3.4

ND: not detected.

^a From Sherah mountains, Petra.

^b From Al-Shoobak.

^c From Madaba.

^d From Kasr Al-Hallabat.

loading the sample. Various water sample volumes were tested. The results shown in Table 2 indicate that the use of 150 mL of the water sample gave 88% recovery, where enrichment factors of 30 can be achieved. This volume of water sample was selected in other extractions.

3.2.5. Analytical figures of merit

Once the optimum extraction parameters have been optimized, the analytical performance of the method was evaluated by calculating the corresponding figures of merit. For that purpose, distilled water was spiked with the following Hg(II) concentrations: 10, 20, 40, 60, 80 and 100 µg L⁻¹; and the optimized SPE procedure was carried out. A linear relationship was drawn between the average absorbance of the solution and the Hg(II) concentration (µg L⁻¹). The linearity of the calibration equation was high ($r^2 = 0.9990$). The relative standard deviation ($n = 3$) ranged between 4.8 and 12.0%. The limit of quantification ($S/N = 10\sigma$) was 12.3 ng L⁻¹, so that the method is linear from 0.0123 µg L⁻¹ till the maximum studied concentration (100 µg L⁻¹). The preconcentration factor was 30, which is slightly lower than that reported by Shang (enrichment factor = 39) [18].

3.2.6. Effect of foreign ions

The effect of the presence of foreign ions was studied by using four different natural mineral waters (from different mineral water resources in Jordan, see Table 3). These are known to contain various nominal amounts of ions. They were treated according to the proposed preconcentration method for mercury determination. Mercury(II) could not be detected in any of these mineral waters. So that they were spiked with 15 µg L⁻¹ of Hg(II) and then treated according to the proposed preconcentration method for mercury(II) determination. Samples were analyzed in five replicates ($n = 5$). The results are shown in Table 3. It was found that the recovery was not significantly affected (spike recovery ranged between 82.0 and 92.1%) and the precision was acceptable (%RSD range 3.4 and 5.7%). This indicates that the proposed method may be precisely used for determination of mercury in natural mineral water without any significant interference from the existing foreign ions.

3.3. Hg(II) determination in real water samples

The proposed method was applied for preconcentration of Hg(II) that presents in tap and reservoir water. Also, the method was applied for preconcentration of Hg(II) that eluted from tobacco leaves and

Table 4
Spike recovery of Hg ($n=5$) from real water samples and digested solid samples.

Matrix	Added Hg(II) level	Found conc. $\pm\%$ SD	Recovery (%) $\pm\%$ RSD
Tap water	10 $\mu\text{g L}^{-1}$	9.0 \pm 0.2 $\mu\text{g L}^{-1}$	89.8 \pm 2.2
	20 $\mu\text{g L}^{-1}$	18.9 \pm 0.3 $\mu\text{g L}^{-1}$	94.6 \pm 1.6
Reservoir water	10 $\mu\text{g L}^{-1}$	8.9 \pm 0.2 $\mu\text{g L}^{-1}$	88.8 \pm 2.2
	20 $\mu\text{g L}^{-1}$	18.3 \pm 0.5 $\mu\text{g L}^{-1}$	91.4 \pm 2.7
Phosphate rock ^a	0	<DL	–
	250 $\mu\text{g kg}^{-1}$	241.5 \pm 1.8 $\mu\text{g kg}^{-1}$	96.6 \pm 2.7
	500 $\mu\text{g kg}^{-1}$	445.4 \pm 2.3 $\mu\text{g kg}^{-1}$	91.6 \pm 2.7
Tobacco leaves ^b	23.2 \pm 1.6 $\mu\text{g kg}^{-1}$ (certified value)	22.3 \pm 1.7 $\mu\text{g kg}^{-1}$	96.1 \pm 3.2

^a Local phosphate rock containing (wt.%): P₂O₅ (33%), CaO (48%) and SiO₂ (10%).

^b Purchased from Poland (INCT-PVTL-6 Polish Virginia Tobacco Leaves).

phosphate rock. The optimized SPE procedure was applied on the unspiked and spiked water samples. Table 4 summarizes the results. For all water samples, the proposed method gave a satisfactory preconcentration recovery (88.8–94.6%), with reasonable random errors (1.6–2.7%). This was close to the results obtained by Shang [18] for natural waters (lake and river waters) where the obtained recoveries ranged from 90 to 96% with RSD values: 2–4%. In fact, the high recoveries indicated the high selectivity of MWCNTs for Hg(II) extraction even in the presence of a high level of other common water ions.

3.4. Method validation: analysis of Hg(II) in digested phosphate rock and certified reference tobacco leaves

The method revealed the absence of Hg(II) in phosphate rock, therefore, the solid samples were spiked with different levels of Hg(II) (0.25–2.50 mg kg⁻¹) and subjected to digestion and SPE to quantify Hg(II) and assess the method efficiency. A linear relationship between the analytical signal and the added concentration as:

$$S_{\text{Hg(II)}} = 0.0958C_{\text{Hg(II)}} - 0.0053$$

with $r^2 = 0.9841$ and a dynamic range of 0.5–2.5 mg kg⁻¹ was achieved. The relative standard deviation ($n = 3$) was acceptable: 0.55–9.30%. The limit of quantification ($10\sigma_{\text{blank}}/\text{slope}$), was found to be 0.03 mg kg⁻¹.

The accuracy of the proposed method and its suitability for Hg(II) quantification in tobacco leaves were carried out by analyzing certified tobacco leaves. The average and RSD values for five determinations are shown in Table 4. The obtained value (22.3 \pm 1.7 $\mu\text{g kg}^{-1}$) was in good agreement with the certified value (23.2 \pm 1.6 $\mu\text{g kg}^{-1}$). The accuracy and precision of the proposed method were assessed by applying t and F tests at 95% confidence levels. The calculated t and F values were 0.5 and 1.12 while the tabulated values are 2.31 and 9.61 at 95% confidence levels, respectively. It is evident from the statistical analyses that there is no significance difference between the obtained results in Hg(II) determination and the results are of comparable precision.

4. Conclusions

The intrinsic adsorption/preconcentration of Hg(II) by MWCNTs is affected by the surface oxidation and geometrical dimensions of the adsorbents. Surface oxidation of L-MWCNT-4060 by nitric acid produced an efficient adsorbent for Hg(II) extraction from natural waters. The optimum SPE procedure was carried out at: 150 mL water sample, pH 7, flow rate 6 mL min⁻¹, elution 5 mL of 1.0 M HNO₃, and mass of adsorbent 200 mg. Analysis revealed that Hg(II) was extracted in the hydroxo form, Hg(OH)₂. Hg(II) can be analyzed with high accuracy (96%) and precision (<3%) in phosphate rock after fast microwave-based digestion producer. The method manifested high accuracy, precision, and short analysis time (30 min) when used for Hg(II) quantification in an independent certified tobacco leaf material.

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