

Effect of oxidation and dimensions of multi-walled carbon nanotubes on solid phase extraction and enrichment of some pesticides from environmental waters prior to their simultaneous determination by high performance liquid chromatography

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Abstract

In this novel study, some factors that affect the enrichment efficiency of multi-walled carbon nanotubes (MWCNTs) towards some pesticides in environmental water samples were studied. The effect of oxidation of MWCNTs with various oxidizing agents and the effect of length and external diameter of MWCNTs were investigated. Model pesticides were selected from various common categories of pesticides, viz. Atrazine, Propoxur, Methidathion. Variables optimized included external diameter and length of the MWCNT, oxidation of the MWCNT, mass of the MWCNT, volume and pH of water sample, composition and volume of eluting solvent and washing solvent. It was found that short-nitric acid oxidized-MWCNT exhibited higher enrichment efficiency, especially for Methidathion, than non-oxidized long MWCNT. The optimized SPE procedure is capable of determining Propoxur (detection limit: 220 ng L^{-1} , linear range: $10\text{--}50 \text{ ng mL}^{-1}$, $<3.0\%$ RSD), Atrazine (detection limit: 57.5 ng L^{-1} , linear range: $10\text{--}100 \text{ ng mL}^{-1}$, $<2.8\%$ RSD) and Methidathion (detection limit: 37.5 ng L^{-1} , linear range: $10\text{--}50 \text{ ng mL}^{-1}$, $<2.5\%$ RSD). Application of the optimized SPE procedure to determine the three target pesticides in real environmental waters (tap water, reservoir water and stream water) gave spike recoveries in the range of 81.0–108%.

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1. Introduction

Environmental pollutants pose great threat to human health even if present in the environment at very low level. To monitor them at such low level, there is a need for an effective sample preconcentration step with high enrichment factor prior to their determination. Solid phase extraction (SPE) is the most common technique for preconcentration of analytes in environmental water samples. It has the advantages of high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, simplicity and ease of operation and the potential for automation. In SPE, the choice of appropriate adsorbent is a critical factor to achieve full recovery and high enrichment efficiency.

Since carbon nanotubes (CNTs) were first prepared by Iijima in 1991 [1], they have become attractive materials for their novel structure characters [2]. CNTs can be visualized as a sheet of graphite which are rolled up into a cylinder and closed by two caps, with either a single-walled or a multi-walled structure [3]. The unique tubular structure makes CNTs a promising adsorbent material, and thus may be used in preconcentration of many pollutants. Cai et al. [4,5] reported that multi-walled carbon nanotubes (MWCNTs) surface has a strong interaction with many phenolics and phthalate compounds. Zhou et al. [6,7] reported that MWCNTs had a high effective enrichment of Atrazine and Simazine in environmental waters. Other recent studies involved CNTs for enrichment of chlorobenzenes [8], chlorophenols [9], sulfonylurea herbicides [10,11], phthalate esters [12], cyanazine, chlorotoluron and chlorbenzuron [13], triasulfuron and bensulfuron-methyl in water samples [14], polybrominated diphenyl ethers in milk samples [15], dicamba herbicide [16], chelates and organometallic compounds [17].

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Tarley et al. [18] reported the use of a simple flow injection mini-column preconcentration system with MWCNTs for determination of cadmium. Fang et al. [19] reported on-line coupling of solid-phase extraction to high-performance liquid chromatography for simultaneous determination of 10 sulfonamides in eggs and pork. CNTs have also been used as sorbents for organic vapor preconcentration [20]. Yu and Lai [21] used molecularly imprinted polypyrrole modified CNTs on stainless steel frit for selective micro SPE of ochratoxin A. MWCNTs were also used for preconcentration of metal ions, such as rare earth elements [22], cadmium and copper [23,24], and silver ions [25]. The above mentioned work revealed that CNTs have great analytical uses as an efficient SPE adsorbent for some pollutants in environmental waters. Recently analytical applications of CNTs have been reviewed by Valcarcel et al. [26]. A special issue for recent advances in analytical applications of CNTs has also been published [27].

Many authors have tried to improve the properties of the CNTs via oxidation with various oxidizing agents. For example, some authors have treated CNTs with nitric acid for opening the caps (tips) of the CNTs and/or for purification purposes [28–32]. Zhang et al. [33] reported that diameter of the single-walled CNT may be enlarged by nitric acid treatment. Other authors reported characterization of the nitric acid oxidized CNTs surface using various physico-chemical techniques [34–37]. Some authors suggested the pretreatment of the CNTs with nitric acid in order to prepare the surface of CNTs to be further modified with various functionalities (modifying materials), such as stearic acid [38], Cu/ZnO [39], various polymers [40], etc.

Liang et al. [41] applied nitric acid-oxidized MWCNTs to concentrate cadmium, manganese and nickel ions. Hennrich et al. [42] reported the modification of adsorption properties of single-walled CNTs via nitric acid exposure. Chakraborty et al. [43] found that treatment of the CNTs with nitric acid/sulfuric acid mixture then baking at 1000 °C increased the surface area.

It seems that Liang et al. [41] are the only group who used nitric acid oxidized MWCNTs for preconcentration of metal ions. In this work, we report the effect of oxidation of MWCNTs with various oxidizing agents (nitric acid, hydrogen peroxide, ammonium persulphate) and the effect of MWCNT's dimensions (length and external diameter) on preconcentration of some model pesticides. Long (5–15 μm) MWCNTs or short (1–2 μm) MWCNTs of various external diameters (10–20,

10–30, 20–40, 40–60, 60–100 nm) were involved in this study. The pesticides selected are model pesticides that represent various categories, viz. Atrazine “a triazine herbicide”, Propoxur “a carbamate insecticide”, Methidathion “an organophosphorus insecticide-acaricide”. To best of our knowledge, the application of MWCNTs as adsorbent for preconcentration of Propoxur and Methidathion pesticides has not been reported in the literature. Additionally none of the studies have explored the effect of carbon nanotube external diameter, length and oxidation on the enrichment performance of the MWCNTs for preconcentration of the above-mentioned pesticides.

2. Experimental

2.1. Chemicals

Atrazine, Propoxur and Methidathion standard material were kindly provided by Vegetarian and agricultural production company/VAPCO (Al-Zarqa, Jordan) as 10 μg mL⁻¹ solution in acetonitrile. Working solutions were prepared daily by appropriate dilution of the stock solutions with water. Acetonitrile, water and methanol were all of HPLC-grade purchased from TEDIA, Ohio, USA. All other solvents and reagents used were of analytical reagent grade unless stated otherwise.

Multi-walled carbon nanotubes were purchased from Shenzhen Nanotechport Co. Ltd., Shenzhen, China. Before use, MWCNTs were dried at 80 °C for 2 h. Six different types of MWCNTs were involved in this study. Dimensions of the MWCNTs as provided by the manufacturer are listed in Table 1. An abbreviation was assigned for each type of carbon nanotubes. The letter L refers to long (5–15 μm), while the letter S refers to short (1–2 μm). External diameter range is also provided following the acronym MWCNT. Other characteristics of all the MWCNTs provided by the manufacturer are as follows: purity >95 vol%; ash ≤0.2 wt.%; amorphous carbon 2%; specific surface area 40–300 m² g⁻¹.

2.2. Oxidation of the L-MWCNT-4060

To study the effect of oxidation of MWCNT with various oxidizing agents on enrichment efficiency towards the target pesticides, L-MWCNT-4060 was used to prepare three oxidized MWCNT adsorbents. Oxidation conditions are shown in Table 2. Adsorbents were then washed with water to remove

Table 1
Dimensions of the MWCNTs and their characteristics

Abbreviation	Range of external diameter (nm)	Length (μm)	MB relative surface area (m ² g ⁻¹)	Iodine number (mg g ⁻¹)	Boehm titrations				
					a	b	c	d	e
L-MWCNT-1020	10–20	5–15	31	23.0	16.7	19.8	10.0	0	9.80
L-MWCNT-1030	10–30	5–15	28	24.8	11.7	19.0	0	0	19.0
L-MWCNT-2040	20–40	5–15	27	31.9	20.0	16.5	0	5.00	11.5
L-MWCNT-4060	40–60	5–15	10	37.2	16.7	10.0	1.00	2.50	6.50
S-MWCNT-4060	40–60	1–2	11	18.0	21.7	18.3	11.8	5.00	1.50
L-MWCNT-60100	60–100	5–15	9	44.7	21.7	26.5	0	0	26.5

(a) Total basic group (μmol g⁻¹), (b) total acidic group (μmol g⁻¹), (c) phenolic groups (μmol g⁻¹), (d) lactonic groups (μmol g⁻¹), (e) carboxylic groups (μmol g⁻¹).

Table 2

Preparation conditions and characteristics of the oxidized MWCNTs with appropriate labelling of the oxidized samples

Oxidized adsorbent abbreviation	Oxidation conditions	MB relative surface area (m ² g ⁻¹)	Iodine number (mg g ⁻¹)	Boehm titrations				
				a	b	c	d	e
L-MWCNT-4060-NA	100 mL of conc. HNO ₃ , 25 °C, 24 h	15	12.4	10.0	23.2	0	0	23.2
L-MWCNT-4060-APS	100 mL of a saturated solution of (NH ₄) ₂ S ₂ O ₈ in 1 M H ₂ SO ₄ , 25 °C, 18 h	8	12.3	0	53.1	0	3.30	49.8
L-MWCNT-4060-HP	Mixture of 50 mL H ₂ O ₂ and 50 mL 1 M H ₂ SO ₄ , 50 °C, 1 h	7	33.2	18.3	14.8	3.3	0	11.5

(a) total basic group (μmol g⁻¹), (b) total acidic group (μmol g⁻¹), (c) phenolic groups (μmol g⁻¹), (d) lactonic groups (μmol g⁻¹), (e) carboxylic groups (μmol g⁻¹).

excess oxidizing agent and other water-soluble species. The produced adsorbents were labelled L-MWCNT-4060-NA, L-MWCNT-4060-HP and L-MWCNT-4060-APS, which refers to L-MWCNT-4060 samples oxidized with nitric acid, hydrogen peroxide and ammonium per-sulphate, respectively (Table 2). The same procedures were used later, as necessary, to oxidize other MWCNT of different dimensions.

2.3. Characterization of the oxidized and non-oxidized MWCNTs

Methylene blue (MB)-relative surface area was estimated as follows [44,45]: 25 mL of aqueous solutions of 10, 20, 30, 40, 50, 60, 70, 90, 110 mg L⁻¹ methylene blue were separately added to 50 mL conical flasks each containing 25 mg of the adsorbent. The tubes were stoppered tightly and left for 1 week in the dark, with shaking from time to time. The remaining concentrations were analyzed spectrometrically at 614 nm using Cary 100Bio UV–vis spectrophotometer. Langmuir adsorption isotherms were plotted to find the monolayer capacity through which MB-relative surface areas were estimated [44,45]. The determination of surface oxides was described by Boehm [46]. Iodine numbers were estimated according to procedure described by ASTM [47].

2.4. Apparatus

MWCNT cartridge was prepared by placing a specific mass of the MWCNT in an empty 6 mL polypropylene SPE-tube “filtration tube” (from Supelco). Polyethylene frits (from Supelco) of 20 μm porosity were used to hold the adsorbent packing in the cartridge. Solid phase extraction process was performed using a visiprep-12-port vacuum manifold (from Supelco). The outlet tip of the manifold was connected to a vacuum pump (KNF NEUBERGER D-7800, Germany) and the flow rate was maintained at 6 mL min⁻¹.

HPLC analyses were performed using a model 785A programmable absorbance detector and a series 200 LC pump. Separations were performed on a spherisorb ODS2 (150 mm × 4.6 mm, 5 μm) from Dr. Maisch GmbH (Germany). A MetaGuard 2.0 mm Polaris 5 μm C18-A guard column was also used. The mobile phase consisted of acetonitrile and water (60/40, v/v), and the flow rate of the mobile phase

was set at 1.0 mL min⁻¹. Chromatographic data were acquired and processed at 210 nm using a Perkin-Elmer 1022 LC Plus system.

2.5. General SPE procedure

0.200 g of the MWCNT adsorbent was packed into the SPE-cartridge and pre-conditioned by washing with 5 mL acetonitrile then with 5 mL water ahead of the preconcentration procedure. Next, 50 mL of the water sample solution (spiked with Atrazine, Propoxur and Methidathion and adjusted to pH 5) was passed through the cartridge. The cartridge was then washed with 10 mL of 10% acetonitrile aqueous solution to remove co-absorbed matrix materials. Subsequently, Atrazine, Propoxur and Methidathion retained on the cartridge were eluted with 10 mL of acetonitrile. Twenty microliter of the eluent was injected into HPLC system for quantitative determination.

In optimization of SPE procedure, detailed description of experimental conditions are provided in appropriate caption of the figures.

2.5.1. Breakthrough curves

Breakthrough curves were estimated by applying the general SPE procedure on clean water samples of various volumes. Water sample volumes tested in this section were 25, 50, 100, 200, 400, 700 and 1000 mL.

2.5.2. Adsorption capacity

Adsorption capacity of S-MWCNT-4060-NA (optimum sorbent) towards the three pesticides was estimated in separate experiments at pH 5 (optimum pH), by passing 50 mL of 5 μg mL⁻¹ of each pesticide solution (separately) into a 0.200 g of S-MWCNT-4060-NA packed in the cartridge and pre-conditioned as described above. The adsorbed pesticide was eluted with 20 mL acetonitrile to ensure full elution.

2.5.3. Analytical performance of the method

Four hundred milliliter of highly purified (doubly distilled de-ionized) water samples were spiked with various concentrations of the three pesticides (simultaneously): 10, 17.5, 25, 37.5, 50, 75, 100 ng mL⁻¹ and then enriched using S-MWCNT-4060-NA (optimum sorbent) according to the optimized preconcentration method described in Section 3.2.6. SPE experiments were

performed in five replicates ($n=5$) and the five extracts were analyzed as separate samples.

2.6. Real water samples

In this work, three types of environmental water samples were used for evaluation of the proposed SPE method; tap water, reservoir water and stream water; using grab sampling in borosilicate glass bottles. Tap water samples were taken after flowing for 10 min from various water taps in our school in different days, and then pooled and used to generate a composite tap water sample. Reservoir water composite sample was generated by collecting various samples from local household reservoirs; which are known to store water for several weeks. Stream water composite sample was generated by collecting various samples from Al-Zarqa stream from various positions at various days. Before use, all the environmental water samples were filtered through 0.45 μm micropore membranes and stored in brown glass bottles at 4 °C.

2.6.1. Application of the proposed method on real water samples

Unspiked real water samples were analyzed according to the optimum SPE procedure. Since real water samples were free of the pesticides according to our procedure, water samples were spiked with the three pesticides (simultaneously) at various concentrations: 10, 17.5, 25, 37.5, 50, 75, 100 ng mL^{-1} (for Atrazine), and 10, 17.5, 25, 37.5, 50 ng mL^{-1} (for Propoxur and Methidathion). SPE experiments were performed in five replicates ($n=5$) and the five extracts were analyzed as separate samples.

To ensure reproducibility of the results, SPE procedures of the unspiked and spiked real water samples were performed in five replicates ($n=5$) then each extract was analyzed for Atrazine, Propoxur and Methidathion as separate samples.

3. Results and discussion

3.1. Characterization of the oxidized and non-oxidized MWCNTs

The oxidized and non-oxidized MWCNTs were characterized in our laboratory by relative surface area estimation by methylene blue adsorption method, iodine number and Boehm titrations. The results are shown in Tables 1 and 2.

The non-oxidized samples showed random variations in relative surface area (as estimated by methylene blue adsorption) (Table 1). There was no clear relationship between the dimensions of the MWCNT (length or external diameter) and the relative surface area. It was only noted that MWCNTs with small external diameter (10–20, 10–30, 20–40 nm) possessed roughly double the MB-relative surface area compared to that of MWCNTs with large external diameters. Oxidation of L-MWCNT-4060 with various oxidizing agents caused variation in MB-relative surface area (Table 2).

It is interesting to note that the iodine number was directly proportional to external diameter of the MWCNT (Table 1),

but short carbon nanotube (S-MWCNT-4060) exhibited lower iodine number value. Oxidation of the MWCNT generally reduced the iodine number (Table 2).

Acidic and basic surface oxides were found in MWCNTs of various dimensions but there were some differences in the amounts of these oxides. A noticeable increase of the carboxyl group was observed for all the oxidized samples in the order L-MWCNT-4060-APS > L-MWCNT-NA > L-MWCNT-4060-HP.

3.2. Optimization of SPE procedure

Optimization of SPE procedure is an important process to get appropriate enrichment efficiency and full recovery. It usually involves water sample volume and pH; washing solvent and its volume; type of eluting solvent and its volume. Effect of oxidation of the MWCNT, its length and external diameter were also investigated in this study. All experiments were performed in five replicates ($n=5$), and RSD was always less than 4.5%.

3.2.1. Effect of adsorbent oxidizing agent and pH of water sample

Enrichment factor is governed by the affinity of the analyte for adsorbent phase and the solubility in the liquid phase. For pesticides with acidic and basic functional groups, the pH of the liquid phase determines the chemical species present (cationic, anionic or neutral) and thus the distribution ratio of the analyte between the two phases.

A series of experiments were executed to investigate the influence of sample pH over the range of pH 3–9. The three oxidized MWCNTs (L-MWCNT-4060-NA, L-MWCNT-4060-HP, L-MWCNT-4060-APS) were tested for SPE of the three pesticides dissolved in aqueous solutions of various pH values, and results were compared with those obtained under identical conditions but with the non-oxidized adsorbent (L-MWCNT-4060). Results and details of the experimental conditions are shown in Fig. 1. It was noted that the highest recoveries were generally observed at pH 5 for all the three pesticides with all the oxidized and the non-oxidized MWCNTs adsorbents. Slightly lower recoveries were obtained in solutions adjusted to pH 7, while very low recoveries were observed at pH 3 and pH 9. An exceptional case was Propoxur with L-MWCNT-4060-APS adsorbent, in which pH 7 gave the highest recovery. Therefore, pH 5 was considered the optimum pH in this study.

The performance of the oxidized MWCNTs was compared with the non-oxidized MWCNT adsorbent at pH 5. It is revealed that oxidation the MWCNT with nitric acid (adsorbent L-MWCNT-4060-NA) increased the recovery for Methidathion by ~17%. For Propoxur and Atrazine, recovery was improved only slightly. Oxidation of the MWCNT with ammonium persulphate (adsorbent L-MWCNT-4060-APS) did not affect the recovery of Methidathion and Atrazine, but reduced the recovery of Propoxur by 60%. Oxidation of the MWCNT with hydrogen peroxide (adsorbent L-MWCNT-4060-HP) did not affect the recovery for Propoxur, but reduced the recovery of both Atrazine and Methidathion by ~15% (relative to L-MWCNT-4060). Due to the significant increase in the recovery for Methidathion upon

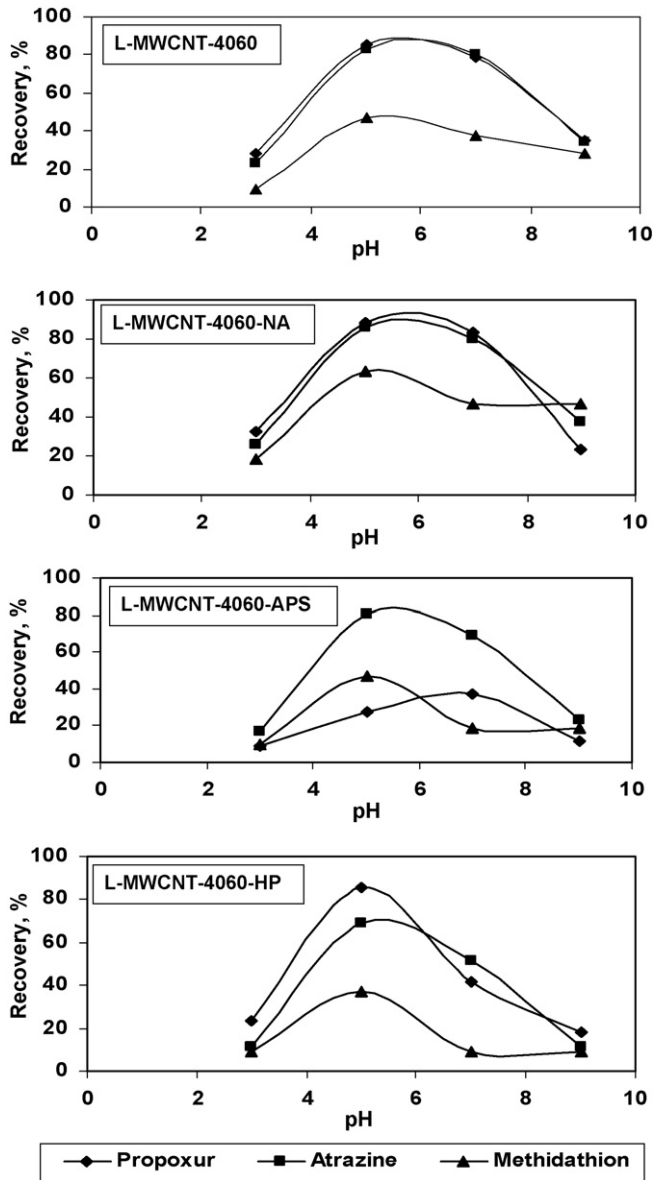


Fig. 1. Effect of oxidizing agent of MWCNT adsorbent and pH of the water sample on % recovery of the pesticides: 100 mL water sample spiked with 50 ng mL^{-1} of the three target pesticides; 0.200 g adsorbent; washing solvent: 10 mL of 10% acetonitrile aqueous solution; eluting solvent: 10 mL of acetonitrile.

oxidation of MWCNT with nitric acid, it was decided to oxidize MWCNT with nitric acid as the preconcentration sorbent in this study.

3.2.2. Effect of dimensions of the MWCNTs

The effect of external diameter on the recovery was investigated by using MWCNTs (all oxidized with nitric acid) of various external diameters but similar length range of 5–15 μm . Results and experimental conditions are shown in Fig. 2. The highest recovery for Atrazine and Propoxur was obtained with L-MWCNT-4060-NA, while for methidathion the highest recover was almost the same with L-MWCNT-2040-NA and L-MWCNT-60100-NA. However, due to higher recoveries obtained for Atrazine and Propoxur by L-MWCNT-4060-NA, it

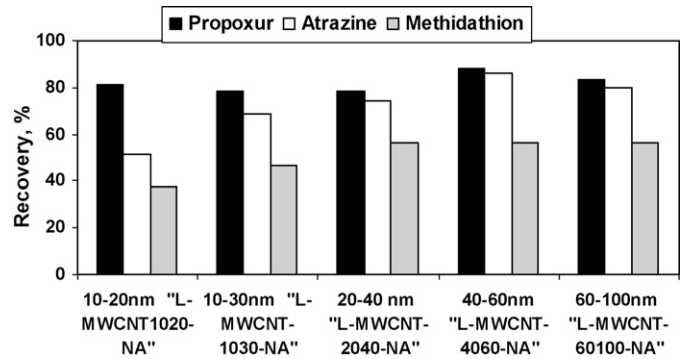


Fig. 2. Effect of external diameter of the MWCNT on % recovery of the pesticides: 50 mL water sample (pH 5) spiked with 50 ng mL^{-1} of the three target pesticides; 0.200 g adsorbent; washing solvent: 10 mL of 10% acetonitrile aqueous solution; eluting solvent: 10 mL of acetonitrile.

was selected for subsequent optimization tests of the proposed method.

To explore the effect of the length of the MWCNT on the % recovery of the pesticides, the SPE procedure was applied using two MWCNTs (oxidized with nitric acid) of different lengths: L-MWCNT-4060-NA which has a tube length range 5–15 μm and S-MWCNT-4060-NA which has a tube length range 1–2 μm . Both have the same external diameter. Results and experimental conditions are shown in Fig. 3. It is generally noted that short multi-walled carbon nanotubes “S-MWCNT-4060-NA” gave better recovery of the pesticides than the long one “L-MWCNT-4060-NA”. The recovery of Methidathion on S-MWCNT-4060-NA is almost double that of the recovery obtained in L-MWCNT-4060-NA. For Atrazine, there was a 15% increase in the recovery when S-MWCNT-4060-NA was used (relative to L-MWCNT-4060-NA), while for Propoxur the increase was only 3%. This may be attributed to the fact that a fixed mass of short MWCNT contains larger number of tubes than the same mass of long MWCNT. Due to the increased % recoveries for Methidathion and Atrazine obtained by short carbon nanotubes, S-MWCNT-4060-NA (short carbon nanotubes

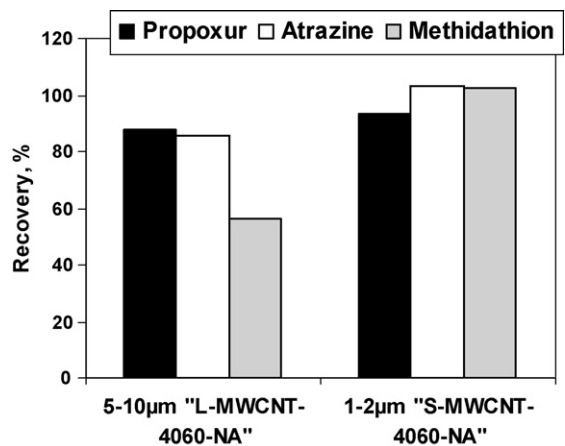


Fig. 3. Effect of length of the MWCNT on % recovery of the pesticides: 50 mL water sample (pH 5) spiked with 50 ng mL^{-1} of the three target pesticides; 0.200 g adsorbent; washing solvent: 10 mL of 10% acetonitrile aqueous solution; eluting solvent: 10 mL of acetonitrile.

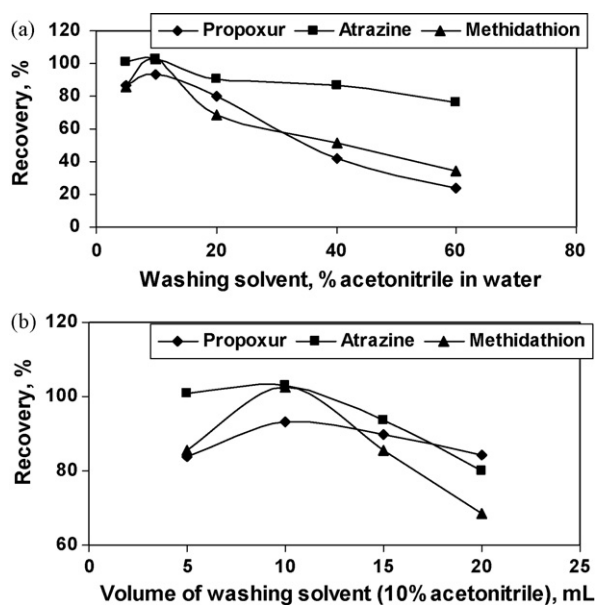


Fig. 4. Effect of (a) type of washing solvent, (b) volume of washing solvent (10% acetonitrile aqueous solution) on % recovery of the pesticides: 50 mL water sample (pH 5) spiked with 50 ng mL^{-1} of the three target pesticides; adsorbent: 0.200 g of S-MWCNT-4060-NA; eluting solvent: 10 mL of acetonitrile.

oxidized with nitric acid and have external diameter range 40–60 nm) was selected for subsequent optimization tests of the proposed method.

3.2.3. Washing solvent and eluting solvent: composition and volume

It is important to remove co-adsorbed species in the cartridge but at the same time, the recovery of the analytes must not be affected. Thus, washing step must be optimized in terms of composition and volume of washing solvent. To remove inorganic contaminants, washing solvent is mainly water mixed with small amount of acetonitrile. Results of studying the effect of washing solvent composition and volume on % recovery of the pesticides, with appropriate experimental conditions, are presented in Fig. 4. It was found that washing the adsorbent with an aqueous solution containing 10% acetonitrile gave the highest recovery (Fig. 4a). Increasing the percentage of acetonitrile in the washing solvent reduced the recovery. Optimum volume of this washing solution was found to be 10 mL (Fig. 4b).

In SPE procedure, it is necessary to elute all the adsorbed analytes on the adsorbent surface to get the highest recovery. Different elution efficiency would be obtained when different eluting solvents are used because of the physical and chemical properties of the involved organic solvents and the characteristics of the adsorbents in the cartridge. However, only two solvents were tested in this study: acetonitrile and methanol. Acetone was excluded because it is too volatile and hence accuracy and precision of analysis may be reduced. Chlorinated solvents (such as dichloromethane and trichloromethane) were also excluded due to their carcinogenic effects. Results of studying the effect of type and volume of eluting solvent, with appropriate experimental conditions, are presented in Fig. 5. The performance of acetonitrile was better than methanol in eluting

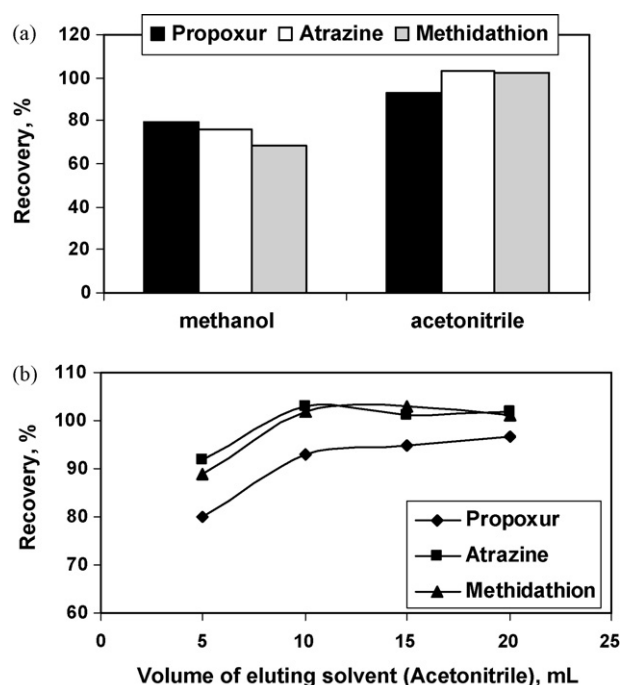


Fig. 5. Effect of (a) type of eluting solvent, (b) volume of eluting solvent (acetonitrile) on % recovery of the pesticides: 50 mL water sample (pH 5) spiked with 50 ng mL^{-1} of the three target pesticides; adsorbent: 0.200 g of S-MWCNT-4060-NA; washing solvent: 10 mL of 10% acetonitrile aqueous solution.

the analytes off the SPE cartridge (Fig. 5a). In the elution step, it is necessary to elute the retained analytes with minimum volume to get the highest enrichment factor. From Fig. 5b, it was found that 10 mL of acetonitrile was sufficient to elute all the adsorbed analytes and gave the highest recovery, above which the pesticide recovery was constant but the concentration of analytes in the eluate was lower.

3.2.4. Breakthrough curves

An important parameter that can be used to reach a concentration that can be detected by the instrument is the volume of sample passed through the adsorbent. Thus detection limit of the method may be lowered further. It is necessary to get the highest enrichment factor with highest recovery. Thus the breakthrough volume needs to be estimated. Results and experimental conditions are shown in Fig. 6. It is evident from Fig. 6 that the breakthrough volume was 400 mL.

3.2.5. Adsorption capacity

The adsorption capacities of S-MWCNT-4060-NA towards the three pesticides at pH 5 were as follows: Propoxur: 0.956 mg g^{-1} , Atrazine: 0.625 mg g^{-1} , Methidathion: 1.11 mg g^{-1} .

3.2.6. The proposed method of analysis

Based on the above discussion, the following optimized method is proposed for simultaneous preconcentration of the three pesticides (Propoxur, Atrazine, Methidathion): 400 mL aqueous solution (containing the three pesticides simultaneously) adjusted to pH 5 is passed through a 0.200 g

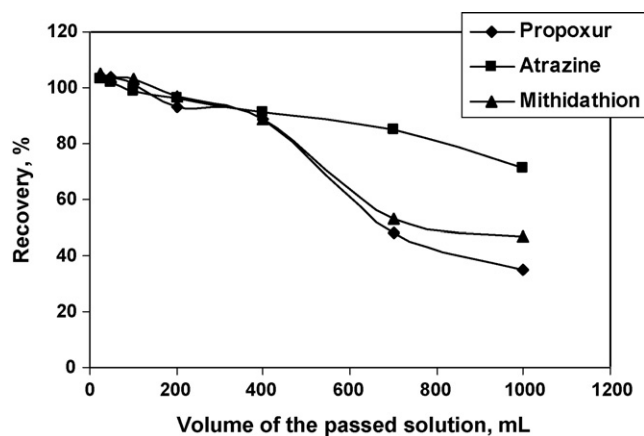


Fig. 6. Effect of volume of water sample on % recovery of the pesticides: water sample (pH 5) spiked with 50 ng mL^{-1} of the three target pesticides; adsorbent: 0.200 g of S-MWCNT-4060-NA, washing solvent: 10 mL of 10% acetonitrile aqueous solution; eluting solvent: 10 mL of acetonitrile.

S-MWCNT-4060-NA packed inside the cartridge and pre-conditioned with 5 mL of acetonitrile and 5 mL of water. The adsorbent is washed with 10 mL of 10% acetonitrile aqueous solution, and then the pesticides are eluted with 10 mL of acetonitrile. Twenty microliter of the eluate is injected into the HPLC instrument operated under the conditions stated in Section 2.4.

3.3. Analytical performance of the method

Some important analytical parameters are to be explored, such as linear range, detection limit, accuracy, precision. A typical chromatogram from the SPE of spiked highly purified water samples is shown in Fig. 7A and analytical performance of the proposed method is presented in Table 3.

The results in Table 3 indicate that precision was satisfactory at a very low level and the relative standard deviations %RSD ($n=5$) was always less than 3.0%. Linear ranges for the three target pesticides were estimated based on the value of the R -squared for the calibration curve. The detection limits of the three pesticides were estimated as three times the standard deviation of the blank signal.

3.4. Application of the method on real water samples

To demonstrate the applicability and reliability of the proposed method for environmental use, three real environmental water samples (tap water, reservoir water and stream water) were used to validate the proposed preconcentration method. The three target pesticides were not found in any of the real

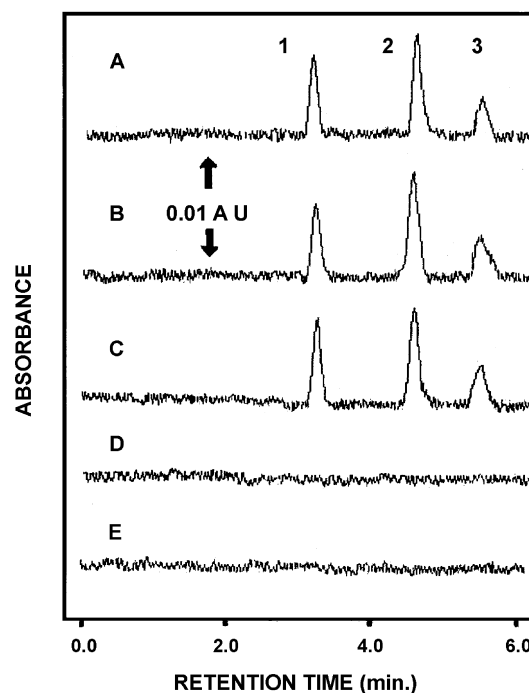


Fig. 7. Chromatograms from the SPE using S-MWCNT-4060-NA according to the proposed SPE method: (A) spiked highly purified water, (B) spiked tap water, (C) spiked reservoir water, (D) tap water, (E) reservoir water; spike concentration: 50 ng mL^{-1} of the three target pesticides. Peaks identification: (1) Propoxur, (2) Atrazine, (3) Methidathion.

Table 4

Spike recovery range for the three target pesticides in real water samples ($n=5$)

	Atrazine (%)	Propoxur (%)	Methidathion (%)
Tap water	90.8–101	86.3–96.4	85.0–96.4
Reservoir water	93.1–108	85.0–107	95.7–104
Stream water	81.0–105	82.0–102	81.0–101

water samples as shown in the chromatograms presented in Fig. 7D and E for tap water and reservoir water, respectively. The chromatograms of the spiked tap water and reservoir water samples are shown in Fig. 7B and C, respectively. Spike recoveries of the target pesticides in real water samples are shown in Table 4. The data in Table 4 indicated that the proposed method could be used in the analysis of real environmental water sample. A series of experiments were executed for comparison of S-MWCNT-4060-NA with C-18 as preconcentrating adsorbent for the three target pesticides. The obtained results demonstrated that S-MWCNT-4060-NA exhibited similar performance to that of C-18 for all the three pesticides (the data are not given).

Table 3

Analytical performance of the proposed SPE method

Compound	Linear range (ng mL^{-1})	R^2	Detection limit (ng L^{-1})	Precision, %RSD range ($n=5$)	Relative error range (%)
Atrazine	10–100	0.9990	57.5	0.21–2.8	–2.0–9.4
Propoxur	10–50	0.9740	220	0.39–3.0	–3.3–9.5
Methidathion	10–50	0.9993	37.5	0.30–2.5	1.6–7.6

4. Conclusion

It was found that oxidation and dimensions of MWCNTs affect the enrichment efficiency of MWCNTs towards some pesticides in water samples. This depends mainly on the nature of the pesticide. Experiments showed that short MWCNT exhibited better enrichment efficiency than long MWCNT towards the targeted pesticides especially for Methidathion (double recovery was obtained). This correlates with the pesticide molecular size. Additionally, nitric acid oxidized MWCNT exhibited better enrichment efficiency at pH 5 (especially for Methidathion) compared with non-oxidized MWCNT. MWCNTs oxidized with hydrogen peroxide and ammonium persulphate either did not affect or reduce the recovery of the pesticides. The proposed method, which involved short MWCNT oxidized with nitric acid and pH of water samples were adjusted to pH 5, was applied satisfactorily for environmental water samples (tap water, reservoir water and stream water). Analytical performance (accuracy, precision, detection limit, linearity) of the new proposed preconcentration procedure was satisfactory.

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