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Extraction and determination of pesticide residues in water using carbon nanotubes coupled with gas chromatography-mass spectroscopy

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Abstract−Multi-walled carbon nanotubes (MWCNT) were used as an adsorbent in a solid-phase extraction (SPE) process to detect pesticide residues in water. The MWCNT were prepared with polyvinyl pyrrolidone and polysilazane liquid by pyrolysis. The morphology and integrity of MWCNT were characterized by Fourier-transform infrared spectroscopy, scanning electron microscope, X-ray diffractometer, and transmission electron microscope. Water samples including pesticides were passed through cartridges containing the MWCNT, where pesticides in the water were concentrated by adsorption. The analytical method for the detection of pesticides in dilute solution was proposed by using MWCNT as an adsorbent with gas chromatography/mass spectrometry for quantification of fenpropathrin, alphacypermethrin, and deltamethrin. The adsorption amounts of pesticides on the MWCNT were analyzed to identify the effects of temperature, flow rate, acidity, ionic strength, and analytes volume. The MWCNT-packed cartridges withstand a high load of water samples in the lowest concentration of 0.03 ng/L passing through for the extraction of pesticide residues at trace levels when compared with the commercial C18 cartridges, due to their large surface area and adsorption capacity.

Keywords: Multi-walled Carbon Nanotubes, Pesticides, Solid-phase Extraction, Adsorption, Water Purification

INTRODUCTION

Nanoparticles are of great scientific interest because they bridge the gap between molecular or atomic structures and bulk materials. Nanoparticles are particles that have one or more dimensions that are 100 nm or less. They have attracted much research interest due to their unique and fascinating properties over bulk materials in a variety of applications, including medicine, engineering catalysis, and environmental remediation. Biological systems have built inorganic-organic nanocomposite structures to improve the mechanical, optical, magnetic and chemical properties in living species [1]. Some flowers demonstrate the ability to self-clean their surfaces because of the combined effects of micro and nano-structured particles with hydrophobic characteristics that repel dirt [2]. Also, nanoparticles can be combined with other materials to make a product such as a rubber tire, which typically is a composite of an elastomer rubber and an inorganic filler of carbon black and silica nanoparticles [3].

The residues of agricultural organic toxicants such as pesticides, herbicides, and fertilizers, in trace quantities, have a large influence on the ecosystem. The fate of pesticides used on the field depends on their characteristics [4], such as evaporation, persistence, adsorption, and leaching. The presence of organic residues in the environment results in water pollution, mainly due to leaching. The accumulation of harmful residues in water reservoirs has resulted in negative effects on ecosystems, including human beings and aquatic species. Despite their presence in trace amounts, many pesticides have been found to cause adverse effects in such low concentrations [5]. To detect the residues at nano and picogram levels, it is necessary to concentrate the residues from the bulk samples before subjecting them to analytical techniques. Continuous monitoring and remedial measures are necessary to maintain an ecological balance necessary for providing a sustainable and safe living environment. Liquid-Liquid extraction has been one of the techniques for the pre-concentration of residues during the past several decades [6]. The restrictions on the use and consumption of organic solvents in large quantities have brought in the study of solid-phase extraction (SPE), which are simple, solvent-free techniques [7-9]. The performance of the SPE techniques mainly depends on the adsorption capacities of adsorbents, which enable simple and fast analysis of residues [10-12].

Porous materials such as alumina, iron [13], carbon [14] and silica [15] are widely used for the removal of many contaminants in the water system based on the adsorption process. In recent years, researchers have discovered the capacity of nanoparticles to adsorb many organic and inorganic contaminants present in environmental substrates. Zhao et al. [16] synthesized silica-magnetite nanoparticles as a sorbent for the extraction of phenolic compounds in water. Nair and Pradeep [15] studied the adsorption of chlorpyrifos and malathion in the water on gold and silver nanoparticles supported on activated alumina for purification of drinking water. Song et al. [16] used super-paramagnetic Fe_3O_4 nanoparticles as an extracting agent for the pre-concentration of triazine herbicides in water by a batch equilibrium process. Liu et al. [1] used porous hollow silica nanoparticles as a carrier for the determination of validamycin in agricultural samples while changing temperature and pH. Geller et

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al. [17] developed a pre-concentration method for residues of organochloride compounds in water by using zirconocene-based colloidal silica particles.

MWCNT has a higher potential to remove pesticide residues and protect the environment than do other adsorbents, including silica nanoparticles [18], magnetic materials [19], organic porous polymers [20] and alumina nanoparticles due to a large specific surface area, high permeability, layered, hollow structure and excellent mechanical and thermal stability [21-26]. Single-walled carbon nanotubes [27] have been used as an adsorbent in the SPE method for the determination of sulfonylurea herbicide residues in water, showing a mean recovery rate of 79 to 102%. Al-Degs et al. [28] developed an analytical method for the simultaneous determination of residues of atrazine, methidathion and propoxur using UV-Vis spectrophotometer and MWCNT as SPE adsorbent for the pre-concentration of residues in water and LOQ of pesticide residues 0.3 μg/mL and 84 to 93% of recovery in tap water with an acceptable 3% RSD (Relative standard deviation). In this research, MWCNT was used as an adsorbent in SPE cartridges combined with GC-MS system for a concentration identification of alphacypermethrin pesticide for the first time, and further studied by using fenpropathrin and deltamethrin pesticides.

The factors influencing the performance of SPE cartridges, such as the amount of adsorbent, pH of the substrate, temperature, eluent solvent, and sample volume, were evaluated by measuring the percent of recovery of pesticide residues using GC-MS. The residues were estimated using a validated GC-MS method with a limit of quantification (LOQ) of 0.03 ng/L and 88 to 96% of recovery an acceptable 2% RSD in water solutions.

MATERIALS AND METHODS

Polyvinyl pyrrolidone (PVP), polysilazane liquid (VL20) and reference analytical standards of fenpropathrin (purity 99.1%), alphacypermethrin (purity 99.3%), and deltamethrin (purity 99.8%) were obtained from Sigma Aldrich. Acetone (Purity-99.5%), Water HPLC grade, ammonia solution (Purity-28.2%) AR grade, and formic acid (Purity-98.8%) AR grade, were obtained from Merck Limited. C18 cartridges with 400 mg of sorbent, were supplied by M/s. Sigma-Aldrich chemicals private limited, Mumbai, India. The tap water samples were collected from our laboratory.

1. Synthesis of MWCNT

The multi-walled carbon nanotubes (MWCNT) were synthesized by using a mixture of polyvinyl pyrrolidone (PVP) and polysilazane liquid (VL 20) [18]. In this process 1.0 g of PVP and 6 mL of VL20 was dissolved in 25 mL of a 2 : 1 ratio solution of ethanol and acetone; with 0.6 g of 2.2-azobisisobutyronitrile (AIBN) added for polymerization of VL20. Then the total composition was stirred under 500 rpm for 3 h at ambient temperature and then heated at 80 °C for 5 h, using a thermostatically controlled water bath. Finally, a solid disc-like sample was obtained after heating at 120 °C for 48 h, followed by calcination at 1,000 °C for 2 h under argon gas. The obtained MWCNT was modified (oxidized) according to the reported literature [29]. The MWCNT produced were then characterized by SEM, TEM, and XRD.

2. Characterization of Carbon Nanotubes

To check the phase purity, a room temperature XRD profile of the synthesized carbon nanotubes was obtained (X'Pert Pro-MPD, PANalytical, Netherlands). For the thermal stability tests, TGA (Scinco TGA N1000, USA) was used [13-15]. The samples were heated to 800 °C with a heating rate (10 °C/min) under N_2 gas flow (50 mL/min). Specific surface area and pore volume were analyzed using a BELSORP-mini instrument (Microtrac BEL, Japan) based on N_2 adsorption-desorption isotherms at 77 K. The BET method was used to determine the particular surface areas of the porous samples. The microstructural analysis performed using scanning electron microscopy SEM (TESCAN, CZ/MIRA I LMH) showed the development of a carbon nanotube matrix. The FTIR (JASCO, FT/IR-6300) was used to identify functionalities in the MWCNT. The size of nanotubes was observed to be 90 nm by TEM (FEI, TECNAI G2 TF20-ST).

3. Preparation of Solid-phase Extraction Cartridges (SPE) with Carbon Nanotubes

The solid-phase extraction (SPE) cartridge was prepared by filling an empty 55 mm, 3 cm cartridge with 500 mg of MWCNT, protected between two polytetrafluoroethylenes (PTFE) frits. The cartridge was then wetted with 10 mL of methyl alcohol, followed by 20 ml of Millipore water to remove the soluble impurities, if present, in the cartridges. The conditioned cartridge was then used for the extraction of pesticide residues present in tap water.

4. Preparation of Standard Solutions

The standard stock solutions for the analysis were prepared by weighing about 5 mg of the respective pesticide into different 50 ml volumetric flasks, adding 10 mL acetone to each flask and sonicating up to 5 min to dissolve the content, then adding acetone up to the mark on the flask. The final stock solutions were prepared by transferring each standard sample of 0.5 mL to 100 mL volumetric flask and adding acetone up to the mark. The solution concen-

Table 1. Concentrations and volumes for the preparation of standard solutions

Stock solution concentration (ng/mL)	Volume taken from the stock solution (mL)	Final make-up volume (mL)	Final concentration (ng/mL)
500	1	10	50
500	0.2	10	10
500	0.1	10	5
5	0.5	10	0.5
5	0.2	10	0.1
0.1	3	10	0.03

trations were 0.5 μg/mL (500 ng/mL).

5. Preparation of Calibration Solutions

Different known concentrations of standard solutions (0.03, 0.1, 0.5, 5.0, 10 and 50 ng/mL) were prepared by diluting the above stock solutions in acetone. The serial dilution details are presented in Table 1.

6. Preparation of Sample Solutions for Assay Accuracy and Repeatability

The assay accuracy of the method was evaluated by spiking two different concentrations, 0.03 and 0.3 ng/L, of pesticide mixture in 100 mL of tap water. The repeatability of the method was determined by analyzing six replicate samples at each concentration level along with two controls for the identification of interference. The concentration of the solvent present in the spiked water sample did not exceed 0.1%. After spiking, the water samples were mixed thoroughly, equilibrated and maintained at 20+2 °C in temperature controlled water bath and passed through the cartridges by means of suction with flow rate 3 to 4 ml per minute. The cartridges were dried under vacuum and residues were then eluted using 5 ml of HPLC grade acetone. Based on the recovery percentage the limit of quantification was established.

7. Preparation of Sample Solution

The sample solution was made by transferring 0.1 mL of standard stock solution (500 ng/mL) into a volumetric flask of 50 mL and filling up to the mark with tap water, producing a sample concentration of 1.0 ng/mL. The solution was used to check the effects of flow rate, adsorption capacity, pH, ionic strength, and temperature.

8. GC-MS Parameters for the Identification of Residues

The configuration of the GC-MS system used included an Agilent/7890N gas chromatograph, together with a 5975C Mass-Selective detection (MSD) unit set in selective ion (EI) monitoring mode. A capillary column DB-1 (30 m length, 0.25 mm inner diameter, 0.25 μm thickness) was used for separation of the pesticide residue peaks. The injector temperature was 295 °C and the transfer line temperature was 300 °C. The column oven temperature was programmed for 100 °C for 3 minutes, increased at 10 °C intervals to 290 °C. The carrier gas used was 1 mL/min helium (He) and the injector volume was 1.0 μL. Agilent Chemstation Software was used for data acquisition and peak area calculation. The retention times for fenpropathrin, alphacypermethrin, and deltamethrin were about 8.4 min, 12.7 min, and 15.4 min, respectively in 20.0 min of total measurement time.

9. Method Validation

Method validation enhances the credibility of the analysis. In this study, parameters such as specificity, linearity, accuracy (recovery), repeatability, and LOQ were considered [20,30]. Recovery tests determined the accuracy of the methods by using samples spiked at 0.03 and 0.3 ng/mL concentrations. Linearity was determined with different known concentrations (0.03 to 50.0 ng/mL), prepared by diluting the stock solutions. The LOQ was determined by the recovery at low fortification levels.

10. Effect of Flow Rate

The dependence of flow rate on pre-concentration of residues was examined by recovery experiments at different flow rates of 1-2 mL, 3-4 mL, 5-6 mL and 7-8 mL/min, which were controlled under vacuum connected to SPE manifold. At these flow rates, 100 mL sample at 1.0 ng/mL was passed through the cartridge to quantify residues adsorbed in cartridges by washing the adsorbed residues with acetone.

11. Effect of pH and Ionic Strength

pH of water samples was controlled by using hydrochloric acid and sodium hydroxide solutions to prepare pH between 5 and 8. After adjusting the desired pH, the water sample was spiked at 1.0 ng/mL level of pesticide mixture. The spiked sample (100 mL) was passed through the cartridges at four different pH levels at 4, 5, 6 and 7, while temperature was controlled at 20±2 °C. The effect of ionic strength was examined by preparing the residues of pesticides with 0.2% and 1% sodium chloride solution in distilled water at 20±2 °C.

12. Effect of Temperature

The temperature effects on adsorption of residues in SPE cartridges filled with MWCNT were tested at 20, 30 and 40 °C. After sample injection, the water samples were homogeneously mixed in a temperature controlled water bath for 30 minutes. And then, 100 mL of sample (1.0 ng/mL) solution was passed through the cartridges with flow rate of 3-4 mL/minute.

RESULTS AND DISCUSSION

1. XRD Pattern of MWCNT

The room-temperature XRD profile for the synthesized MWCNT is shown in Fig. 1. A peak at about 25° indicates the presence of carbon. Another peak obtained at about 43° indicates the presence of oxygen. The XRD profile clearly shows the formation of the cubic spinel phase in our fabricated sample. These conscientious results are in good agreement with JCPDS No. 88-0315. The diffraction peaks at 25.8° and 43.5° correspond to the lattice spacing of the carbon (002) and (100) [31,32]. Further, no impurity peak was observed in the complete XRD pattern, confirming the formation of pure phase material.

2. TGA Analysis

TGA curves for the MWCNT are shown in Fig. 2. The process was initiated at ambient temperature, and the temperature was increased to 700 °C at a heating rate of 20 °C/min in air. A significant loss in weight did not occur until 200 °C. The weight loss detected in the range of 50-180 °C was attributed to the elimination

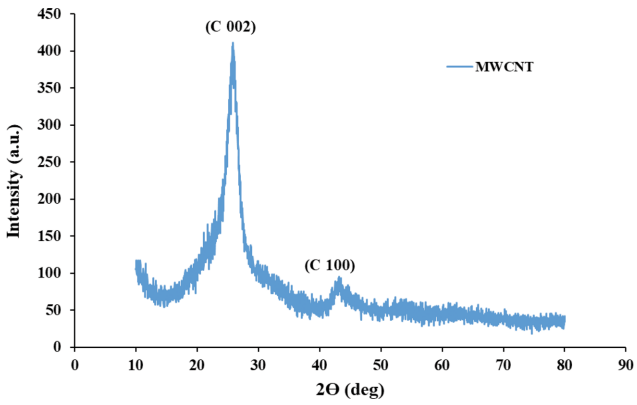


Fig. 1. XRD patterns of MWCNT.

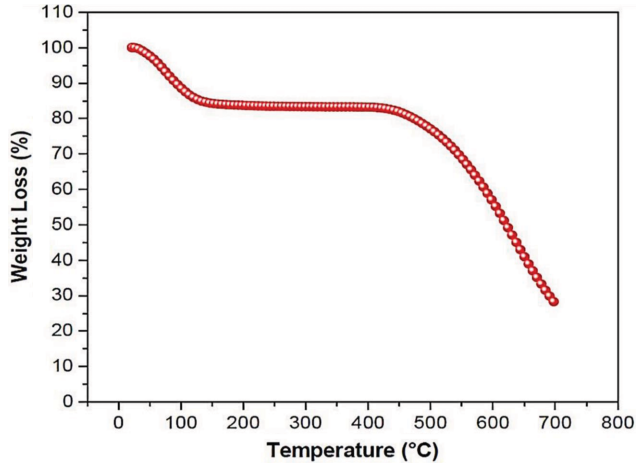


Fig. 2. TGA curve of MWCNT.

of physisorbed water on the MWCNT surface. There was a significant decrease in the weight of the MWCNT between 500-700 °C.

3. Adsorption Isotherm Measurements

N_2 adsorption-desorption assessment and the non-local density functional theory (NLDFT) technique determined the BET specific surface area and textural characteristics of the sample. Because of the presence of microporous material, all curves were type IV isotherms (Fig. 3), typically with type H_3 hysteresis. The MWCNT exhibited a pore volume of 1.38 cm^3/g and a surface area of 198.35 m^2/g. As seen in Fig. 3(b), the pore size distribution was also verified by MWCNT calculated using the non-local functional density theory (NLDFT) technique, showing three pore ranges of 1-3.5 nm, 3.5-6.5 nm, and 7.5-10 nm.

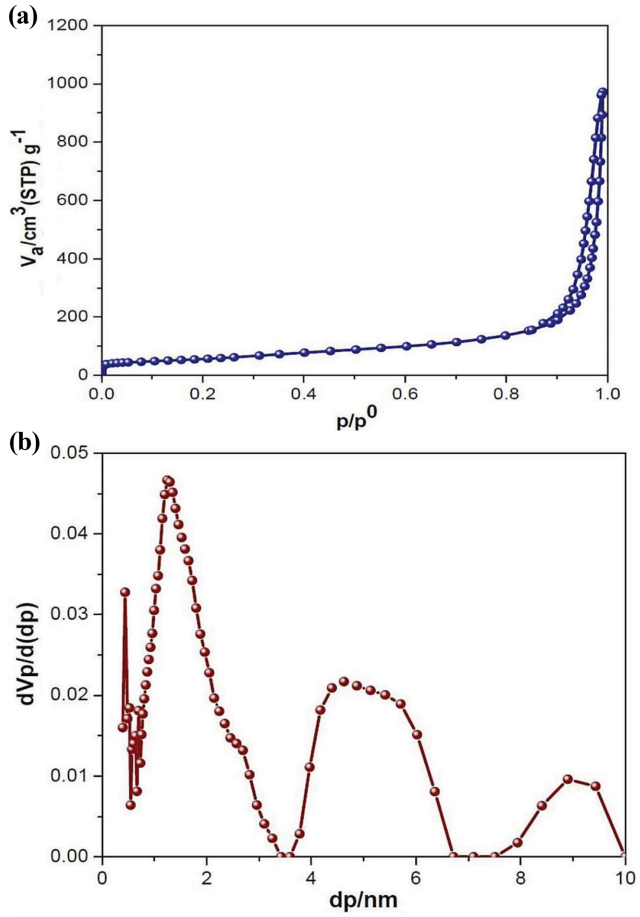


Fig. 3. (a) N_2 adsorption-desorption isotherm at 77 K, (b) pore size distribution of MWCNT.

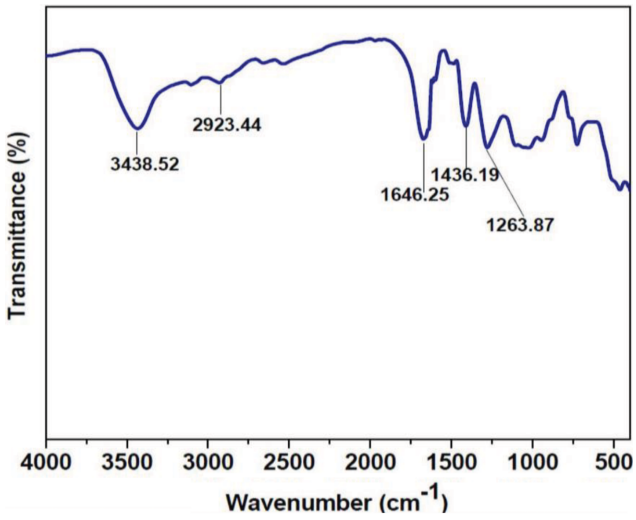


Fig. 4. FTIR spectrum of MWCNT.

4. FTIR Analysis of MWCNT

The FTIR spectrum of oxidized MWCNT analysis (Fig. 4) shows that there is a broad peak at about 3,438.52 cm^{-1} due to O-H stretching vibration in carboxyl groups (O=C-OH and C-OH) [29,33]. The peak at 2,923.44 cm^{-1} corresponds to the asymmetric (CH_2) and symmetric (CH_2) stretching vibration by the C-H bond. The 1,646.25 cm^{-1} peak is due to the stretching of C=C [34]. The vibration (O-H) in the carboxyl groups appears at a wavenumber of 1,466 cm^{-1} and the wavenumber of 1,263.87 cm^{-1} shows stretching C-O vibrations [31].

5. SEM Analysis of MWCNT

The microstructure of the sample was investigated using SEM. The SEM images of the MWCNT (Fig. 5) clearly show that the MWCNT is composed of nanotubes with irregular shapes and sizes. Also, in some regions, the interconnectivity of the nanotubes has increased, which has given rise to agglomerated regions within the sample.

6. TEM Analysis of MWCNT

The characteristic morphology of MWCNT was estimated by TEM analysis. Clear, hollow cylindrically shaped shells were observed with significant aggregation (Fig. 6). The distribution histogram of length of nanotubes from TEM observation showed a wide distribution with an average length 90 nm.

7. Specificity

Aliquots of standard solution (5 ng/mL), sample solution (1.0 ng/mL), control sample solution (Tap water), and acetone were assayed to check the specificity. No matrix peaks were observed in the chromatograms which can interfere with the analysis of different residues (Fig. 8). Furthermore, the retention times of fenpropathrin, alphacypermethrin and deltamethrin were about 8.4 min, 12.7 min,

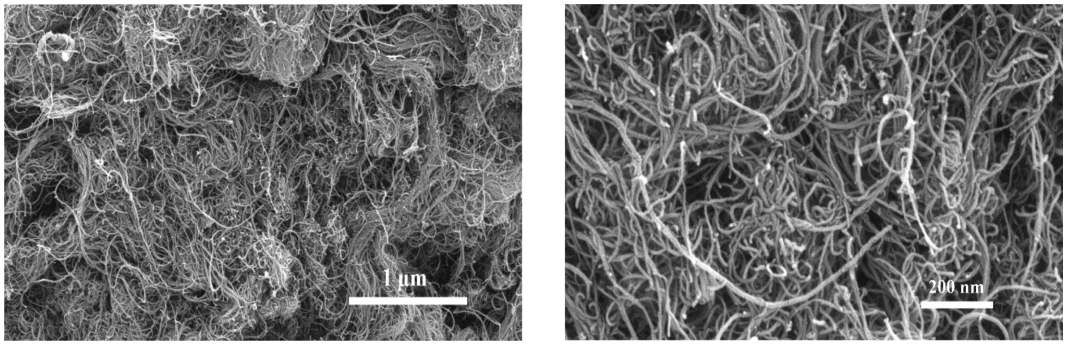


Fig. 5. Scanning electron microscope images of MWCNT with low (a) and high (b) magnification.

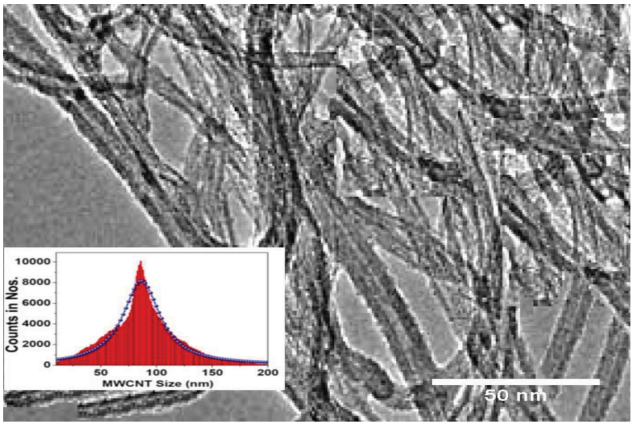


Fig. 6. TEM image of a nanotubes length distribution curve of MWCNT.

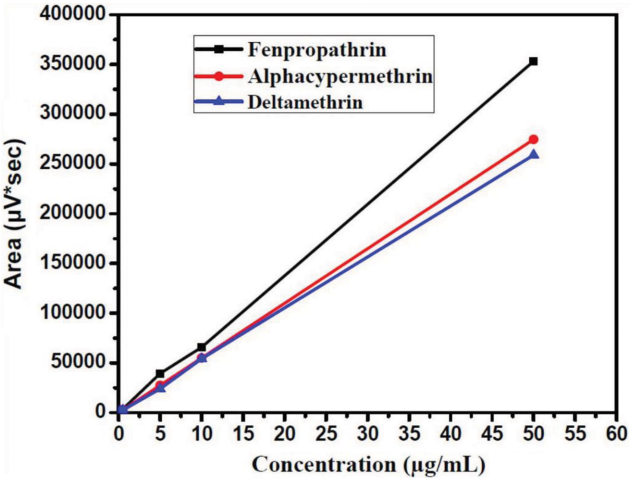


Fig. 7. Calibration curve of pesticides using GC-MS.

and 15.4 min, respectively.

8. Linearity

A calibration curve was plotted for concentrations of standard solution injected and the peak areas that were observed (Fig. 7). All the pesticide residues resulted in abundant molecular ion peaks. The amount of residues was analyzed according to the fragments of molecular ion peaks. The data of the limit of detection, retention time, fragmentation ions, and molecular mass of pesticide residues are presented in Table 2 (see Fig. S1 and S2 in supporting information).

9. Assay Accuracy (Recovery), Repeatability and Limit of Quantification

The recovery percentages of samples were evaluated by fortifying at two levels, 0.03 and 0.3 ng/L, of standard stock solution in 100 mL of tap water. The repeatability of the method was examined by operating with six replicate samples at each fortification level with two controls for each to identify any interferences. Based on the recovery percentage, the LOQ was determined. The average recovery percentage for each pesticide in tap water is presented in Table 3.

10. Effect of Flow Rate

The study of flow rate effect (Fig. 8) shows that the increase in flow rate resulted in decrease in the recovery rate of the MWCNT-SPE cartridges. The recoveries of pesticides were decreased with increases in flow rate, showing recovery of more than 90% up to 2 mL/min because the interaction time of pesticides in MWCNT-SPE decreased with increase in flow rate. The increase in flow rate

Table 2. Details of parameters for GC-MS analysis

Pesticides	Retention time (min)	Linearity range (ng/mL)	R^2	LOQ (ng/mL)	Molecular mass (m/z)	Fragment ions (m/z) used for quantification
Fenpropathrin	8.4	0.03-50	0.9996	0.03	349	181, 208
Alphacypermethrin	12.7	0.03-50	1.0000	0.03	416	163, 181
Deltamethrin	15.4	0.03-50	0.9998	0.03	505	181, 253

Table 3. The Average recovery of pesticide residues using MWCNT-packed SPE cartridges

Pesticides	Percent recovery in MWCNT	
	0.03 ng/mL	0.3 ng/mL
Fenpropathrin	91	96
Alphacypermethrin	89	93
Deltamethrin	88	92

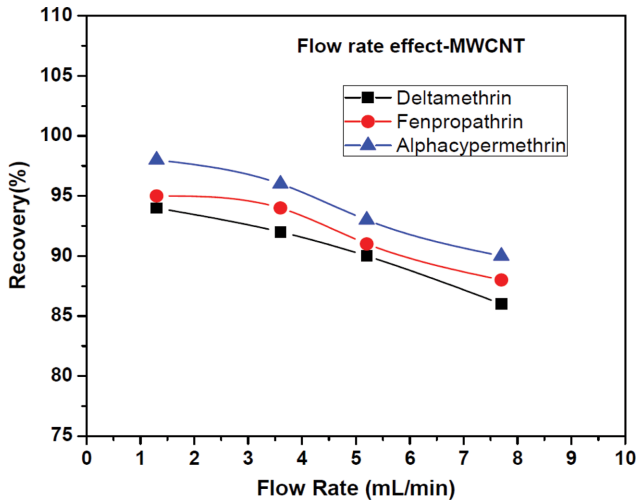


Fig. 8. Effect of flow rate in the extraction of pesticide residues.

over 5 mL/min showed further decreases in recovery percentage.

11. Effect of Sample Volume

A comparative study of conventional C18 cartridges was carried out to compare with the effects of MWCNT-SPE cartridges. The MWCNT based cartridges exhibited more capacity to collect the pesticide residues when compared with the conventional C18 cartridges (Fig. 9). The trapping capacity of the MWCNT based cartridges shows relatively high recovery even after passing 600 mL, but the recovery percentages were reduced from 93-96 to 84-89 for MWCNT and from 90-93 to 84-86 for C18 with increases in sample volume. The adsorption capacity of the C18 cartridges was also reduced after passing 200 mL of fortified water samples.

12. Effect of pH, Ionic Strength and Temperature

The effects of pH in preconcentration of residues were conducted in pH range of 4-7 by adjusting pH of water solutions using 0.1% hydrochloric acid or 0.1% sodium hydroxide solution. Recovery rate increased up to pH 5 and decreased after that (Fig. 10(a)). Most recoveries were maintained above 90% in pH of 4-7. The influence of pH value on the extraction efficiency depends on the analyte properties and was investigated previously in a range of 2 to 10 [35] and a range of 3 to 12 [36], showing that the highest recoveries were observed under acidic conditions [35]. According to the structure of pesticide, it was unstable and decomposed easily in an alkaline medium, leading to decreased recovery above pH 6. There were no significant changes in residue recovery rates during variation in the ionic strength showing 93 to 98% recovery with water sample with 0.2 and 1% of sodium chloride, respectively, at 1.0 ng/mL level (Fig. 10(b)). Ionic strength determined

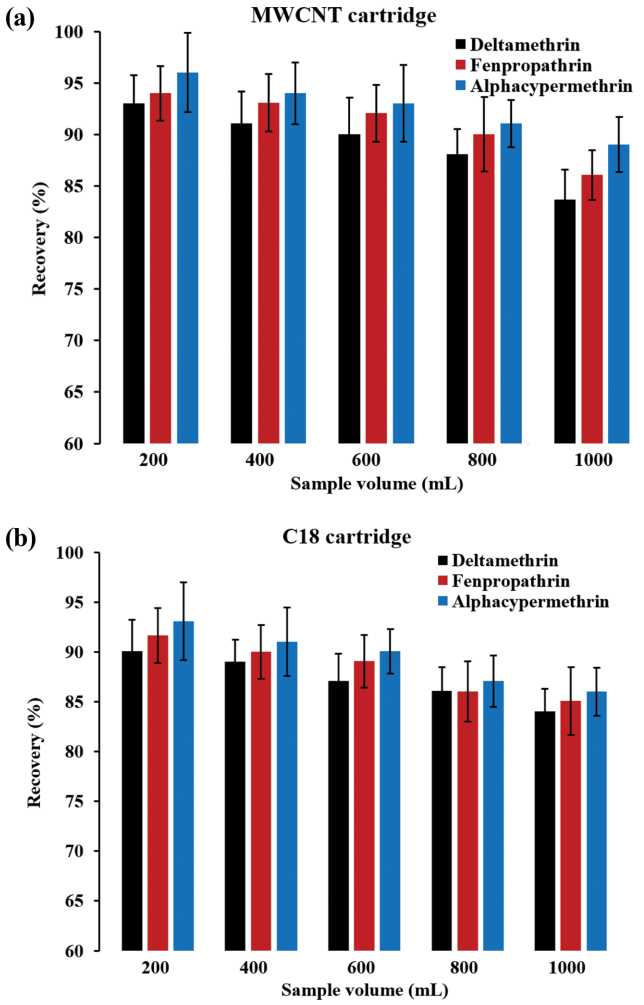
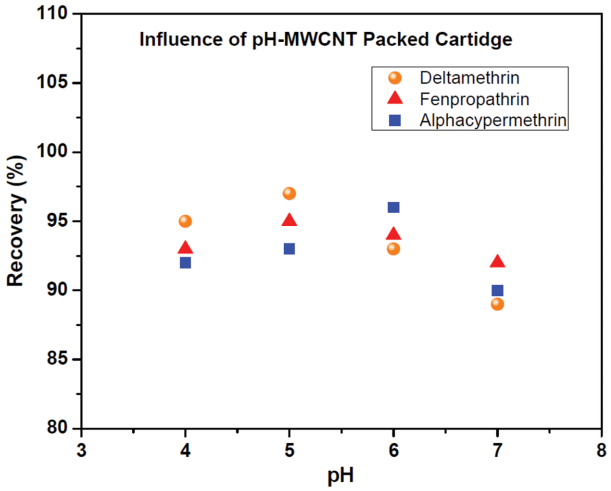


Fig. 9. Effect of the sample volume in the extraction of pesticide residues (a) MWCNT cartridge; (b) C18 cartridge.

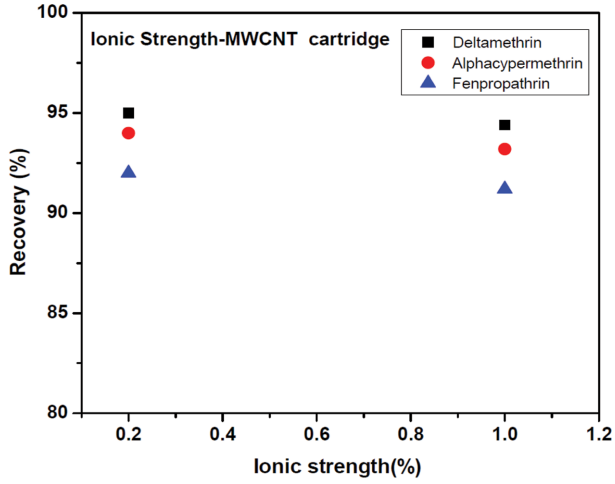
the concentration of ions in that solution, but due to variation in ionic strength little change in preconcentration capacity of residue was observed [37]. The effect of temperature was analyzed at three different temperatures. All the cartridges showed increases in recovery of the pesticides with temperature increase (Fig. 10(c)) due to increase in mobility of pesticide molecules in aqueous solution and MWCNT adsorbents in a cartridge, which leads to improvement in recovery rate.

CONCLUSIONS

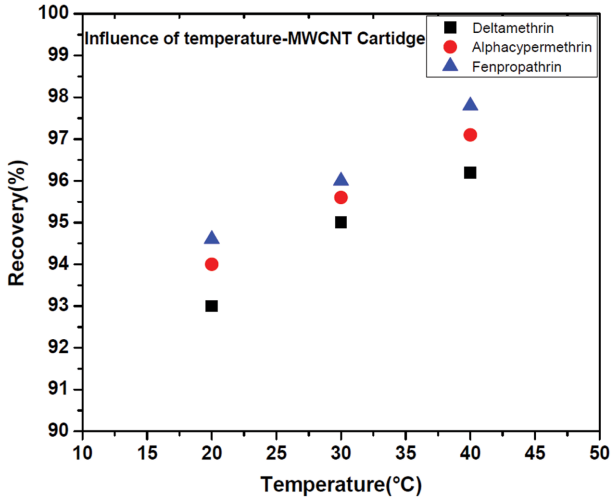
MWCNT was applied in SPE cartridges for the preconcentration of pesticide residues from water solutions. The performance of MWCNT cartridges presented a high recovery rate, retention efficacy and pH stability when compared with silica nanoparticles based cartridges. Thus, MWCNT is a potential alternative as a solid adsorbent for the pre-concentration of organic residues in environmental water. The cartridges operated with high flow rates of water samples for the pre-concentration of residues and proved the detection of residues from a dilute solution, which is an advantage over conventional columns. The concentration of alphacypermethrin



(a) Effects of pH



(b) Effects of ionic strength



(c) Effects of temperature

Fig. 10. Effects of pH, ionic strength, and temperature on extraction of pesticide residues.

pesticide was analyzed from a dilute solution with MWCNT adsorbent system for the first time.

The analytical method developed for the detection of residues in water solutions by using GC-MS has determined the lowest concentration of an LOQ 0.03 ng/L with MWCNT-packed SPE. The study shows that temperature increase brought in increased adsorption amounts of residues, while there were no differences in recovery rates with an increase in ionic strength for the three pesticide residues. More than 90% of each of the pesticide residues was adsorbed in the MWCNT cartridges. The results are comparable with the C18 cartridges, influenced by the volume of the sample, the recovery to a greater extent with the MWCNT cartridges [33]. The employed method was tested and found to be successful for the extraction and identification of pesticide residues in water samples by using MWCNT-SPE cartridges at different pH levels. The cartridges MWCNT-SPE will also be extended to withstand an increased number of water samples passing through at trace levels of residues for detection over conventional columns.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Extraction and determination of pesticide residues in water using carbon nanotubes coupled with gas chromatography-mass spectroscopy

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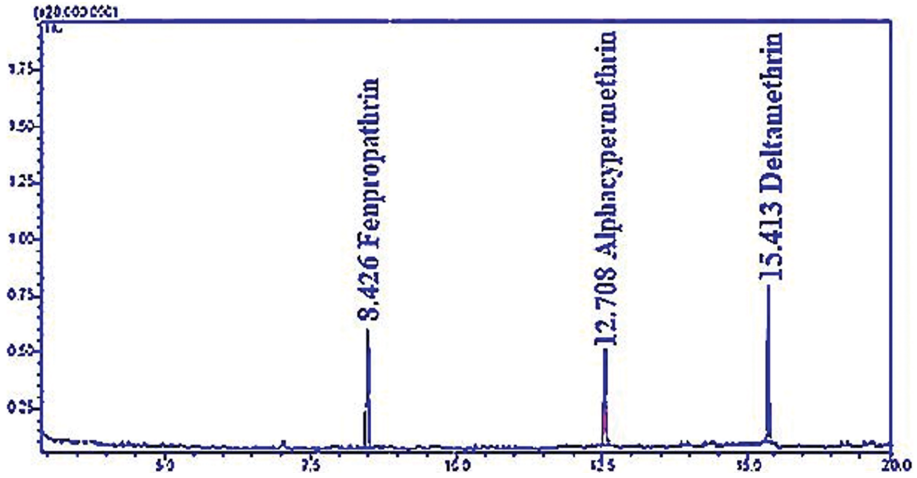


Fig. S1. GC-EI-MS total ion chromatogram for recovery samples of pesticides using MWCNT-packed SPE cartridges.

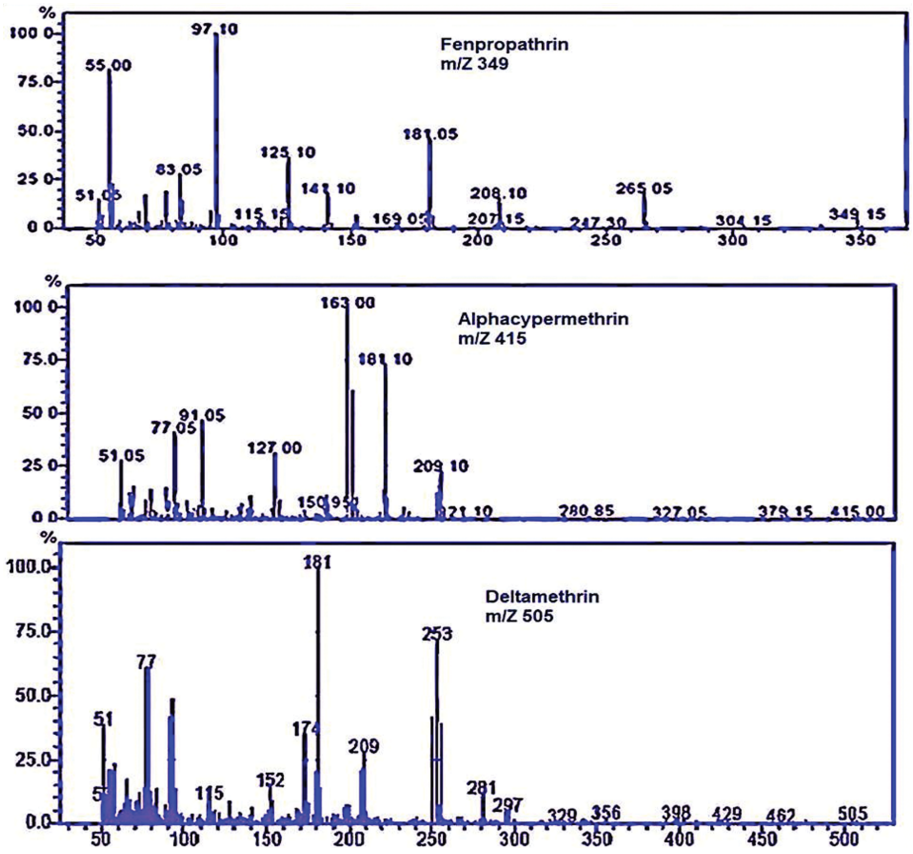


Fig. S2. GC-MS mass spectra of pesticides.