

Application of Single Wall Carbon Nanotube-wrapped Silica Composite Adsorbents as a Solid Phase Extraction Material to Measure Organophosphorus Pesticides in Water

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Abstract: In this paper, single wall carbon nanotube (SWCNT) suspensions were added dropwise to silica particles before volatilising the solvent to prepare a core-shell composite adsorbent with SWCNTs wrapped around silica particles (SWCNTs@Silica). The composite adsorbent was used as packing for the solid phase extraction (SPE) and the enrichment of organophosphorus pesticides (OPPs) in water. The results indicate the SWCNTs entirely wrap the silica particle surfaces to form SWCNT shells. This preparation method is simpler and more efficient than existing methods. SWCNTs@Silica composite materials can reduce the number of SWCNTs required and improve their utilization. The extraction capacity for OPPs in water was higher than for C₁₈ but below HLB. The developed SPE-GC-FPD method exhibited a limit of detection (LOD) and limit of quantitation (LOQ) of 0.593~1.759 µg/L and 1.95~5.80 µg/L, respectively and satisfactorily measured Jiulong river and farmland water samples.

Keywords: Organophosphorus pesticides, silica gel, single wall carbon nanotubes, solid phase extraction.

1. INTRODUCTION

The broad usage of organophosphorus pesticides (OPPs) results in their appearance in environmental waters. Due to potential biosafety risks, many countries, including the US and China, have set clear limits on the environmental residual concentration [1-3]. Currently, the primary pretreatments for OPPs include Soxhlet extraction, ultrasonic extraction and solid phase extraction (SPE) [1-4]. Of these, the China National Standard recommends Soxhlet extraction [2, 3, 5]; however, this method wastes significant amounts of toxic organic solvents; is complicated, time consuming and labour intensive; and cannot extract highly water-soluble polar pesticides. The emergence of new solid phase adsorptive material is expected to allow SPE to replace Soxhlet extraction [6, 7]. Numerous reports have used carbon nanotubes (CNTs), which demonstrate excellent adsorption properties [8-11], as SPE packing to extract OPPs in water. However, these studies all use pure CNTs as the packing and consumed a large amount of material (100-200 mg) with low utilization, and the minicolumn exhibited significant resistance with a low flow velocity. Composite adsorbents prepared from CNTs and other inorganic or organic carriers *via* wrapping, embedding and grafting can resolve these issues to some extent. However, these preparation methods are extremely complicated [12-17]. This paper leveraged the self-polymerization of SWCNTs at high

concentrations to prepare a silica composite adsorbent wrapped with SWCNTs (SWCNTs@Silica) *via* a simple hot air drying method. This composite material inherits both the superior adsorptive properties of SWCNTs and the low column pressure of silica and is expected to lessen the above issues. In this paper, target OPPs with different polarities were used to determine the properties of SWCNTs@Silica, and an analysis method was developed and used to measure environmental water samples.

2. MATERIALS AND METHODS

2.1. Equipment and Reagents

An Agilent 6890 gas phase chromatograph with a flame photometric detector (FPD), USA with an EQUITY-1701 chromatogram column (30 m×0.32 mm×0.25 µm, SUPELCO, USA), 12-bit SPE equipment (CNW Co., Germany), electrothermal air blow drying cabinet (Shanghai Yiheng Technical Instrument Co. Ltd., China), stereomicroscope (XTB-1 type, Jiangnan Optical Instrument Factory, China), SWCNTs (Chengdu Organic Chemical Co. Ltd., China, specific surface area 380 m²/g), silica (reagent grade, 100-200 mesh column chromatography silica gel, Qingdao Jiyida Silica Gel Reagent Factory), C₁₈ bonded silica minicolumn (BOND ELUT-C₁₈, 200 mg, 3 mL, VARIAN Co., USA), and Oasis HLB SPE minicolumn (200 mg, 6 cc, Waters Co., USA) was used for these experiments.

Mevinphos, dimethoate, malathion, chlorpyrifos and triazophos (analytical grade, Sigma-Aldrich Shanghai Trading Co., Ltd., Shanghai, China); NN-dimethylformamide (DMF, analytical grade, Xilong Chemical Co., Ltd.,

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Guangdong, China); methanol, acetone, hexane, and ethyl acetate (HPLC grade, Tedia Co., USA); and ultra-pure water (Millipore Simplicity System, Germany) were obtained.

A 10.0 mg sample of each pesticide standard was placed in a 10 mL brown flask, and dissolved with acetone to obtain 1000 mg/L single standard stock solutions. A corresponding volume from each stock solution was placed in a single 10 mL brown flask and diluted with acetone to obtain mixed standard stock solutions of mevinphos, dimethoate, malathion, chlorpyrifos, and triazophos with concentrations of 10, 20, 30, 20, and 10 mg/L, respectively. Either ultra-pure or actual water samples were added during testing according to the requirements to create spiked water samples with different concentrations.

2.2. Extraction Column Preparation

The SWCNTs were oxidized and a suspension prepared according to reference [18]. A 5 mg/mL SWCNT/DMF suspension was obtained. The SWCNT suspension was added dropwise to 200 mg of prepared silica in a beaker until it was barely moistened, and then placed in a 160°C hot air drying cabinet for 10 min to remove the DMF. The beaker was then removed, and a glass rod was used to gently press and separate the clustered particles before again adding the proper suspension dosage. The above process was repeated until all 10 mL of the suspension was consumed to obtain the SWCNTs@Silica. The SWCNTs@Silica was collected in a beaker and weighed to determine that the SWCNTs@Silica material contained 7.5 mg of SWCNTs, 3.6% of the total weight. An optical stereomicroscope was used to observe the surface wrapping.

A 200 mg SWCNTs@Silica sample was placed in a 6 mL empty plastic syringe with sieves at the bottom. Push the sieve from the top to obtain a SWCNTs@Silica SPE minicolumn. Before reusing, the minicolumn was washed with 10 mL of methanol, acetone, and ethylacetate in sequence and drained for future use.

2.3. Chromatogram Separation Condition

The chromatogram column cabinet temperature program: the initial temperature was 80°C, increased by 20°C/min to 250°C, held at 300°C for 3 min post run using a 260°C sample inlet temperature. The carrier gas (high purity nitrogen) flow rate was 2.0 mL/min using a splitless injection and measurement temperature of 230°C. A phosphorus filter was used with a 60.0 mL/min makeup gas (high purity nitrogen) flow rate, 75.0 mL/min hydrogen flow rate, and 100 mL/min air flow rate. The pre-tests indicate that 5 OPPs can be separated in 8.5 min under such conditions.

2.4. Column Flow Speed Comparison

A silica column under a 20 Kpa negative pressure was used as control group to examine the prepared SWCNTs@Silica minicolumn flow speeds. Three minicolumns of each type were used. Every 10 min, a graduated cylinder was used to measure the water volume passing through the extraction minicolumn, and the average flow speed was calculated. This process was repeated thrice for each column.

2.5. SPE Operation

In SPE equipment, 3 mL of methanol and 6 mL of ultra-pure water were used sequentially to activate the minicolumn. The water sample flowed through the minicolumns at the rate of 5~6 mL/min, was dried using negative pressure and eluted using a 6 mL mixed acetone/ethyl acetate solution ($v/v=1:3$). The eluent was concentrated to 1 mL using a nitrogen purge, and a 1 μ L sample was injected.

2.6. Measurement the Volume Penetration

The widely used commercial C₁₈ bonded silica gel and Oasis HLB minicolumns were compared to the SWCNTs@Silica minicolumn. Three penetration volumes for the minicolumns were measured, and it was operated as in section 2.5. All three microcolumns were spiked with 15 μ L of the mixed standard stock solution with 1, 100, 200, 300, 400 and 500 mL of ultra-pure water. These experiments were repeated 3 times.

2.7. Effect of pH

The effect a pH of 2, 4, 6, and 8 for a 100 mL spiked water sample had on the SWCNTs@Silica minicolumn recoveries was examined for 5 targets.

2.8. Water Sample Collection and Storage

Water samples were collected from the north (117.0815°E, 25.1740°N) and west branches (117.8125°E, 24.5033°N) of the Jiulong River; farmland water was collected from farms in Shamei Village, Xiang'an, Xiamen (118.3280°E, 24.6178°N). The water samples were filtered through a 0.45 μ m glass fiber membrane and stored in a brown bottle at 4°C for future use. Measurements were performed with in 12 h.

3. RESULT AND DISCUSSION

3.1. SWCNTs@Silica Characteristics

A stereomicroscope was used to observe the prepared SWCNTs@Silica. Fig. (1a) shows that a black SWCNT layer wrapped around the SWCNTs@Silica surface, and the particles were uniformly distributed with no hardened block. Fig. (1b) simultaneously shows the colourless transparent silica gel and black SWCNTs@Silica. The SWCNTs@Silica were similarly shaped and sized to the silica particles with coarser and edgy surfaces. This trait may result from the uneven precipitation and polymerization of SWCNTs on the surface. Studies have shown that SWCNTs have small tube diameters, large length-diameter ratios, and strong Van der Waals interactions between tubes with self-polymerization being likely after dispersion [19]. In this paper, an excessive SWCNT concentration in each drop added during the preparation, likely forms a hardened block between particles, while a low-dosages have difficulty wrapping the entire particle, and the SWCNTs layer commonly peels off. The optimal result was obtained when the silica gel is barely moistened. Once hot air removes the solvent, the SWCNTs self-polymerize and deposit on the silica surface due to the

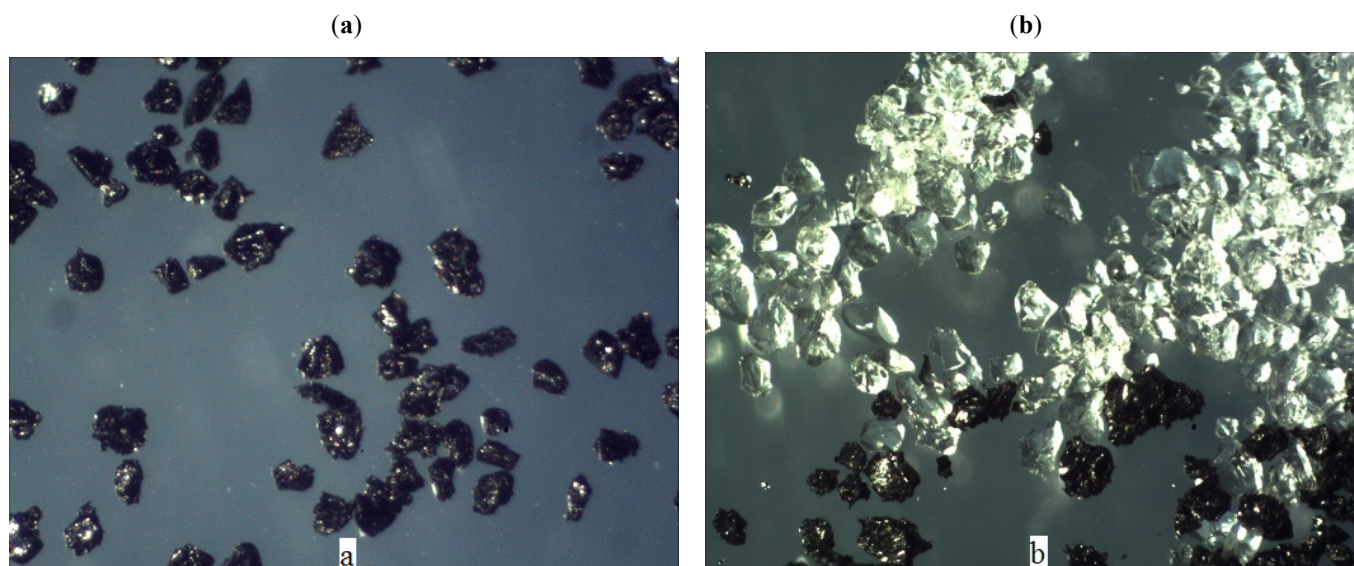


Fig. (1). Images of SWCNTs@Silica and Silica Gel under a Microscope (a) SWCNTs@Silica ($\times 50$); (b) Silica gel (colourless) and SWCNTs@Silica (black) ($\times 50$).

Van der Waals forces. Multiple precipitations form overlapping SWCNT layers that completely wrap the silica particles without shedding. This method requires few steps and simple operations without requiring adhesives or other additives; the end product has no extra impurities with high SWCNT utilization. This technique is superior to existing preparation methods.

3.2. Comparison of Column Flow Speed

Because CNTs are normally powders, packing pure CNTs into a SPE minicolumn yields a large resistance and unstable flow speed that negatively affects the extraction result [20-22]. In this paper, the average measured silica column flow rate was 5.53 mL/min (RSD=9.0%, $n=3$), while the SWCNTs@Silica minicolumn averaged a 7.70 mL/min flow rate (RSD=10.3%, $n=3$). The T test was under the confidence interval of 95%, which indicates there was no significant difference between two minicolumn flow rates. This result indicates that the SWCNTs@Silica minicolumn inherited the silica minicolumn's low column pressure.

3.3. Penetration Volume Measurements

The penetration volume is an important parameter for measuring the SPE minicolumn's adsorption capabilities. Fig. (2) indicates the extraction result for the Oasis HLB packing's that was best followed by SWCNTs@Silica with C₁₈ bonded silica being the worst. For a 300 mL water sample, the recovery for each target using a HLB minicolumn remained approximately 80%-120%. Increasing the water sample volume further reduced the recovery. This result indicated that the minicolumn was penetrated and the targets had begun to leak. Similarly, the SWCNTs@Silica minicolumn's recoveries declined rapidly from 100 mL to 200 mL for dimethoate and mevinphos, which are strongly polar; this result indicated that the penetration volume was approximately 100 mL. C₁₈ bonded silica exhibited the worst

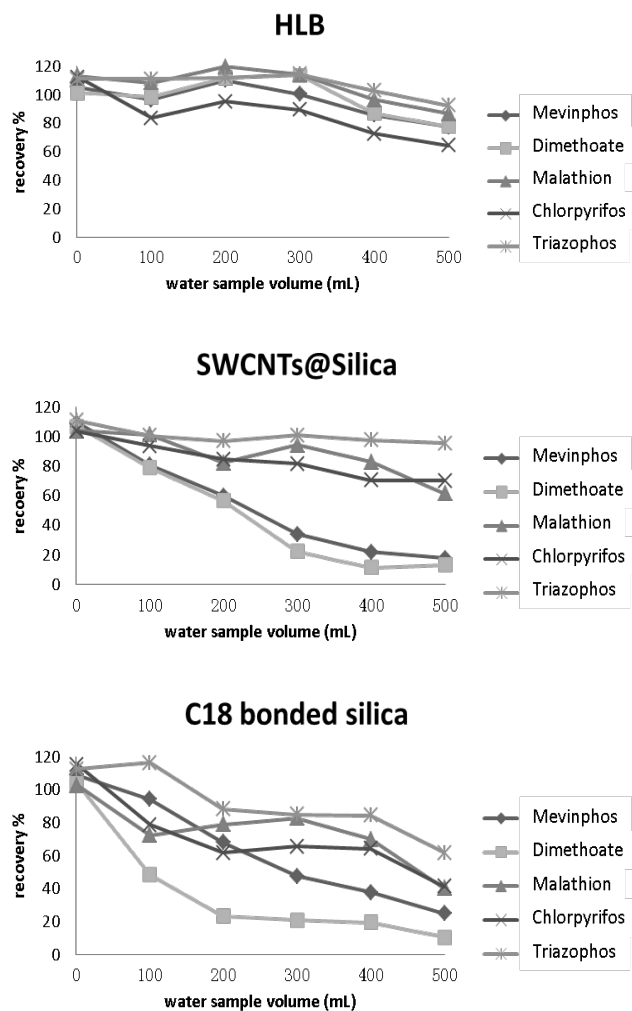


Fig. (2). Relationship between the recovery and water sample volume (RSD < 10%, $n=3$).

extraction result. The recovery of dimethoate rapidly declined from 1 mL to 100 mL to below 50%, which indicates the penetration volume was approximately 1 mL.

The 5 selected targets had N-octanol/water partition coefficients ranging from 0.7~4.7. Mevinphos and dimethoate were strongly polar, could mix with water and were difficult to extract. Oasis HLB is a bi-polar packing that can simultaneously extract polar and non-polar compounds. Therefore, it yielded excellent extraction results for all 5 targets. In contrast, C₁₈ bonded silica is a non-polar packing and exhibited the worst extraction results for the two polar compounds, Mevinphos and dimethoate. SWCNTs@Silica contains both oxidized polar groups and its inherent non-polar groups. Therefore, its overall extraction results were better than C₁₈ bonded silica and worse than HLB. However, because SWCNTs@Silica only contain 3.6% SWCNTs, preparing SWCNTs@Silica with higher concentrations may enhance the extraction capacity.

3.4. Effect of pH on the Extraction

SWCNTs@Silica exhibited better extraction result when the pH value ranged from 2~6. Above a pH of 8, the chlorpyrifos and malathion recoveries declined significantly.

Therefore, water sample should be processed before measuring to maintain a pH from 2~6.

3.5. Linear Range, LOD and LOQ

The SWCNTs@Silica minicolumn was used to extract a 100 mL water sample with a flow rate of 3-4 mL/min using 6 mL of an acetone/ethyl acetate mixed solution. The eluent was concentrated to 1 mL, a 1 μ L sample was injected, and a GC-FPD measurement was performed. The analysis for the 5 OPPs in water was developed under these conditions.

A series of 100 mL ultra-pure spiked water samples with different concentrations were prepared and measured using the developed method. The chromatogram peak area was used to develop a working curve; the linear range and correlation coefficients for the 5 targets were obtained using these working curves. A signal-noise ratio of 3 and 10 times were used to determine the method's LOD and LOQ, respectively; the results are shown in Table 1. All OPPs exhibited excellent linearity in the predefined concentration range with a correlation coefficient (R^2) of 0.9979~0.9995 and RSD of 3.2%~8.3% ($n=3$). The method yielded a LOD of 0.593~1.759 μ g/L and LOQ of 1.95~5.80 μ g/L for the targets.

Table 1. Characteristic data for the developed method.

Targets	Linear Range (μ g/L)	Correlation Coefficient	LOD (μ g/L)	LOQ (μ g/L)	RSD (n=3, %)
Mevinphos	2~200	0.9979	0.593	1.95	8.3
Dimethoate	4~400	0.9994	1.161	3.83	5.3
Malathion	6~600	0.9984	1.759	5.80	6.8
Chlorpyrifos	4~400	0.9995	0.875	2.88	4.3
Triazophos	2~200	0.9992	0.465	1.53	3.2

Table 2-1. Recoveries and precision for samples from the north branch of the Jiulong River.

Targets	Recovery ^a (%)	RSD ^a (% , n=3)	Recovery ^b (%)	RSD ^b (% , n=3)
Mevinphos	77.3	8.2	107.5	4.9
Dimethoate	70.4	2.0	96.4	7.3
Malathion	87.8	4.0	90.3	6.3
Chlorpyrifos	91.4	5.5	113.3	7.7
Triazophos	95.2	8.7	114.7	7.6

a. The spiked concentrations were 5, 10, 15, 10, and 5 μ g/L (low concentration), respectively; b. the spiked concentrations were 150, 300, 450, 300, and 150 μ g/L (high concentration), respectively.

Table 2-2. Recoveries and precision for sample from the west branch of the Jiulong river.

Targets	Recovery ^a (%)	RSD ^a (% , n=3)	Recovery ^b (%)	RSD ^b (% , n=3)
Mevinphos	86.0	6.4	100.7	1.4
Dimethoate	95.3	4.3	94.8	8.9
Malathion	93.9	6.6	108.7	6.6
Chlorpyrifos	91.8	3.8	116.5	3.3
Triazophos	95.2	2.0	107.4	1.3

a. The spiked concentrations were 5, 10, 15, 10, and 5 μ g/L (low concentration), respectively; b. the spiked concentrations were 150, 300, 450, 300, and 150 μ g/L (high concentration), respectively.

Table 2-3. Recoveries and precision for farmland water samples.

Targets	Recovery ^a (%)	RSD ^a (%; n=3)	Recovery ^b (%)	RSD ^b (%; n=3)
Mevinphos	76.7	9.7	90.6	9.1
Dimethoate	77.7	1.6	96.5	5.7
Malathion	81.5	4.1	102.6	5.7
Chlorpyrifos	102.0	1.8	119.3	3.5
Triazophos	97.2	5.4	112.2	1.7

a. The spiked concentrations were 5, 10, 15, 10, and 5 µg/L (low concentration), respectively; b. the spiked concentrations were 150, 300, 450, 300, and 150 µg/L (high concentration), respectively.

3.6. Actual Water Sample Measurements

No target was detected when the developed method was used to measure water from the west and the north branches of the Jiulong river and farmlands. Recoveries from 3 water samples were measured after adding a standard, and the results are shown in Tables 2-1, 2-2 and 2-3. These tables indicate that the targets all had spiked recoveries between 70%-110% with a 10% precision (RSD%, n=3). Samples with higher spiked concentrations had slightly higher recoveries than those with lower spiked concentrations. This method can be applied to actual water sample measurements with satisfactory result.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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