

# Solid-phase extraction of polar organophosphorous pesticides from aqueous samples with oxidized carbon nanotubes

Quanlong Li,\* Xuefeng Wang and Dongxing Yuan

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The development of new sorbents, which are able to trap polar compounds, is a growing research field in solid-phase extraction (SPE). In this study, multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) were oxidized in air at 600 °C and 500 °C, respectively, for 2 h. MWCNTs, SWCNTs, air oxidized MWCNTs (OMWCNTs) and SWCNTs (OSWCNTs) (200 mg of each) were packed in SPE cartridges. The four cartridges obtained, together with a commercial Oasis HLB cartridge, were used to extract six polar organophosphorous pesticides (OPPs), *i.e.*, dichlorvos, methamidophos, acephate, omethoate, monocrotophos and dimethoate, from an aqueous sample. The results showed that the oxidation process significantly enhanced the adsorption abilities of both SWCNTs and MWCNTs for polar OPPs. A comparative study indicated that OSWCNTs were more effective than Oasis HLB for the extraction of methamidophos and acephate and as effective as Oasis HLB for the other four OPPs from aqueous samples. When 100 mL of a natural sample was spiked with OPPs and extracted with OSWCNTs, the recoveries of five of the six polar OPPs (methamidophos excepted) ranged from 79.1 to 101.9%. The detection limits of the method based on OSWCNTs was found to be 0.07–0.12 µg L<sup>-1</sup>.

## 1. Introduction

Organophosphorous pesticides (OPPs), acting as cholinesterase inhibitors, are extensively used in agriculture all over the world. However, OPPs are toxic not only to pests but also to all animals including humans, all of which produce acetylcholinesterase. Obviously, therefore, the residues of OPPs in the aqueous environment will have lethal effects on non-target organisms. For an ecological risk assessment of low concentration OPPs in aquatic systems, analytical methods of high sensitivity are required. Many papers have been published on the determination of OPPs in aqueous samples.<sup>1–6</sup> GC and GC-MS are the most commonly used techniques for the analysis of OPPs,<sup>1–4</sup> but LC and LC-MS techniques have also been reported.<sup>5,6</sup> The OPPs in water samples are usually extracted with liquid–liquid extraction (LLE),<sup>1</sup> solid-phase extraction (SPE),<sup>2</sup> solid-phase microextraction (SPME),<sup>4,5</sup> or stir bar sorptive extraction (SBSE).<sup>3</sup> However, the physico-chemical properties of different OPPs, such as water solubility and  $K_{ow}$ , vary significantly (see Table 1). Some of the most polar OPPs, such as acephate, methamidophos, monocrotophos and omethoate, are of high polarity and extremely water soluble,<sup>6</sup> and thus cannot be effectively extracted from water with common LLE, SPE, SPME and SBSE procedures. As a result, they have often been missed in the studies described in the literature.<sup>1–5</sup>

SPE is the most widely used sample preparation technique in environmental analysis. SPE sorbents are usually divided into

three groups: chemically bonded silica, carbon materials, and porous polymeric materials. Due to their hydrophobic nature, the conventional sorbents such as C<sub>18</sub> silica, graphitized carbon black, and macroporous PS-DVB, show low retention for polar compounds.<sup>7,8</sup> In order to improve the SPE efficiency for polar compounds, many hydrophilic materials have been developed. The commercially available hydrophilic SPE sorbents include Amberlite XAD-7 from Room & Hass, Oasis HLB and Porapak RDX from Waters, Absolut from Varian, and Discovery DPA-6S from Supelco.<sup>7</sup> Besides these commercial sorbents, many laboratory-made hydrophilic SPE sorbents have been reported recently. For example, conductive resins based on polyaniline,<sup>9</sup> poly-*N*-methylaniline, polydiphenylaniline,<sup>10</sup> and polypyrrole,<sup>11</sup> were synthesized and applied to extract phenols. Marce's group prepared several SPE sorbents by polymerizing a polar monomer and crosslinking agent, and used the obtained polymers to extract phenols and polar pesticides.<sup>12–14</sup> In brief, the development of new sorbents, which are able to trap polar compounds, is a growing research field in SPE.<sup>7,8</sup>

Carbon nanotubes (CNTs) are a kind of carbonaceous nanomaterial and have received significant attention in many fields. There are two types of CNTs, namely, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs possess a cylindrical nanostructure, formed by rolling up a single graphite sheet into a tube. MWCNTs are arrangements of coaxial tubes of graphite sheets. The applications of MWCNTs as SPE sorbents for the preconcentration of environmental pollutants such as phenols,<sup>15,16</sup> phthalate esters,<sup>17</sup> triazine herbicides,<sup>18</sup> sulfonyleurea herbicides,<sup>19,20</sup> OPPs<sup>21,22</sup> and metal ions,<sup>23,24</sup> are reported. In comparative studies, MWCNTs are found to be more effective than, or as effective as, C<sub>18</sub> silica and

State Key Laboratory of Marine Environmental Science, Environmental Science Research Center, Xiamen University, Xiamen, 361005, P. R. China. E-mail: liql@xmu.edu.cn

**Table 1** Properties of the organophosphorous pesticides used in this study<sup>a</sup>

Pesticides	Water solubility/g L <sup>-1</sup>	Log K <sub>ow</sub>	Structure
Dichlorvos	8.0	1.47	
Methamidophos	1000.0	-0.8	
Acephate	818.0	-0.85	
Omethoate	1000.0	-0.74	
Monocrotophos	1000.0	-0.2	
Dimethoate	25	0.78	

<sup>a</sup> Data from <http://chem2.sis.nlm.nih.gov/>.

other polymer sorbents.<sup>15,17,18</sup> All the results reported indicate that CNTs are a suitable sorbent for SPE.

However, most of the reported work has focused on the application of MWCNTs, and the target chemicals were limited to low polar compounds and metal ions. SWCNTs have a much higher specific area and thus a stronger retention ability for polar compounds than MWCNTs. Some oxygen-containing functional groups will be present at the ends and on the walls of CNTs when they are oxidized.<sup>25-27</sup> Consequently, oxidized CNTs would be more retentive for polar compounds than those not oxidized. To the best of our knowledge, the application of oxidized SWCNTs (OSWCNTs) as SPE sorbents for the pre-concentration of high polar compounds has not yet been reported. In this study, both SWCNTs and MWCNTs were oxidized with air to enhance their polarity and used as SPE sorbents to enrich six typical polar OPPs, *i.e.* dichlorvos, methamidophos, acephate, omethoate, monocrotophos and dimethoate, in aqueous samples. The adsorption abilities of Oasis HLB for the above OPPs were also investigated and compared under the same experimental conditions. Finally, an SPE method based on an OSWCNTs packed cartridge was developed and applied to the analysis of environmental water samples.

## 2. Experimental

### 2.1 Chemicals and standards

MWCNTs prepared by the decomposition of CH<sub>4</sub> on a Ni-MgO catalyst<sup>28</sup> and with a specific surface of 100 m<sup>2</sup> g<sup>-1</sup> were kindly provided by the State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University, Xiamen, China). Commercially available SWCNTs, prepared using chemical vapour

decomposition and with a purity of more than 90%, an outer diameter of 0.8–1.6 nm, a length of 5–30 μm and a specific surface of 380 m<sup>2</sup> g<sup>-1</sup>, were purchased from Chengdu Organic Chemicals Co., Ltd. (Chengdu, China). The acephate, methamidophos, monocrotophos, omethoate, dichlorvos and dimethoate standard solutions of 100 mg L<sup>-1</sup> were supplied by China Standard Technology Development Corp. (Beijing, China), and used to prepare the stock solution containing 5 mg L<sup>-1</sup> of each compound in acetone. Acetone, methanol and ethyl acetate of analytical reagent grade were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The Oasis HLB cartridge (6 mL, 200 mg) was obtained from Waters Corporation (Milford, MA, USA). Purified water was supplied from a Milli-Q ultra-pure water system (Millipore, Billerica, USA) and used throughout the experiments.

### 2.2 Instrumentation

A model 5890 GC (Hewlett-Packard, Palo Alto, CA, USA) equipped with a flame photometric detector and an EQUITY-1701 capillary column (30 m × 0.32 mm × 0.25 μm, Supelco, Bellefonte, PA, USA) was used to separate OPPs. Chromatograms were recorded and analyzed using HW chromatographic data processing software (Qianpu Software Co., Ltd., Nanjing, China). The temperatures of the injection port and the detector were set at 200 °C and 250 °C, respectively. The column head pressure was 14 psi. The column temperature was kept at 50 °C for 2.0 min, then increased to 250 °C at a rate of 20 °C min<sup>-1</sup> and maintained for 2.0 min. A splitless injection mode was adopted.

Nexus 470 Fourier transform infrared spectroscopy (Thermo Nicolet Corp., Madison, WI, USA) was run on KBr pellets containing 0.5 wt% CNTs samples in order to characterize the

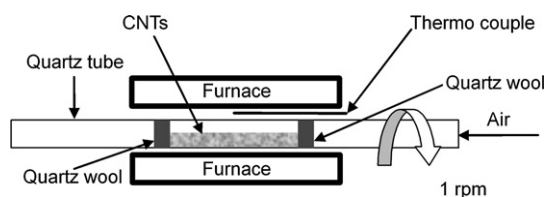


Fig. 1 Schematic diagram of the oxidizing apparatus.

oxygen-containing functional groups. Acid-based titration as described by Hu *et al.*<sup>29</sup> was applied to determine the coverage of the carboxylic group on the OSWCNTs.

### 2.3 SPE cartridge preparation

The MWCNTs and SWCNTs were refluxed in 6 M HCl for 8 h prior to use to remove any catalyst from them. A specially designed apparatus, as shown in Fig. 1, was applied to oxidize CNTs. CNTs (1.5 g) were placed in the quartz tube (60 cm in length, 1.8 cm in inner diameter) and immobilized at both ends with quartz wool. The quartz tube was then placed in the tube furnace, and an air flow of 50 mL min<sup>-1</sup> was introduced. The furnace temperature was set at 500 °C for SWCNTs and 600 °C for MWCNTs. The quartz tube was rotated at 1 rpm to allow the CNTs to be evenly exposed to air. After oxidation in air for 2 h, the weight loss of the CNTs sample was about 50%. The obtained CNTs were refluxed in 6 M HCl for 8 h for the further removal of catalyst. The HCl refluxed CNTs sample was then washed repeatedly to neutral pH with purified water, and dried at 150 °C for 3 h.

MWCNTs, SWCNTs, oxidized MWCNTs (OMWCNTs) and OSWCNTs (200 mg of each) were packed in 6 mL polypropylene cartridges. The sorbent was retained by a polyethylene frit at each end of the cartridge. Before use, the cartridge was washed with 6 mL of acetone followed by 6 mL of ethyl acetate.

### 2.4 SPE procedure

Prior to loading the water sample, the cartridge was conditioned with 3 mL of methanol followed by 3 mL of purified water. If the sample volume was 10 mL or less, the sample passed through the cartridge simply driven by gravity. When the sample volume was more than 10 mL, the sample was loaded at a flow rate of 3 mL min<sup>-1</sup> using a peristaltic pump (Baoding Longer Precision Pump Co., Ltd., Hebei, China) connected to the outlet of the cartridge. After sample loading, compressed air flow was applied to blow the cartridge to dryness. Acetone and methanol were chosen to elute the polar OPPs from the cartridge. The eluate was put in a water bath set at 45 °C and evaporated gently to 1 mL with high purity nitrogen gas flow; and 1 µL of the obtained solution was used for GC analysis. External calibration curves were used for the quantification. The recoveries of OPPs under different conditions were obtained by comparing the amounts of OPPs determined with that added to the water samples.

### 2.5 Water samples

In this study, two environmental water samples, seawater and reservoir water, were analyzed. The seawater sample was collected

from the Jiulongjiang estuary and the reservoir water came from the Lingyun reservoir in Xiamen University. The water samples were filtered through 0.45 µm membranes and then extracted with SPE cartridges packed with either OSWCNTs or Oasis HLB.

## 3. Results and discussion

### 3.1 Elution optimization

The OPPs adsorbed onto an SPE cartridge should be eluted as completely as possible in the SPE procedure. The type and volume of eluent have a great effect on the eluting efficiency, and thus need to be optimized. Optimization was performed only for OSWCNTs due to its strongest retention ability for OPPs among the sorbents investigated. The polar organic solvents, acetone and methanol, were tested as eluent for the polar OPPs. Spiked water (1 mL) containing 20 µL of stock solution was extracted with the cartridges. The retained OPPs were eluted with 6 mL of methanol and different volumes of acetone. Recoveries of OPPs as listed in Table 2 were used to evaluate the efficiency of the eluents. When 6 mL of acetone was applied as the eluent, the recoveries of six OPPs were near 100%, indicating that the target OPPs were completely desorbed. However, desorption of OPPs was incomplete with 6 mL of methanol. As a result, 6 mL of acetone was chosen to elute the OPPs in the SPE procedure.

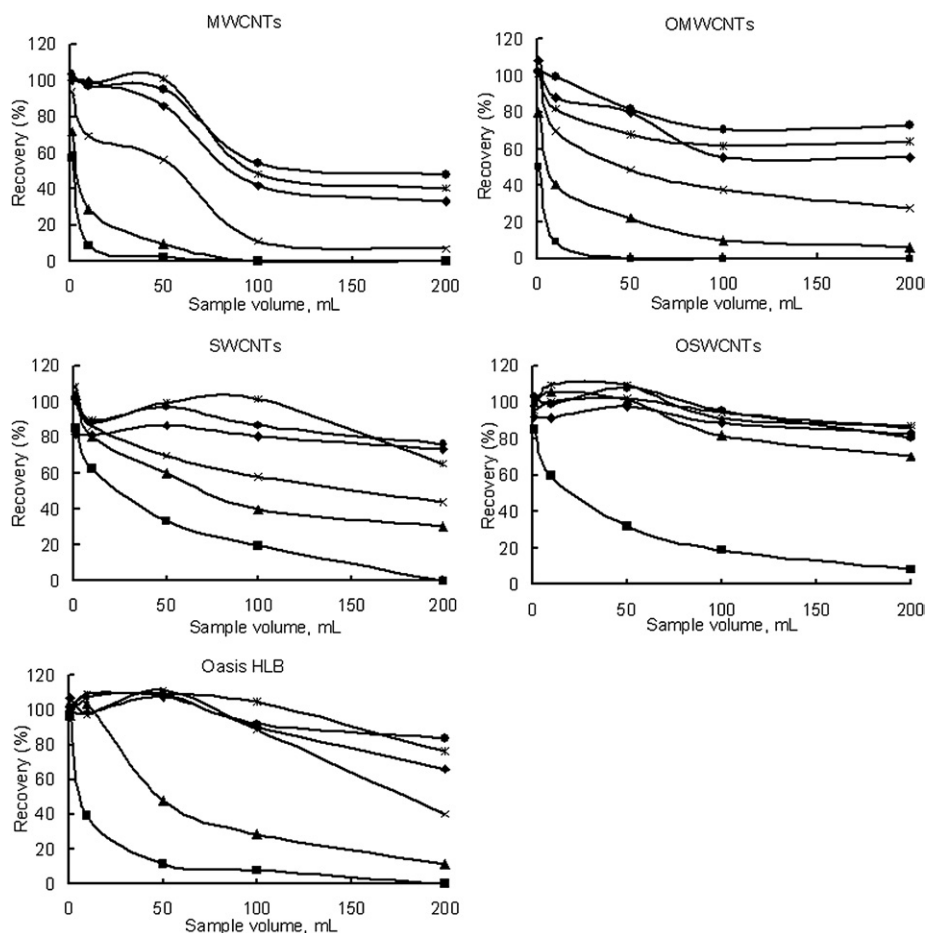
### 3.2 Retention of polar OPPs on the sorbents

Purified water (1, 10, 50, 100 and 200 mL) was spiked with 20 µL of stock solution to prepare a series of sample solutions at concentrations of 100, 50, 25, 5 and 0.5 µg L<sup>-1</sup>, respectively. These samples were concentrated with the cartridges packed with MWCNTs, SWCNTs, OMWCNTs, OSWCNTs and Oasis HLB. The test was performed in triplicate for every sorbent using different volumes. The recoveries of six OPPs on different sorbents at different volumes are shown in Fig. 2.

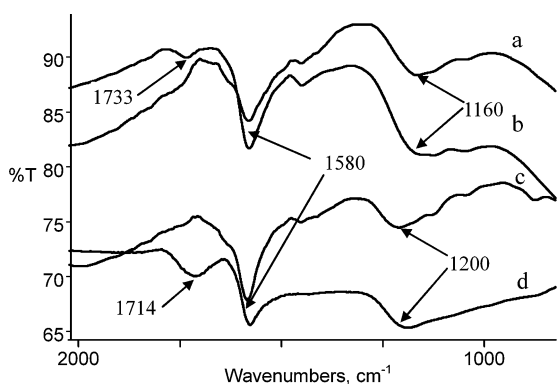
The results in Fig. 2 indicate that the recoveries of the six OPPs on OMWCNTs and OSWCNTs were higher than those on MWCNTs and SWCNTs, when the sample volume was more than 100 mL. These results implied that the oxidation process significantly enhanced the retention of polar OPPs on CNTs. The FTIR spectra of the CNTs samples are shown in Fig. 3. The vibrational mode at ~1580 cm<sup>-1</sup>, existing in every sample, corresponds to C=C bonds, and was assigned to the nanotube phonon mode. The peaks at ~1160 cm<sup>-1</sup> for SWCNTs and OSWCNTs, and ~1200 cm<sup>-1</sup> for MWCNTs and OMWCNTs,

Table 2 Recoveries of OPPs on oxidized SWCNTs with different eluents (%) (*n* = 3)

OPP	Eluent and its volume/mL			
	Acetone			Methanol 6
	2	4	6	
Dichlorvos	83 ± 9	96 ± 3	92 ± 7	70 ± 1
Methamidophos	76 ± 4	88 ± 5	85 ± 2	22 ± 2
Acephate	86 ± 8	88 ± 5	100 ± 3	30 ± 3
Omethoate	63 ± 8	90 ± 1	100 ± 5	22 ± 3
Monocrotophos	54 ± 12	82 ± 7	102 ± 3	32 ± 8
Dimethoate	43 ± 10	87 ± 5	108 ± 7	84 ± 5



**Fig. 2** Recoveries of six OPPs on different sorbents at different volumes, RSD ( $n = 3$ ) < 10% (◆, dichlorvos; ■, methamidophos; ▲, acephate; ×, omethoate; \*, monocrotophos; ●, dimethoate).



**Fig. 3** FTIR spectra of CNTs samples: (a) OSWCNTs, (b) SWCNTs, (c) MWCNTs and (d) OMWCNTs.

resulted from the C–O groups. The peaks at  $\sim 1733\text{ cm}^{-1}$  for OSWCNTs and  $\sim 1714\text{ cm}^{-1}$  for OMWCNTs were assigned to carboxylic groups. These FTIR results demonstrated that the oxidation process introduced carboxylic groups onto the surface of the CNTs, and this is confirmed by other researchers.<sup>25–27</sup> It is believed that the carboxylic groups present on the oxidized CNTs would enhance the polarity of the CNTs, and therefore improve their retention of polar OPPs.

Oasis HLB is a macroporous copolymer (divinylbenzene-co-*N*-vinylpyrrolidone) designed to have hydrophilic-lipophilic balance. The occurrence of the polar functional group, pyrrolidone, improves its adsorption for polar compounds. Oasis HLB gives high and reproducible recoveries for acidic, basic and neutral compounds. The recoveries of the OPPs on Oasis HLB with different sample volumes are shown in Fig. 2 for comparison with OSWCNTs. At the sample volume of 100 mL, the recoveries of dichlorvos, omethoate, dimethoate and monocrotophos on Oasis HLB were more than 85%, and similar to those on OSWCNTs (more than 80%). However, the recoveries of methamidophos and acephate on Oasis HLB were only 7.6% and 28.3%, respectively, and lower than those on OSWCNTs (18.9% and 82%, respectively). The results indicated that both methamidophos and acephate broke through on Oasis HLB, while acephate was trapped effectively on OSWCNTs. From the comparison, it could be found that OSWCNTs were more effective than Oasis HLB for the extraction of methamidophos and acephate and as effective as Oasis HLB for the extraction of the other four OPPs investigated in aqueous samples. The SWCNTs used in this study had nanometer pores and a specific surface area of  $380\text{ m}^2\text{ g}^{-1}$ . The occurrence of carboxylic groups on the OSWCNTs was verified using the FTIR spectra shown in Fig. 3, and the coverage of the carboxylic groups determined

with acid–base titration was found to be 2.7%. The high adsorption of polar OPPs by OSWCNTs probably resulted from their special structure and oxygen-containing groups.

### 3.3 Effect of sorbent drying during sample loading

When traditional reversed-phase sorbents such as chemically-bonded silica are applied in SPE, a conditioning step is needed. If the sorbent dries out before or during sample loading, its condition can be destroyed and the analyte will be less well retained, resulting in breakthrough. In 1996, Waters introduced the Oasis HLB sorbent, a reversed-phase and water wettable resin, whose performance is not affected by sorbent drying. In our study, the effect of sorbent drying on OSWCNTs was examined and compared with that of Oasis HLB. Two duplicate samples of 50 mL, spiked with 20  $\mu\text{L}$  stock solution, were prepared. The first aliquot was loaded after the cartridge was conditioned and equilibrated. When 25 mL of the sample had passed through, the cartridge was dried by blowing compressed air through it at a flow rate of 500  $\text{mL min}^{-1}$  for 10 min, and then the remaining 25 mL of the sample was loaded. The second aliquot was extracted without the drying step. This test was performed in triplicate. Fig. 4 shows the recoveries of six OPPs by OSWCNTs and Oasis HLB, with and without drying during sample loading. The recoveries on both OSWCNTs and Oasis HLB were not affected by the drying step. Similar to pyrrolidone on Oasis HLB, the oxygen-containing groups on the OSWCNTs reduced the interfacial tension between the sorbent surface and the water sample, improving the wetting characteristics, and thus enhanced the contact between the OPPs and OSWCNTs. As a result, the retention of OPPs on OSWCNTs was not affected by sorbent drying during sample loading.

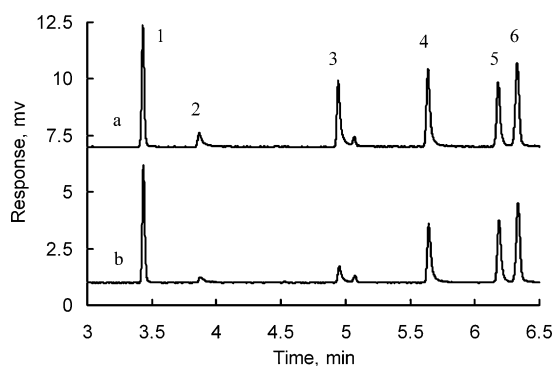
### 3.4 Analytical performance

The analytical performance of the OSWCNTs method was evaluated using 100 mL of spiked purified water. There was a linear correlation ( $r > 0.99$ ) between the peak area and the OPPs concentrations from 1 to 200  $\mu\text{g L}^{-1}$ . The detection limits ( $S/N = 3$ ) of dichlorvos, acephate, omethoate, monocrotophos and dimethoate were 0.07, 0.08, 0.09, 0.12 and 0.08  $\mu\text{g L}^{-1}$ , respectively. No methamidophos data was obtained, because of its low extraction efficiency on OSWCNTs. For an SPE cartridge packed with a given sorbent, the maximum sample volume (breakthrough volume) is related to the amount of the sorbent. If more OSWCNTs are packed into the cartridge, a greater water

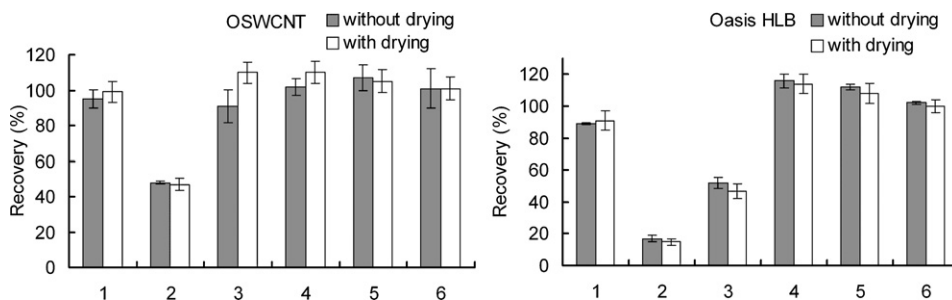
sample can be extracted and more OPPs retained, and therefore the detection limits of the method would be lowered. Evaporating the eluate in the water bath to a smaller volume during the SPE procedure could be another way to lower the detection limits.

Filtered reservoir water and seawater (100 mL of each) were concentrated using the cartridges packed with OSWCNTs and Oasis HLB. Both water samples could be used as matrix blanks, since no target OPPs were found in either. The two water samples were spiked at a concentration of 1.0  $\mu\text{g L}^{-1}$  for each compound and extracted with the OSWCNTs and Oasis HLB cartridges, and Fig. 5 shows the chromatograms of the six OPPs in the spiked seawater. The OPPs were completely separated, and the peak heights of methamidophos and acephate extracted with OSWCNTs were much higher than those extracted with Oasis HLB. The recoveries of the OPPs in spiked natural samples are listed in Table 3. On the OSWCNTs cartridge, the recoveries of methamidophos ranged from 17.9% to 19.0% and the others from 79.1% to 101.9%. On the Oasis HLB cartridge, the recoveries of methamidophos and acephate were less than 7.0% and 25.0%, respectively, and the others were in the range 82.1% to 105.1%. The results showed that OSWCNTs were more effective than Oasis HLB for the extraction of methamidophos and acephate and about as effective as Oasis HLB for the other four OPPs investigated.

The results for spiked purified water are also presented in Table 3 for comparison. No significant differences in the



**Fig. 5** Chromatograms of six OPPs ( $1.0 \mu\text{g L}^{-1}$ ) in the spiked seawater extracted with: (a) OSWCNTs and (b) Oasis HLB (1, dichlorvos; 2, methamidophos; 3, acephate; 4, omethoate; 5, monocrotophos; 6, dimethoate).



**Fig. 4** Recoveries of OPPs on OSWCNTs and Oasis HLB with and without drying during sample loading (1, dichlorvos; 2, methamidophos; 3, acephate; 4, omethoate; 5, monocrotophos; 6, dimethoate).

**Table 3** Recoveries of OPPs in spiked water samples with different sorbents (%)<sup>a</sup>

OPPs	OSWCNTs			Oasis HLB		
	Reservoir water	Seawater	Purified water	Reservoir water	Seawater	Purified water
Dichlorvos	87.3	82.6	88.7	92.2	95.3	90.3
Methamidophos	19.0	17.9	18.9	6.6	5.9	7.6
Acephate	83.0	79.1	75.4	23.6	21.3	28.3
Omethoate	97.1	101.9	99.2	82.4	82.1	93.5
Monocrotophos	101.0	98.9	95.6	111.2	105.0	116.5
Dimethoate	94.3	97.4	100.2	105.1	101.9	96.7

<sup>a</sup> The values are the average of 6 measures, RSD ( $n = 6$ ) < 10%.

recoveries of OPPs were found between the spiked seawater, the reservoir water and purified water. This revealed that the adsorption ability of both OSWCNTs and Oasis HLB towards the OPPs studied was not affected by the matrix.

For the evaluation of the reproducibility of the oxidizing process, three cartridges packed with 200 mg of OSWCNTs from three different batches were applied to extract the reservoir water sample spiked at 1.0  $\mu\text{g L}^{-1}$ . The relative standard deviations of the peak areas of the OPPs (except for methamidophos) were less than 10%.

It should be noted that the price of SWCNTs is higher than that of the Oasis material at present. However, the high cost of SWCNTs results from the preparation process and this will become lower with development of a suitable preparation technique in the near future.

#### 4. Conclusions

In this study, the potential for using oxidized CNTs in SPE to extract polar OPPs was investigated. The oxidation process introduced polar functional groups onto the surface of the CNTs, and significantly improved the adsorption ability of both SWCNTs and MWCNTs for polar OPPs. A comparative study suggested that OSWCNTs had a higher extraction efficiency than Oasis HLB for the extraction of methamidophos and acephate and about the same for the other four OPPs in aqueous samples. However, the improvement was not significant, and OSWCNTs could supplement Oasis HLB for the extraction of polar OPPs. The extracting efficiency of OSWCNTs remained constant even if they were dried during sample processing. When 100 mL of natural sample spiked with OPPs was extracted with OSWCNTs, the recoveries (except for methamidophos) ranged from 79.1% to 101.9%. The method detection limits with OSWCNTs were found to be 0.07–0.12  $\mu\text{g L}^{-1}$ .

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