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Carbon Nanotubes as a New Solid-Phase Extraction Material for Removal and Enrichment of Organic Pollutants in Water

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Abstract: Among carbonaceous materials, carbon nanotubes (CNTs) distinguish many unique electronic, mechanical and chemical properties, high surface and excellent strength. They have been also proven to possess great potential as superior adsorbents. The characteristic structures of carbon nanotubes allow them to interact strongly with organic molecules, via non-covalent forces, such as hydrogen bonding, π-π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. This review presents a summary of the performance of CNTs for the removal and enrichment of different classes' organic pollutants in water. The use of carbon nanotubes as a tool in filters, membranes and sorbent material for solid phase extraction is discussed along with their sorption capacities and process parameters.

Keywords: Carbon nanotubes, adsorption, organic pollutants, water samples

INTRODUCTION

In recent years, the release of various harmful organic compounds into the environment has attracted great attention because of their toxicity and widespread use. Therefore, it is crucial to develop simple, rapid and efficient methods for monitoring the environment. The most widely used methods for analyzing these organic contaminants are chromatographic and electrophoretic techniques. In spite of improvements in sensitivity

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and selectivity of modern analytical detection systems, conventional separation techniques are frequently used to overcome interferences from matrix elements and to improve detection limits through concentration of the analytes (1, 2). Among different separation and enrichment techniques, batch and column techniques in which analytes are sorbed on different water-insoluble materials and eluted with acids or other reagents have been widely used (3, 4). For the materials to be beneficial in solid phase extraction (SPE), given analytes should be easily, quantitatively and reproducibly collected and eluted with minimum efforts exerted in experimental procedures. SPE in analysis of water samples and aqueous extracts offers a number of important benefits in comparison with laborious classical liquid-liquid extraction, such as reduced solvent usage and exposure, low disposal costs and short extraction times for sample preparation. Today, SPE is the most often used method in environmental analysis for sample enrichment as it is easily automated and a wide range of phases is available.

Several materials have been proposed for solid phase extraction, such as C_{18} bonded silica (5, 6), polymeric sorbents (7, 8), carbonaceous materials (8, 9), zeolites (10) or polyurethane foam (11). The mechanism of sorption depends on the nature of the sorbent, and may include simple adsorption, ion-exchange, chelation or ion-pair formation. Adsorption occurs through van der Waals forces or hydrophobic interactions, which occur when the solid sorbent is highly non-polar. The most common sorbents of this type include octadecyl-bonded silica and styrene-divinylbenzene copolymers that provide additional π-π interactions, when π-electrons are present in the analytes. The presence of appropriate functional groups in solid matrices is needed for chelating trace elements. The choice of specific sorbent should be based on analyte, sample matrix and technique for final detection, whereas higher enrichment factors can be obtained using adequate experimental conditions (time of loading sample, sorbent mass, etc.).

Among carbonaceous materials, activated carbon was certainly one of the first materials applied in SPE. It has been widely used in water and wastewater treatment, primarily as an adsorbent for the removal of organic and inorganic contaminants (12, 13). More recently, fullerenes and carbon nanotubes (CNT) were discovered, and this opened a new perspective beyond that of carbon materials based on the flat graphite-like hexagonal layers. CNTs possess many unique electronic, mechanical and chemical properties, high surface and excellent strength. Presently three main methods employed for CNTs synthesis are arc-discharge, laser ablation and chemical deposition (14, 15). Synthesis methods are quickly improved year by year to produce large amount of size-controlled CNTs for commercial applications. Carbon nanotubes have been the subject of intense research because of their novel physical, chemical and electrical properties. Over the past 20 years, more and more potential applications such as catalyst supports, electronic and optical devices, reinforced materials, hydrogen storage, field-emission materials or biomedical use have been found. In numerous applications, including the analytical ones (such as gas sensors, electrochemical detectors, biosensors with immobilized biomolecules), modification of their surface and interfacial engineering are essential (16–19). CNTs are expected to play important roles in future sensing and separations techniques because they represent a novel class of material with varied functionality to facilitate adsorption.

The purpose of this paper is to summarize the applications of carbon nanotubes for the removal and enrichment of different classes' organic pollutants in water samples and some aqueous extracts. The use of carbon nanotubes as a tool in filters, membranes and sorbent material for solid phase extraction is discussed along with their sorption capacities and process parameters.

SORPTION PROPERTIES OF CNTS

Carbon nanotubes can be visualized as a sheet of graphite that has been rolled into a tube, with either single-walled (SWCNTs) or multi-walled (MWCNTs) structures. Whereas SWCNTs have diameters ranging from 0.3 to 3 nm, the MWCNTs are composed of a concentric arrangement of many cylinders and can reach diameters of up to 100 nm (20). The internal pores of the CNTs are large enough to allow small molecules to penetrate. Large sorption surfaces are also available on the outside and in the interstitial spaces within the nanotube bundles that are held together by van der Waals force. The surface morphology of CNTs examined by scanning electron microscopy (SEM) showed that they are open-ended, with adsorption sites on both internal and external surfaces (Fig. 1A),

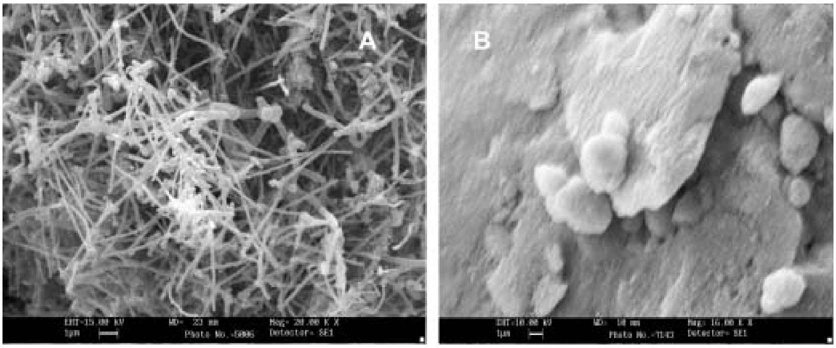

Figure 1. SEM images of carbon nanotubes (A) and graphitized carbon (B).

while graphitized carbon black (GBC) has a nonporous structure with a planar graphite surface (Fig. 1B).

The characteristic structures of carbon nanotubes allow them to interact strongly with organic molecules, via non-covalent forces, such as hydrogen bonding, π-π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions. These interactions as well as hollow and layered nanosized structures make them a good candidate for use as adsorbents. The surface, made up of hexagonal arrays of carbon atoms in graphene sheets, interacts strongly with the benzene rings of aromatic compounds. In 2001, Long and Yang (21) observed that dioxins, which have two benzene rings, were strongly adsorbed on CNTs. The amounts of dioxin adsorbed were 10^4 and 10^{17} times greater than that on activated carbon and γ-Al_2O_3, respectively. Dioxins after enrichment step could be removed from the adsorbent by temperature-programmed desorption.

The sorption equilibrium data for organic compounds are mostly related either with the Langmuir or the Freundlich equations (or both) tried to find a link between empirical isotherms and heterogeneity of the surfaces (22–27). The Langmuir equation describes localized, monolayer adsorption on homogeneous surfaces while in the Freundlich model the surface is mainly considered heterogeneous. Using these models the isotherm constants related to adsorption capacity are usually obtained; for example the values of adsorption capacity for trihalomethanes decreased in order: $CHCl_3 > CHBrCl_2 > CHBr_2Cl > CHBr_3$ (25). For polycyclic aromatic hydrocarbons, adsorption seemed to be related with their molecular size, e.g., the larger the molecular size, the lower the adsorbed volume capacity (27). Agnihotri et al. (26) found that increasing the sample temperature reduced the relative error between experimental and predicted data irrespective of isotherm model used. Increasing the temperature allows adsorption to occur predominantly on sites with higher activation energy, which makes them appear less heterogeneous. The negative free energy changes accompanied by a positive entropy changes indicate that the adsorption reactions are spontaneous and removal of 1,2-dichlorobenzene is an endothermic reaction (22). Moreover, the increase in temperature results in a rise in diffusion rate across the external boundary layer and within the pores of CNTs due to the result of decreasing solution viscosity (24).

The surface chemistry of carbons is determined to a large extent by the number and the nature of the surface functional groups or complexes. Oxidation of CNTs with nitric acid is an effective method to remove the amorphous carbon, carbon black and carbon particles introduces by their preparation process (28). It is known that oxidation of carbon surface can offer not only a more hydrophilic surface structure, but also a larger number of oxygen-containing functional groups, which increase the ion-exchange capability of carbon material. Gas phase oxidation of activated carbon increases mainly the concentration of hydroxyl and carbonyl surface groups, while oxidation in the liquid phase increase particularly the content of carboxylic acids (29). The amount of carboxyl and lactone groups on the CNTs treated with nitric acid was higher in comparison that this process was conducted using H_2O_2 and $KMnO_4$ (30). The chemical and thermal treatment processing could have great impact on the adsorption capability of CNTs, particularly for metal ions removal, because the performance of carbon materials is mainly determined by the nature and concentration of the surface functional groups (30, 31).

The covalent functionalization of the CNTs utilizing open-end and sidewall chemistry also opens additional possibilities for sorption of different molecules. Several examples for the use of such nanotubes in the fabrication of polymeric carbon nanocomposites, the probing of nanotube-molecule interactions, and the conjugation with biological species have been already presented (18, 32, 33). Microbeads obtained by encapsulation of carbon nanotubes in Ba^{2+}-alginate were applied for elimination of dibenzeno-*p*-dioxin, dibenzofuran, and biphenyl from contaminated water (34). Recently, Salipira et al. (35) reported that copolymerization of cross-linked nanoporous polymers with functionalized CNTs resulted in novel polymers capable of efficient removal of organic pollutants from water. The cyclodextrin-based polymers removed *p*-nitrophenol by 99% from a 10 mg/L spiked water sample, whereas granular activated carbon removed only 47%. Moreover, these polymers have also demonstrated ability to remove trichloroethylene (10 mg/L spiked sample) to non-detectable levels (detection limit $< 0.01\,\mu g/L$) compared to 55% and 70% for granular activated carbon and native cyclodextrin polymers, respectively. The investigations into the use of cross-linked cyclodextrin polyurethanes copolymerized with functionalized carbon nanotubes as adsorbents for organic pollutants has yielded very useful results that may have an impact in future water treatment applications (36).

Carbon nanotubes can also be used as support for adsorption materials significantly enhanced their sorption capacity. MnO_2/CNTs composites were efficient for removal of Pb(II) ions (37), while cerium oxide supported on carbon nanotubes with high surface area (in excess of 189 m^2/g) exhibited excellent characteristics for removal of chromium(VI) (38) and arsenate (39) from drinking water.

Jin et al. (40) proposed magnetic Fe nanoparticle functionalized MWCNTs for the removal of benzene and related derivatives. They not only displayed improved water solubility, but could also be recovered easily from the solution by magnetic separation. The scheme for the preparation of functionalized water-soluble MWCNTs (Fe-MWCNT-CH_2COONa) is presented in Figure 2. Briefly, MWCNTs were dispersed in $Fe(NO_3)_3$ solution with the help of an ultrasonic bath. After draining

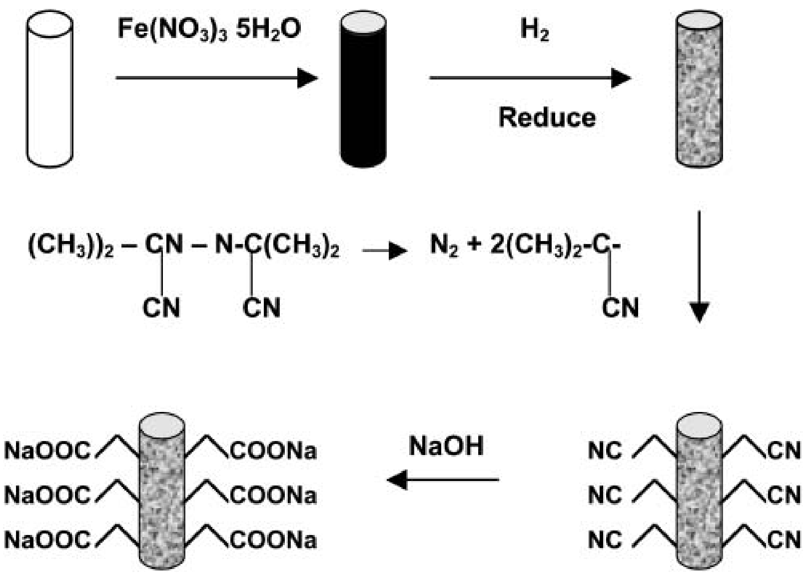

Figure 2. Scheme for the preparation of magnetic Fe nanoparticle functionalized water-soluble multiwalled carbon nanotubes (40). (Copyright The Royal Society of Chemistry. Reproduced with permission).

excess of water on a rotary evaporator with a vacuum pump, the resulting materials were reduced using hydrogen at 560°C and 900°C successively. Thus, Fe nanoparticles were deposited inside the inner cavities of carbon nanotubes. Then they were attacked by carbon radicals generated by the thermal decomposition of azodiisobutyronitrile. The produced Fe-MWCNTs-cyano material was refluxed in sodium hydroxide aqueous solution-methanol mixture. The applicability of the obtained sorbent was studied using four model compounds—benzene, toluene, dimethylbenzene and styrene. Their mixture was shaken at room temperature with 10 mg of the prepared sorbent for a few minutes to form a homogeneous black dispersion. Then CNTs were collected from the black dispersion by discarding supernatant liquid with the help of magnet and the adsorbed compounds were eluted with 0.2 mL of methanol. The recoveries of studied compounds were higher than 80% (40). Notably, after being several times with methanol and dried in vacuum, this sorbent can be re-used.

APPLICATIONS

In several papers, sorption on CNTs has been examined for different aromatic compounds, such as chloorobenzenes (22, 23), polycyclic aromatic hydrocarbons (27), three endocrine disruptors (bisphenol A, 4-*n*-nonylphenol and 4-*tert*-octylphenol) (41), several phtalate esters (42), chlorophenols (43), triazine (44, 45) and sulfonylurea herbicides (46–48), phenoxyalkanoic (49, 50) and organochlorine pesticides (51), diazinon (52), uraemic toxins (53), microcystins (54) as well as polychlorinated dibenzo-*p*-dioxins and related compounds (34). These works demonstrate the application of carbon nanotubes used as the packing of SPE cartridge in trace analysis of environmental pollutants in natural water samples in combination with high-performance liquid chromatography. Fang et al. (55) applied CNTs as a sorbent for on-line solid-phase extraction of 10 different kinds of sulfonamides before their simultaneously determination in eggs and pork. Carbon nanotubes were also applied for trapping volatile organic compounds (26, 56–58). The presentation concerning applications of CNTs for removal and enrichment of several organic compounds is given in Table 1 for an easier approach and comparison.

Solid-phase extraction of dicamba (3,6-dichloro-2-metoxybenzoic acid) using different polymeric sorbents (Oasis, Strata-X, Lichrolut SAX) and C_{18} BondElut or phenyl-silica gave unsatisfactory results (59). This herbicide is present in several environmental compartments due to a large scale of application, persistence, polar nature and water solubility. Carbon nanotubes have a much greater herbicide adsorption capability compared to that of graphitized carbon black (GBC) and C_{18} adsorbents as it shown by Figure 3 (50). The absorption capacity increases remarkably at lower pH of sample solution as dicamba is a highly acidic compound ($pK_a = 1.9$). The decrease of pH leads to decrease in ionization of the analyte and simultaneously to neutralization of the carbon surface charge.

The thermodynamic characteristics of adsorption of several organic compounds on carbon nanotubes were determined by gas chromatography and compared with those for GBC and molecular crystals of fullerene C_{60} (60). The comparison of adsorption data for compounds with different functional groups showed similarity of adsorption properties of CNTs and graphitized carbon black, but there were significant differences in molecular interaction of adsorbed molecules with crystal C_{60}.

The application of carbon nanotubes, C_{18} bonded silica and activated carbon for enrichment of four chlorobenzenes were compared under the same experimental conditions (columns packed with 15 mg of each sorbent materials, sample volume 100 mL, analytes at 5 ng/mL concentration level) (23). The highest recoveries were found for CNTs (Fig. 4). Moreover, carbon nanotubes exhibit the highest adsorption ability towards these analytes, which was concluded from the obtained values of the apparent constant K in Freundlich model.

Table 1. Examples for adsorption of organic pollutants on carbon nanotubes.

Compounds	Sample	pH	Eluent	Recovery (%)	Remarks	Ref.
Chlorobenzenes	Natural and polluted waters		methanol	80–103	Adsorption capacity 237 mg/g; higher than for C_{18} and activated carbon. The experimental data were fitted to Freundlich isotherm	23
Trihalomethanes	Standards	3–7			Static adsorption experiments. Adsorption capacity of 0.92–2.41 mg/g. Comparison with C_{18}.	25
Organic vapors (toluene, methyl ethyl ketone, hexane, cyclohexane)	Standards				The relative adsorption capacities decreased in the order: toluene > methyl ethyl ketone > hexane > cyclohexane. The Freundlich isotherm equation fitted the experimental data more closely than the Langmuir or Dubin-Radushkevich models.	26
Polycyclic aromatic hydrocarbons	Standards				For different PAHs, adsorption seemed to relate with their molecular size – the larger the molecular size, the lower the adsorbed volume capacity. The nonlinear isotherm models (Freundlich, Langmuir, Brunauer-Emmer-Telelr, Dual-mode and Polanyi-Manes) were tested to fit experimental data.	27
Bisphenol A, 4-*n*-nonylphenol, 4-*tert*-octylphenol	Natural waters	5–8	methanol	90–104	Linear range 0.2–200 µg/L. CNTs have better ability for the extraction than C_{18} and XAD-2 copolymer.	41

(*continued*)

Table 1. Continued.

Compounds	Sample	pH	Eluent	Recovery (%)	Remarks	Ref.
Phthalate esters	Tap, river, seawater		acetonitrile	80–105	Linear range 2–100 µg/L. Sample volume up to 3000 mL.	42
Chlorophenols	Tap and river water	5–9	methanol	88–109	The recoveries decreased slightly with the increase of sample volume higher than 200 mL.	43
Antrazine and simazine	Natural waters	6–7	acetonitrile	83–104	The recoveries were constantly at the flow rate in the range of 2–7 mL/min.	44
Propoxur, atrazine, methidathion	Tap, reservoir and stream water	5	acetonitrile	70–96	Adsorption capacity of CNTs was larger than those of activated carbon and C_{18} silica. CNTs may be re-used over 100 times after proper cleaning and re-conditioning.	45
Triasulfuron and bensulfuron-methyl	Tap, reservoir, well water, seawater	3	acetonitrile + 1% (v/v) acetic acid	79–108	The recovery of bensulfuron-methyl from seawater sample was only 44%. No significant differences in the enrichment efficiencies were observed even if the sample solution was up to 1500 mL for 100 mg CNTs packing.	47
Organochloro pesticides	Underground, tap and reservoir waters	7	dichloromethane	90–116	The precision at the 0.4 µg/L was in the range of 2.3–2.6% RSD. The recoveries were almost constant when the flow rate was change over the range of 2–8 mL/min for sample loading.	51
Diazinon	Tap water	6–7	acetonitrile	94–97	Preconcentration factor of 200 was achieved for 1000 mL of sample volume. Linear range of 0.3–10 000 µg/L.	52

Creatinine, vitamin B_{12}	Standards			Static adsorption experiments. Adsorption capacity of vitamin B_{12} was 47.18 mg/g which is 5.5 and 10.8 times of that of macroporous resin and activated carbon, respectively.	53
Microcystins	Drinking water	7		Static experiments. The size of CNTs tube pore that is fit for molecular dimension of microcystins plays a dominate role. Adsorption capacity up to 14.8 mg/g. Comparison with activated carbon and clays.	55
Sulfonamides	Eggs, pork	4–5	water-methanol (78:22)	Sample loading time up to at least 23 min for the flow rate of 4.5 mL/min. CNTs gave lower detection limit, higher enrichment factor and better precision than C_{18} silica.	56

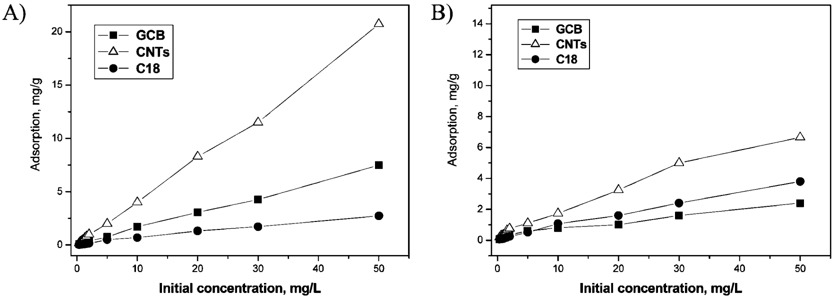

Figure 3. Adsorption isotherms of dicamba onto GCB, CNTs and C_{18} at pH 3 (A) and pH 7 (B). Adapted from Ref. (49).

The ability of CNTs to adsorb the most prevalent microcystines (MCs) produced by cyanobacterial bloom, has also been evaluated (54). Cyanobacteria bloom in natural waters has become a growing environmental problem worldwide due to the increased discharge of nitrogen- and phosphorous-containing wastewater into rivers and lakes. Generally, MCs are very stable in the water body and resistant to removal from drinking water by traditional water treatment technology. Compared to

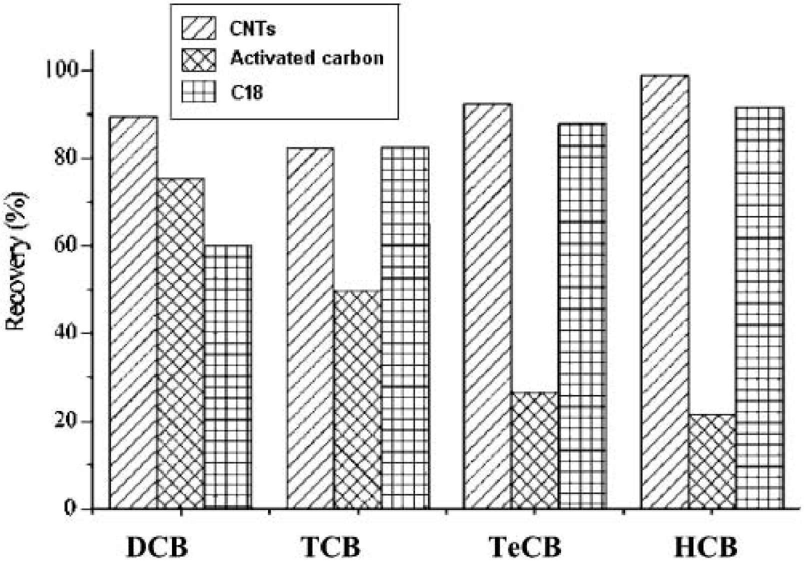

Figure 4. Recoveries of chlorobenzenes using CNTs, activated carbon and C_{18} sorbents. Sample volume, 100 mL, sample concentration 5 ng/mL, eluent, 2 mL of methanol. DCB – dichlorobenzene, TCB – 1,2,4-trichlorobenzene, TeCB – 1,2,4,5-tetrachlorobenzene, HCB - hexachlorobenzene (24). (Copyright Taylor & Francis. Reprinted with permission).

wood-based activated carbon and clays, the amounts of MCs adsorbed onto CNTs from lake water were four times higher (54), suggesting that CNTs may be potentially promising nanomaterials or the removal of microcystine from drinking water.

A novel, carbon nanotubes-supported micro-solid-phase extraction (μ-SPE) procedure has been developed (60). A 6-mg sample of CNTs was packed inside a (2 cm × 1.5 cm) sheet of porous polypropylene membrane whose edges were heat-sealed to secure the contents. The μ-SPE, which was wetted with dichloromethane, was then placed in a stirred sewage sludge sample solution to extract organophosphorous pesticides, used as model compounds. After extraction, analytes were desorbed in hexane and analyzed using gas chromatography with mass spectrometry detection. No analyte carryover effect was observed and each μ-SPE device could be used for up to 30 extractions. The comparison with hollow fiber protected solid-phase microextraction (HFM-SPME) and headspace solid-phase microextraction (HS-SPME) showed that this procedure is accurate, fast and the proposed device is easy to prepare in-house at reasonable cost. Figure 5 shows the chromatograms of extracts after μ-SPE with porous membrane-protected carbon nanotube, HFM-SPEM and HS-SPME of sewage samples spiked at 5 μg/L individual organophosphorous pesticides. All three procedures gave comparatively clean extracts; however, μ-SPE is more sensitive. The limits of detection were in the low part-per-trillion (ppt) ranges (1–7 pg/g), while LOD values for HFM-SPME and HS-SPME were 10–67 pg/g and 21–93 pg/g, respectively. Potentially, this developed microextraction technique can be used to extract complex matrices, such as biological fluids, sewage sludge and sludge samples, preventing coextraction of extraneous materials. One drawback is that is not easily automated.

Zhou et al. (48) compared the trapping efficiency of MWCNTs and C_{18} packed cartridge using sulfonylurea herbicides as the model compounds. When the matrices of the samples were very simple, such as tap water and reservoir water, the enrichment performance between these two adsorbents had no significant difference. However, MWCNTs become much more suitable to extract herbicides from complex matrices (seawater and well-water). The comparison of carbon nanotubes, activated carbon and C_{18} silica in terms of analytical performance, application to environmental waters, cartridge re-use, adsorption capacity and cost of adsorbent has been also made for propoxur, antrazine and methidation herbicides (45). The adsorption capacity of CNTs was almost three times that of activated carbon and C_{18}, while activated carbon was often preferred to the other two sorbents due to its low cost.

Carbon nanotubes can also remove and preconcentrate volatile organic compounds. Saridara et al. (61) described a microtrap

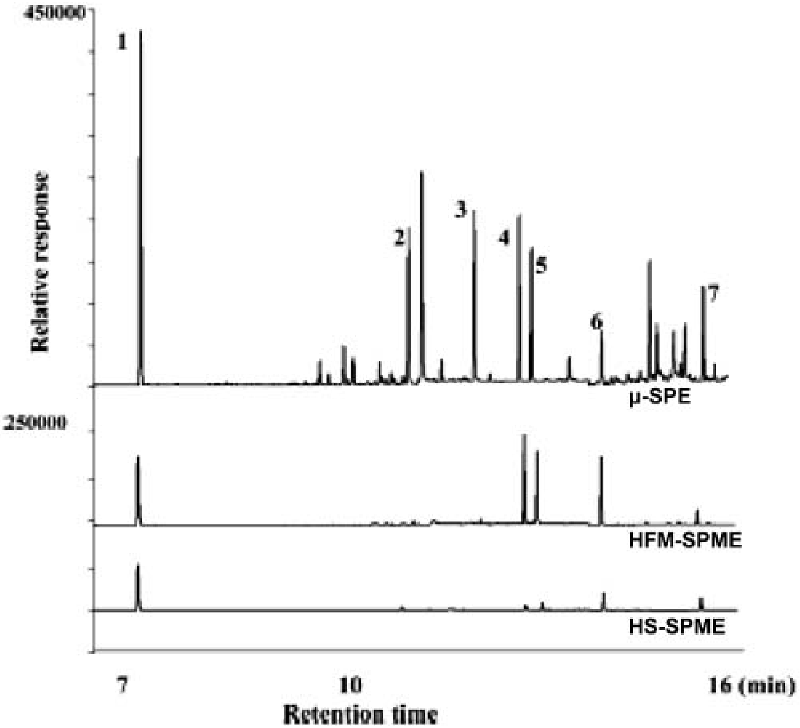

Figure 5. GC-MS chromatograms of spiked sewage sludge extracts after μ-SPE, HFW-SPME and HS-SPME. Peaks: (1) triethylphosphorothioate, (2) thionazin, (3) sulfotep, (4) phorate, (5) disulfon, (6) methyl parathion, (7) ethyl parathion (60). (Copyright American Chemical Society. Reproduced with permission).

operating as a nanoconcentrator and injector for gas chromatography. A thin layer of CNTs was deposited by catalytic chemical vapor deposition on the inside wall of a steel capillary in order to fabricate the microtrap. The obtained film provides an active surface for fast adsorption and desorption of small organic molecules such as hexane and toluene. Stronger sorption of toluene in comparison with hexane could be explained by possible π-π interactions between the carbon nanotube side-wall and the toluene aromatic ring. The purge-and-trap system was used for evaluation of carbon nanotubes as an adsorbent for trapping 16 volatile organic compounds from gaseous mixtures and indirectly from water samples (58). Due to their porous structure, CNTs were found to have much higher breakthrough volumes than that of graphitized carbon black (Carbopack B) with the same surface area.

CONCLUSIONS

The need for efficient methods for sample concentration and clean-up in environmental application is constantly growing. In recent years, efforts to investigate the possibility of CNTs as an adsorbent for the removal and enrichment of environmental pollutants yielded positive results, particularly with those containing benzene rings. Their large sorption capacity is linked to well developed internal pore structure and surface area. In several comparative studies carbon nanotubes exhibit higher adsorption capacity for organic pollutants than commonly used adsorbents such as C_{18} bonded silica, activated carbon or macroporous resins (35, 41, 45, 49, 51, 53, 55, 58) and it takes less contact time for CNTs to reach equilibrium (24, 25, 53). As it was reported, CNTs may be re-used over 100 times after proper cleaning and re-conditioning (45). However, the wider practical application of CNTs may be hampered by their relatively high unit cost. Thus, further works on developing a cost-effective way of CNTs production are recommended.

Whilst the above studies indicate that CNTs are potentially efficient adsorbents for a variety of pollutants in both drinking and environmental waters, their toxicity and biocompatibility needs to be thoroughly investigated. The studies indicated that the raw carbon nanotubes may posses some degree of toxicity (*in vivo* and *in vitro*), predominantly due to the presence of metal catalysts, while chemically functionalized CNTs have not demonstrated any toxicity so far (62, 63).

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