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Review

Carbon nanotubes as sorbents in the analysis of pesticides

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ABSTRACT

With increasing public concerns for agrochemicals and their potential movement in the ecosystem, very sensitive, selective and precise methods for the analysis of pesticides are needed. Because these substances are present usually at trace levels, the extraction and preconcentration steps are so far essential for their detection. Discoveries of novel nanomaterials with unique properties have significant impact on their use also in extraction techniques. This overview reports the recent application of carbon nanotubes in the analysis of pesticides. The largest numbers of reported applications of carbon nanotubes concern their role as a sorbent materials in solid-phase extraction and microextraction techniques.

Contents

1. Introduction

The history of carbon nanostructures began in 1985, when the Buckminsterfullerene C_{60} was discovered by Kroto et al. (1985). Since that time, the number of discovered structures has rapidly increased. The examples of them include nanotubes discovered by Ijima (1991), the family of fullerenes (Kuzuo et al., 1994; Dorset and Fryer, 2001), carbon nanocones (Ge and Sattler, 1994), carbon nanohorns (Nisha et al., 2000) and other different allotropic carbon nanoparticles. Some examples of carbon nanostructures are presented in Fig. 1. The extreme properties of these materials, such as high surface areas, large aspect ratios, remarkably high mechanical strength as well as electrical and thermal conductivities have spurred a broad range of applications. However, carbon nanotubes (CNTs) are presently the hottest carbon nanostructured material. They can be described as a graphite sheet rolled up into a nanoscale-tube. Two structural forms of CNTs exist: single-walled (SWCNTs) and multi-walled (MWCNTs) nanotubes (Fig. 1). CNT lengths can be as short as a few hundred nanometers or as long as several microns. SWCNT have diameters between 1 and 10 nm and are normally capped at the ends. In contrast, MWCNT diameters are much larger (ranging from 5 nm to a few hundred nanometers) because their structure consists of many concentric cylinders held together by van der Waals forces (Wepasnick et al., 2010).

At present, the three main methods for CNT synthesis are arc-discharge, laser ablation and chemical vapor deposition (Huczko, 2002; Kingston and Simard, 2003). The last method seems to be the most promising for possible scale-up due to the relatively low growth temperature, high yields and high purities that can be achieved. It should be mentioned, however, that low synthesis temperature often results in high defect density of the obtained CNTs. Because as-prepared CNTs usually contain carbonaceous or metallic impurities, purification is an essential issue to be addressed. Considerable progress in the purification of CNTs has been made and a number of purification methods including chemical oxidation, physical separation, and combinations of chemical and physical techniques have been developed for obtaining CNTs with

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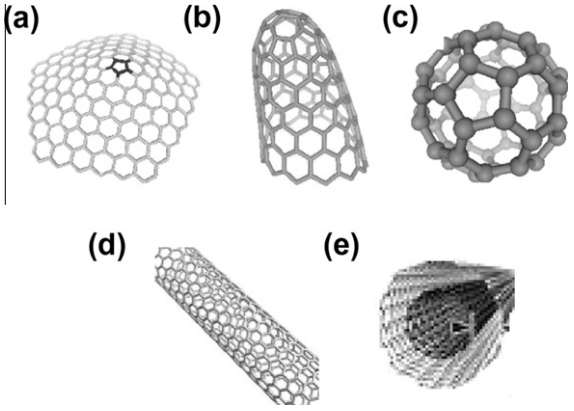

Fig. 1. Examples of carbon nanostructures; (a) carbon nanocone; (b) carbon nanohorn; (c) fullerene; (d) single-walled carbon nanotube; (e) multi-walled carbon nanotube.

desired purity (Hou et al., 2008). Extensive reviews covering chemical and structural characterization of various carbon nanostructures have been published recently (Baer et al., 2010; Wepasnick et al., 2010; Zhang and Yan, 2010).

The exceptional properties that these materials possess open new fields in science and engineering. In the field of environmental monitoring, the properties of carbon nanostructures offer opportunities for a wide range of applications for detection and remediation of different contaminants and wastewater treatment. Pesticides continue to be studied more than any other environmental contaminant, because they are widely used to protect plants from disease, weeds and insect damage. They could undergo a variety of transformations that provide a complex pattern of metabolites. Because of their toxicity and environmental fate the European Union has included pesticides in their list of priority pollutants and has established the maximum levels for pesticide residues according to the regulation (EC) No. 396/2005 amending Council Directive 91/414/EEC. The Framework Directive 2009/128/EC, which became law in November 2009, aims to reduce the risks and impacts on human health and the environment related to the use of pesticides. Thus, the development of analytical methods for their determination in various of environmental media at the required maximum residue limits demands state-of-art techniques for sample preparation, analyte separation, detection and quantification (Lagana et al., 2002; Andreu and Picó, 2004).

Taking into account the widespread interest in carbon nanostructures, it is not surprising that they are also found some application in analysis of pesticides. This article illustrates a growing number of application of CNTs in separation techniques; for preconcentration and enrichment using solid-phase extraction and microextraction. This survey will attempt to cover the state of-the art from 2006 to 2010. The general application of carbon nanotubes in analytical sciences has been discussed in the earlier reviews (Merkoçi, 2006; Valcárcel et al., 2007, 2008; Pyrzynska, 2008; Ravelo-Perez et al., 2010).

2. Solid-phase extraction

Because of their advantageous characteristics (high adsorption capacity, good thermal stability, wide pH range of application), carbon nanostructures have been employed in the extraction techniques such as solid-phase extraction (SPE) and solid phase microextraction (SPME). A considerable number of chromatographic and electrophoretic methods using SPE technique have been described. Mostly, SPE cartridges filled with CNTs were applied for the preconcentration of pesticide and herbicide residues form environmental waters.

The characteristic structures and electronic properties of carbon nanotubes (CNTs) allow them to interact strongly with organic molecules, via non-covalent forces, such as hydrogen bonding, $\pi-\pi$ 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 sorbents. The surface, made up of hexagonal arrays of carbon atoms in graphene sheets, interacts particularly strongly with the benzene rings of aromatic compounds. Long and Yang (2001) 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.

Oxidation of CNTs with nitric acid is an effective method to remove the amorphous carbon, carbon black and carbon particles introduced in their preparation process (Yang et al., 2006). This process 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 carbon increases mainly the concentration of hydroxyl and carbonyl surface groups, while oxidation in the liquid phase increases particularly the content of carboxylic acids (Dastgheib and Rockstraw, 2002). Functional groups can change the wettability of CNTs surfaces and consequently make them more hydrophilic and suitable for sorption of relatively low molecular weight and polar compounds. On the other hand, functional groups may increase diffusional resistance and reduce the accessibility and affinity of CNTs surfaces for organic compounds (Cho et al., 2008).

In several published papers, sorption on CNTs has been examined for different compounds, such as triazines (Zhou et al., 2006a; Yan et al., 2008; Min et al., 2008; Al-Degs et al., 2009; Katsumata et al., 2010), sulfonylureas (El-Sheikh et al., 2007; Zhou et al., 2007a; Niu et al., 2008; Springer and Lista, 2010), phenoxyalkanoic acids (Biesaga and Pyrzynska, 2006; Pyrzynska et al., 2007), organophosphorous pesticides (Du et al., 2008; Ravelo-Pèrez et al., 2008; Asensio-Ramos et al., 2009; Li et al., 2009), organochloride pesticides (Lü et al., 2007), Wu et al., 2009), and multi-class pesticides (Wang et al., 2007; El-Skeikh et al., 2008; Asensio-Ramos et al., 2008; Dong et al., 2009a,b; Lopez-Feria et al., 2009). The recent applications of carbon nanotubes for removal and enrichment of these compounds are presented in Table 1.

The effect of CNT external diameter on the recovery of some pesticides was investigated by using carbon nanotubes oxidized with nitric acid of various external diameters but similar length range of 5–15 μm (El-Sheikh et al., 2007). For atrazine and propoxur the highest recovery was obtained with CNTs with external diameters of 40–60 nm, while for methidathion similar results were obtained with CNTs of 20–40 and 60–100 nm diameters. Moreover, short carbon nanotubes (1–2 μm length) gave better recovery of the pesticides than the long one (5–15 μm). The recovery of methidathion on the shorter CNTs was almost double that of the recovery obtained using longer nanotubes with the same external diameter. This may be attributed to the fact that a fixed mass of short CNTs contains larger number of tubes.than the same mass of long ones, thus increasing the surface/volume ratio and consequently sorption rate.

Zhou et al. (2007a) compared the trapping efficiency of CNTs and C_{18} packed cartridge using sulfonylurea pesticides 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

Table 1
Recent examples for sorption of pesticides onto CNTs.

Analytes	Sample	Eluent	Recovery%	Remarks	Reference
Sulfonylurea compounds	Water	Acetonitrile + 1% acetic acid, pH 3	84–111	100 mg of CNTs for 2000 mL of sample volume	Zhou et al., 2006a
Atrazine, simazine	Water	Acetonitrile	83–104	Flow rate of 7 mL min^{-1} for elution	Zhou et al., 2006b
Thiamethhhoxam, imidacloprid, acetamiprid	Water	Methanol	87–110	pH of 4 as optimum	Zhou et al., 2006c
Dicamba	Water	Acetonitrile + NH_3 (80:20, v/v)		Backflush mode for elution	Biesaga and Pyrzynska, 2006
Sulfonylurea compounds	Water	Acetonitrile + 1% acetic acid, pH 3	60–95	Comparison with $C1_8$ silica	Zhou et al., 2007a
Triasulfuron and bensulfuron-methyl		Acetonitrile + 1% acetic acid, pH 3	44–108	Up to 2000 mL of sample could be preconcentrated	Zhou et al., 2007b
Atrazine, propoxur, methidation	Water	Acetonitrile	81–96	Dimensions of CNTs affect the enrichment efficiency	El-Sheikh et al., 2007
Phenoxyalkanoic acids	Water	Acetonitrile + NH_3 (80:20, v/v)	83–97	Comparison was made with C_{18} silica	Pyrzynska et al., 2007
Organochlorine pesticides	Water, wastewater	Thermal desorption	45–116	Carbon nanotube filter coating for microextraction	Lü et al., 2007
Multi-class pesticides	Water	Acetone/*n*-hexane (1:1, v/v)	82–104	0.1 g of CNTs	Wang et al., 2007
Atrazine and its metabolities	Water, soil	Ethyl acetate	72–109	Extraction from soil by methanol/water solution (50%, v/v)	Min et al., 2008
Organophosphorous pesticides	Fruit juices	Dichloromethane	73–103	Low amount of sorbent(40 mg) is required	Ravelo-Perez et al., 2008
Various pesticides	Water	Acetonitrile	81–108	Comparison was made with C_{18} and activated carbon	El-Skeikh et al., 2008
Pesticides	Mineral water	Dichloromethane with formic acid (5% v/v)	53–94	Optimum pH for enrichment was 8.0	Asensio-Ramos et al., 2008
Methyl parathion	Garlic	Desorption by electrochemical method	97–104	Square-wave voltammetric detection	Du et al., 2008
Triazines	Water	Acetonitrile/methanol (50%, v/v)	84–104	Optimization of SPE parameters by partial least squares method	Al-Degs et al., 2009
Organophosphorous pesticides	Seawater	Acetone or methanol	79–102	CNTs could supplement Oasis HLB	Li et al., 2009
Organophosphorous pesticides	Soil	Dichloromethane	54–91	Ultrasound-assisted extraction of the soils with methanol/acetonitrile (1:1)	Asensio-Ramos et al., 2009
Chloroacetanilide	Tap and river water	Ethyl acetate	77–104	pH 7 as optimum	Dong et al., 2009a
Sulfonylurea compounds	Water	Acetonitrile + 1% acetic acid, pH 3	79–102	Carbon nanotube disk compared with C_{18} and an activated carbon disks	Niu et al., 2008
Sulfonylurea compounds	Soil	Chlorobenzene	76–93	Dispersive solid-phase extraction	Wu et al., 2009
Chotoluron, diuron, atrazine, simazine, tertbutylazin-desethyl, dimetoathe, malathion, parathion	Virgin olive oils	Ethyl acetate	79–105	The cartridge with CNTs can be reused at least 100 times without losing performance	Lopez-Feria et al., 2009
Chlorsulfuron and metsulfuron methyl	Water	Water–methanol (50%, v/v)-acetonitrile (2%, v/v)		6 mg of CNTs	Springer and Lista, 2010
Atrazine and simazine	Water	Acetone	87–110	Enrichment factor from 200 mL of sample was about 4000	Katsumata et al., 2010

difference. However, carbon nanotubes become much more suitable to extract these compounds 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 (Ravelo-Perez et al., 2008). The adsorption capacity of CNTs was almost three times higher than that of activated carbon and C_{18}, while activated carbon was superior over the other sorbents due to its low cost. It is noteworthy to add that oxidation process of activated carbon with various chemical agents reduced the recovery of some pesticides (Ravelo-Perez et al., 2008). A comparative study suggested that carbon nanotubes had a higher extraction efficiency than Oasis HLB for the extraction of methamidophos and acephate, particularly for seawater samples (Li et al., 2009). Fig. 2 shows the chromatograms of six organophosphorous pesticides in the spiked seawater sample extracted using CNTs and Oasis HLB sorbent. For other tested polar organophosphorous pesticides (dichlorvos, omethoate, monocrotophos and dimethoate) improvement was not significant, thus CNTs could supplement Oasis HLB for the extraction of these compounds.

Generally, multi-walled carbon nanotubes offer better sorption capabilities than SWCNTs due to the existence of concentric layers of grapheme. Lopez-Feria et al. (2009) compared the MWCNTs sorbent capability with that provided by carboxylated single-walled carbon nanotubes (c-SWCNTs). Fig. 3 shows that the capacity of c-SWCNTs was markedly better than that of MWCNTs for all the analytes, which can be ascribed to the additional interaction provided by the carboxylic moiety present in the c-SWCNTs.

Carbon nanotubes could be also used in a format of disc. Incorporating sorbents of small particle size, the disc format possesses a larger surface area than the cartridge, resulting in good mass transfer and fast flow rates (Thurman and Snavely, 2000). To enhance the sorption capacity of the disks, double or even triple disks were

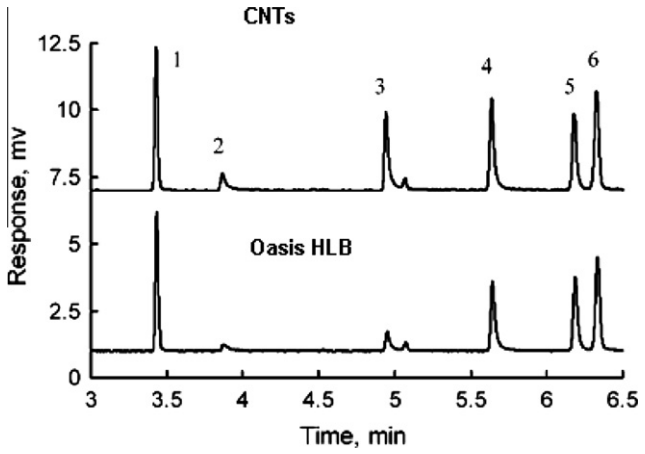

Fig. 2. Chromatograms of organophosphorous pesticides (1.0 μg L^{-1}) in the spiked seawater extracted with CNTs and Oasis HLB. Peaks identification: 1-dichlorvos, 2-methamidophos, 3-acephate, 4-omethoate, 5-monocrotophos, 6-dimethoate. Adapted from Li et al. (2009).

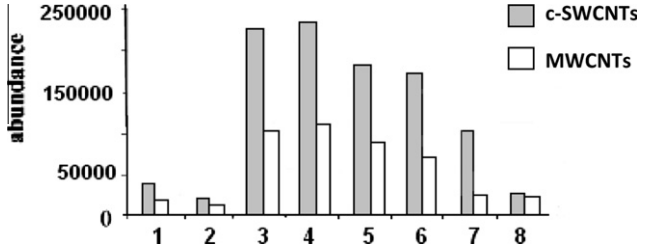

Fig. 3. Comparison of the performance of c-SWCNTs and MWCNTs for the isolation of the selected pesticides from virgin olive oil samples. Compounds: 1 – chlortoluron; 2 – diuron; 3 – terbutylazin-desethyl; 4 – dimetoate; 5 – simazine; 6 – atrazine; 7 – malathion; 8 – parathion. Adapted from Lopez-Feria et al. (2009).

used together (Niu et al., 2008). A comparison study showed that the double-disk system (comprising two stacked disks with 60 mg of CNTs) exhibited extraction capabilities that were comparable to those of a commercial C_{18} disk with 500 mg sorbent for nonpolar or moderately polar compounds. Moreover, the former system was more powerful than the latter for extracting polar analytes. The triple layered CNTs disk system showed good extraction efficiency when the sample volume was up to 3000 mL. Katsumata et al. (2010) obtained very high enrichment factor for preconcentration of atrazine and simazine (3900 and 4000, respectively, for 200 mL of sample solution when only 30 mg of MWCNTs was used in the format of disk.

Carbon nanotubes could be also readily immobilized into the pore structure of a polymeric membrane for improving the membrane extraction process (Hylton et al., 2008). The aqueous dispersion of CNTs nanotubes were injected through a polypropylene hollow fiber under pressure, trapped and held within the pores facilitating solute exchange from the donor to the acceptor phase. The enrichment factor measured as the ratio of analyte concentrations in the acceptor phase to the donor phase could be increased by more than 200% compared to plain polypropylene membrane.

Carbon-encapsulated magnetic nanoparticles (CEMNPs) are core–shell materials with similar surface characteristics to carbon nanotubes and this similarity enables to use them as solid sorbents. They are comprised of the magnetic core (10–100 nm in diameter), which is tightly coated by a carbon coating built from parallel stacked graphitic layers (Li et al., 2007). Encapsulation approach primarily protects the nanoparticles against the external environment, hampers aggregation and also provides the ability for surface functionalization. This process may improve also the dispersion stability of core–shell nanomaterials in a wide range of suspending solvents. A unique and attractive property of CEMNPs is that magnetic nanoparticles can readily be isolated from sample solution by the application of an external magnetic field. Magnetic nanoparticles were also applied in SPE for preconcentration of several organic compounds from environmental water samples (Jin et al., 2007; Zhao et al., 2008a,b). In order to enhance their sorptive tendency towards organic compounds, cetylpyridinium chloride was added, which adsorbed on the surface of nanoparticles and formed mixed hemimicelles. Compared with non-magnetic nanoparticles, the proposed sorbent material avoids the time-consuming column passing and filtration operation and shows great analytical potential in preconcentration of large volumes of real water samples.

3. Solid phase microextraction

Similarly to SPE, the SPME technique also employs a solid adsorbent for the purification and preconcentration of analytes. However, SPME applies a short, thin rod of fused silica coated with the adsorbent, which is immersed in the liquid sample. CNTs with high porosity and large adsorption area seems to be a good candidate for SPME coating. In addition, the more thermal and physical resistance of carbon nanotubes in comparison with commercial SPME coatings, are the other important characteristics from the practical point of view.

Lü et al. (2007) proposed novel coating for solid phase microextraction by attaching SWCNTs onto a stainless steel wire through organic binder. Compared with the commercial polydimethylsiloxane coating, the CNTs fiber exhibited better thermal stability (over 350 °C) and longer life span (over 150 times). The developed method was applied to determine trace organochlorine pesticides in lake water and wastewater samples with external standard calibration. Liu et al. (2009) reported a chemical bonding method for fabricating MWCNTs/fused-silica fiber based on the surface modification of both materials (Fig. 4). Briefly, carbon nanotubes were oxidized by mixed acids ($H_2SO_4 + HNO_3$) to create –COOH groups. The silica fibers were firstly hydroxylated by NaOH solution in order to break the Si–O–Si bond to form Si-OH groups, which were then transformed to $–NH_2$ groups by reacting with 3-aminopropyltriethoxysilane (APTS). CNTs/SPME fibers were formed in reaction between –COOH and $–NH_2$ groups upon heat treatment.

Recently, a novel microextraction technique, termed solid phase membrane tip extraction (SPMTE), was developed involving the use of tiny cone-shaped membrane tip protecting MWCNTs (See et al., 2010). This technique was evaluated for extraction of selected triazine herbicides in river water samples prior to micro-liquid chromatography. The SPMTE scheme is presented in Fig. 5. The enriched analytes were then desorbed by ultrasonication in 100 μL of acetonitrile. Zeng et al. (2010) proposed an approach using MWCNTs/Nafion composite coating as a working electrode for electrochemically enhanced solid phase microextraction. Carbon nanotubes and Nafion are well known to be electro-conductive and MWCNTs posses a high surface area-to-volume ratio that exhibit a strong π–π conjugated interaction with the benzene rings of the analytes (See Fig. 6). Compared to direct SPME mode (without applying potential), this technique presented more effective and selective extraction of charged analytes primarily via electrophoresis and complementary charge interaction.

4. Conclusions

Several hundred pesticides of different chemical structure are used world-wide in agriculture. Due to their persistence, polar

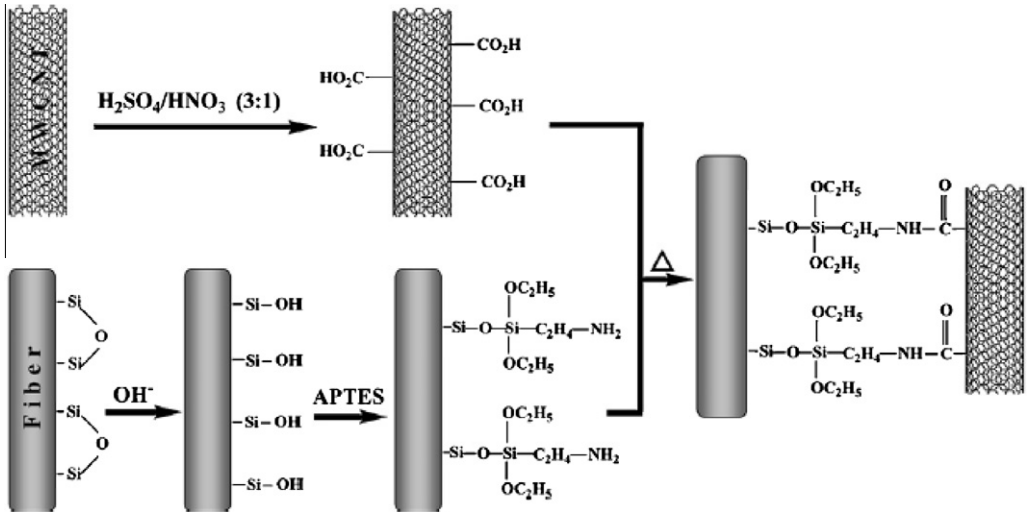

Fig. 4. Scheme for the preparation of MWCNTs/fused-silica fiber. Adapted from Liu et al. (2009).

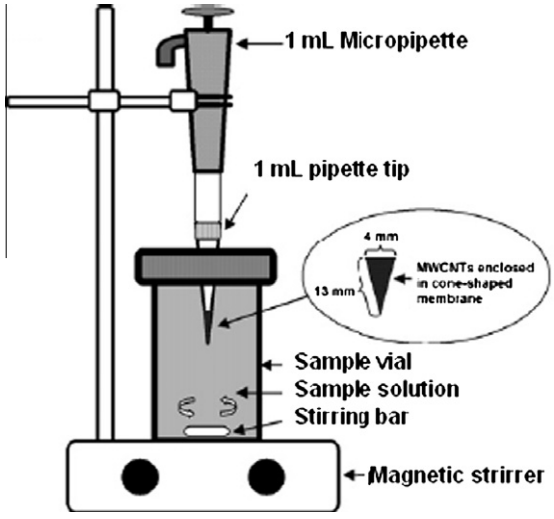

Fig. 5. Scheme of the SPMTE device. Adapted from Zeng et al. (2010).

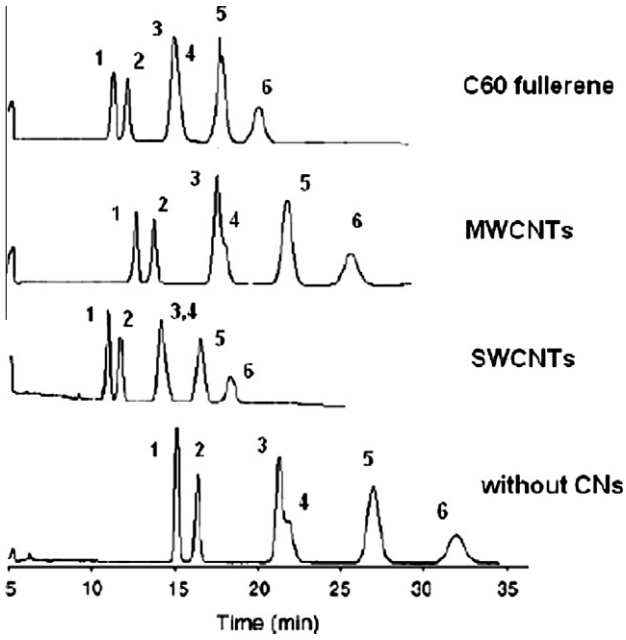

Fig. 6. Comparison of resolution of triazines without carbon nanostructures (CNs) and in the presence of surfanctant-coated SWCNTs, MWCNTs and C60 fullerenes. SDS concentration 60 mM. Peaks: 1-atrazine, 2-*ter*-butazine, 3-ametryn, 4-propazine, 5-prometryn and 6- terbutryn (all at concentration of 33 mg L^{-1}). Adapted from Moliner-Martinez et al. (2008).

nature and water solubility, they are dispersed in the environment and their residues and transformation products are present in several environmental matrices. With increasing public concerns for agrochemicals and their potential movement in the ecosystem, many countries have severely restricted the maximum acceptable concentration of pesticides in drinking water and in vegetable foods. Therefore, the availability of sensitive, selective, precise and rapid analysis methods is essential. Pesticides residue analysis generally requires several steps such as extraction from the sample of interest, removal of interfering co-extractives, analytes enrichment and quantification of their content.

Carbon nanotubes have a strong adsorption affinity for a wide variety of organic compounds, including pesticides and are also characterized by their high sorption surface. These interesting properties have been exploited in some analytical methodologies, where they have been used as a sorbent material in solid-phase extraction. The use of carbon-encapsulated magnetic nanoparticles avoids the time-consuming column passing and filtration operation and shows great analytical potential in preconcentration of large volumes of real water samples. Carbon nanotubes were also readily immobilized into the pore structure of a polymeric membrane to improve membrane extraction process. Recently, CNTs have been proposed as a coating material in solid phase microextraction fibers for the determination of residue pesticides in environmental and food samples. Their higher thermal and physical resistance in comparison with commercial SPME coatings are very important from the practical point of view.

Since their discovery, carbon nanostructures have been considered as a promising material, being extensively studied in order to make use of their structure and properties. Wider application of CNTs in the analysis of pesticides have been facilitated by the improvement in their production. In all carbon nanostructured materials, cost has been a main factor in limiting commercialization. However, it is widely believed that if production volumes increase, costs would decrease markedly. Recently, new solvent-free process for producing MWCNTs from used polymer *via* thermal

dissociation in the presence of catalysts in the closed reactor under the inert or air atmosphere has been proposed (Pol and Thiyagarajan, 2010).

From the other side, there has been a great concern if carbon nanotubes are toxic and could enter the environment as suspended particulate matter of respirable sizes. The toxicological hazard assessment of potential human exposures to airborne CNTs have been discussed (Lam et al., 2006; Kolosnjaj et al., 2007; Brar et al., 2010). Although further research is required, results presented today clearly demonstrate that, under certain conditions, especially those involving chronic exposure, carbon nanotubes can pose a serious risk to human health. However, some parameters such as structure, size distribution, surface area, surface chemistry and charge, agglomeration state as well as purity of the samples, have considerable impact on the reactivity of carbon nanotubes.

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