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Carbon Nanotubes as a New Solid Phase Extraction Sorbent for Analysis of Environmental Pollutants

Bele Constantin

University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca, Romania

1. Introduction

Pretreatment is often considered to be a fundamental step in the process of successful analysis of environmental pollutants, because it helps not only to achieve low detection limits but also to clean up the sample matrix. Solid phase extraction (SPE) is an effective sample handling method and is used as an enrichment technique when low concentrations of analytes need to be determined. SPE provides higher enrichment efficiency and requires a lower volume of solvent than the traditional method of liquid-liquid extraction.In addition, SPE is simpler and easily to be automated and operated.In the procedure of SPE, the type of sorbent, its structure and its interactions with the solute play an important role in obtaining higher enrichment efficiency of analytes. Until now, several kinds of materials such as C18, Oasis HLB, bonded silica, styrenedivinyl-benzen (SDB), zeolites, carbonaceous materials have been proposed as adsorbents for SPE cartridge.

In recent years, carbon nanotubes (CNTs), a novel member in the carbon family , have attracted great attention due to its advantages that can be used for many different applications in terms of its chemical, electronic and mechanical properties as well as the unique tubular structures and large length / diameter ratio. CNTs are to be considered as a sheet of graphite that has been rolled into a tube and be classified as single – walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) . Over the past 20 years, CNTs have been exploited in analytical and other fields such as biosensors with immobilized biomolecules, electrochemical detectors, gas sensor, catalyst supports and so on. Because CNTs surfaces have a strong interaction with other molecules, particularly with those containing benzene rings, they possess excellent adsorption ability and substitute active carbon. CNTs as SPE adsorbents has been investigated to extract organic compounds such as pesticides (carbofuran, iprobenfos, parathion-methyl, prometryn, fenitrothion etc.), polycyclic aromatic hydrocarbons, antibiotics, sulphonylurea herbicides, sulfonamides, phthalate esters, endocrine disruptors, triazines, microcystines, pyrethroids and polybrominated diphenyl ethers . In several comparative studies CNTs exhibit similar or higher adsorption capacity for environmental pollutants than silica-based sorbents or macroporous resins. CNTs can also preconcentrate volatile organic compounds.CNTs were

used as SPE adsorbents for preconcentration of metal ions, such as copper, nichel, cobalt, vanadium, silver, cadmium, rare earth elements etc.

This chapter is organized in four sections including the introduction. Section 2 is devoted to the sorption properties of CNTs. Section 3 summarize the most important applications of CNTs for the enrichment of environmental pollutants.The potential factors affecting SPE and the sorption capacities of CNTs are also disscussed. The whole chapter is then concluded in Section 4.

2. Adsorption properties of carbon nanotubes

CNTs usually have a diameter in the range comprized within a tenth to tens nanometers and a length of up to centimeters. The ends of CNTs are normally capped by a fullerene-like structure. As fullerene, CNTs also exhibit limited solubility. Depending on their diameter and helicity of the graphitic sheets CNTs can be either metallic or semi-conducting (Valcarcel et al., 2008). The characteristic structures of carbon nanotubes allow a strong interaction with organic molecules via non-covalent forces, such as hydrogen bonding, π -π stacking, electrostatic forces, van der Waals forces and hydrophobic interactions (Pyrzynska et al., 2008). The presence of functionalized carbon nanotubes allows the possibility of incorporating one or more of these interactions which increase the selectivity and the stability of the system.

It was stated that CNT derivatization is required when developing special applications (e.g. retention of metals). CNTs were purified by sodium hypochlorite solutions and were employed as adsorbents to study the adsorption characteristics of zinc in water (Lu & Chiu, 2006). The properties of CNTs such as purity, structure and nature of the surface were considerably improved after purification by sodium hypochlorite which made CNTs become more hydrophilic and suitable for adsorption of Zn^{2+} from water . The adsorption of Zn^{2+} onto CNTs rises proportional to the pH increase within 1- 8 range, fluctuates very slight and reaches a maximum in the pH range of 8-11; the adsorption curve decreases at a pH of 12. The contact times to reach equilibrium are 60 min for SWCNTs and MWCNTs. The maximum adsorption capacities of Zn^{2+} calculated by the Langmuir model are 43.66 and 32.68 mg / g with SWCNT and MWCNT, respectively, at an initial Zn^{2+} concentration range of 10-80 mg/ L.

It was found that the acid treatment with a mixture of nitric acid and sulfuric acid made CNTs become more hydrophilic and suitable for adsorption of low molecular weight and relatively polar trihalomethanes (THMs) in water (Lu et al., 2005). The adsorption of THMs onto CNTs can be suitably described by both Langmuir and Freundlich models. The smallest molecule $CHCl_3$ is the most preferentially adsorbed onto CNTs, followed by $CHBrCl_2$, $CHBr_2Cl$ and then by $CHBr_3$. THMs absorption onto CNTs fluctuates very slightly in the pH range of 3 –7 but decreases with pH value when pH exceeds 7.

It was shown that carbon nanotubes can also be used as supports for adsorption materials, and the new composites have a good affinity to many metals . MWCNTs filled with Fe_2O_3 nanoparticles have been prepared and employed as adsorbent for the magnetic separation of dye contaminants (Methylene Blue and Neutral Red) in water (Qu et al., 2008). The magnetic nanoparticles have been prepared via hydrothermal reaction of shortened MWCNTs in ferric nitrate solution and subsequent calcinations. The prepared magnetic MWCNTs can be well dispersed in water and easily magnetic separated from the medium

after adsorption. As compared with other adsorbents, the magnetic nanoparticles not only have high adsorption efficiency to dyes, but can also be easily manipulated by external magnetic field.

MWCNT / iron oxide magnetic composites were prepared and used for adsorptions of Ni (II) and Sr (II) (Chen et al., 2009). Scan electronic microscopy (SEM) image shows an entangled network of MWCNTs with clusters of iron oxides attached to them suggesting the formation of MWCNTs / iron oxide magnetic composites. Ni (II) adsorption on the magnetic nanoparticles is pH and ionic strength dependent and can be easily desorbed from the magnetic nanoparticles by adjusting the solution pH values.The Langmuir model fitted the adsorption isotherm data of Ni (II) better than the Freundlich model.

MnO_2 / CNTs composites were efficient for Pb (II) ion removal from aqueous solution (Wang et al., 2007b) . The optimum MnO_2 loading indicating the best performance of Mn O_2 on the Pb(II) removal is 30 wt %.The application to experimental results of the Langmuir and Freundlich models show that the Langmuir model gives a better correlation coefficient.

It was found that CNTs present a marked tendency to aggregation, which negatively affects adsorption by reducing their active surface (Valcarcel et al., 2008). In addition, when cartridges or home-made columns are employed, this tendency may increase pressure in the flow systems .

Special configurations are developed for specific applications. A complex sheet of SWCNT and polyaniline was used as a new adsorbent to remove bilirubin from plasma (Ando et al., 2009) . Bilirubin, a red- brown bile pigment, is a metabolite of heme produced from the senescent hemoglobin. If a bilirubin concentration exceeds a certain level in blood, it may cause kernicterus or liver diseases. Bilirubin CNTs adsorption capacity has been found to be much higher versus the conventional materials because of their large surface area and considerable adsorption capability for polycyclic compound molecules due to their structure similar to graphite.

A recently introduced immobilization method to link the aminoacid L-tyrosine to CNTs was described (Pacheco et al., 2009). The amount of aminoacid immobilized on CNTs surface was 3174 µmol / g. The material was tested for Co retention using a minicolumn inserted in a flow system. A 10 % (v/v) HNO_3 solution was chosen as eluent. The pH study revealed that Co binding increased at elevated pH values. The retention capacity was compared to other bivalent cations and showed the following tendency : $Cu^{2+} > Ni^{2+} > Zn^{2+} >> Co^{2+}$.

The influence of the surface functionalization on the colloidal stability of CNTs, as well as on the sorption of heavy metals was investigated (Schierz & Zanker, 2009). Uranium (VI), a chemical element of considerable public concern, was chosen as an example of a toxic heavy metal. The results indicated that acid treatment increases the amount of acidic surface groups on the CNTs. Acid treatment has an intensifying effect upon the colloidal stability of the CNTs, and on their adsorption capacity for U (VI).

The analytical potential of MWCNTs modified with a Schiff base ligand was examined for simultaneous preconcentration of Au (III) and Mn (II) in aqueous samples prior to their flame atomic adsorption spectrometric assessment (Shamspur & Mostavafi, 2009) . It was found that the sorption is quantitative in the pH range 5.0- 7.5, whereas quantitative desorption occurs instantaneously with 4.0 mL of 0.1 mol / L $Na_2S_2O_3$.

The application of the hemimicelle capped carbon nanotubes–based nanosized SPE adsorbents in environmental analysis is reported for the first time using arsenic as model

target (Li et al., 2009a). The end functionalized of CNTs can introduce oxygen-containing negatively functional groups such as – COOH, - OH, or - C= O on their surface site. If cationic surfactant, such as cetyltrimethylammonium chloride (CTAC) was added to the functionalized CNTs, interactions like hydrophobic and ionic may lead to the formation of hemimicelle / admicelle aggregates on the CNTs ; this way, a new kind of adsorbents is acquired, namely hemimicelle capped CMMWCNTs. Arsenic can be quantitatively retained on the hemimicelle capped CMMWCNT at pH 5 – 6 from sample volume up to 500 mL, and subsequently eluted completely with 2 mol/ L HNO_3 in the presence of 10 mg / L CTAC.

Carbon nanotubes have also been proposed as material coatings in SPME fibers for the determination of flame retardants like polybrominated diphenyl ethers   (PBDEs) in environmental and food samples (Wang et al., 2006a). The home-made fibers, which were prepared according to the method used for constructing composite electrodes, were evaluated quantitatively and compared with commercial fibers. The results demonstrated that the MWCNT coating was effective for extracting the analytes described above, and provided better enhancement factors than activated carbon and poly (5 % dibenzene- 95 % dimethylsiloxane) coatings.

3. CNTs as adsorbents in solid-phase (micro) extraction

Most CNT applications published have been developed for the extraction of water samples, which are probably the less complex samples to work with. Up to now, only few works have used CNTs (basically MWCNTs) for the extraction of environmental pollutants from matrices different than waters.

Some reprezentative examples of the use of carbon nanostructures as sorbent materials in SPE and solid phase microextraction (SPME) are given in Table 1 for an easier approach and comparison.

Carfentrazone-ethyl (a relatively novel triazolinone herbicide) residue in water was enriched by use of MWCNTs (Dong et al., 2009a). Relevant studies were developed to examine several factors affecting the recovery of the analyte,   for example the pH of the water samples , sample volume, polarity and volume of eluents . It was found that MWCNT was an effective SPE adsorbent for preconcentration of carfentrazone-ethyl   in water and the recovery of this herbicide from fortified water was 81.49-91.08 %.The detection limits and quantification were 0.01 and 0.03 μg / L. It was also shown that under the optimized SPE procedure, the MWCNT-packed cartridge needed only 100 mg adsorbent .

The extraction efficiency of MWCNT as a new SPE adsorbent followed by GC-ECD for the analysis of chloroacetanilide herbicides (alachlor, acetochlor, metolachlor and butalochlor) was investigated (Dong et al. 2009b). It was found that the amount of adsorbent was much less for MWCNT in comparison with the commonly used adsorbent, such as C18. As an example, in this method were used only 100 mg MWCNT, whereas for the environmental analysis routine work were applied 500 mg to 1000 mg C18 cartridges. The detection limits were situated within the range of 0.01-0.03 μg / L.

The adsorptive potential of MWCNTs was used for the extraction and clean up of eight pesticides in agricultural, ornamental and forestal soils (Asensio- Ramos et al., 2009) . Soils were first ultrasound extracted with a mixture of methanol/ acetonitrile and the evaporated

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Analyte	Sample	Combined technique and detection limit (ng / mL)	Remarks	References
Carfentrazone-ethyl	Water	GC-ECD 0.01-0.03	Only 100 mg of MWCNTs as adsorbent was needed Comparison with C 18 silica	Dong et al., 2009a
Pesticides	Agricultural, ornamental, forestal soils	GC- NPD 2.97- 72.4	Low cost CNTs were used (10-15 nm o.d., 2-6 nm i.d. and 0.1-10 µm length) Satisfactory recovery values (54-91 %) were obtained	Asensio-Ramos et al., 2009
Amines	Water	GC-MS 0.005-0.016	Comparison with Lichrolut EN ,Oasis HLB, RP-C18, graphitized carbon black and fullerenes	Jurado-Sanchez et al., 2009
Pesticides	Olive oils	GC-MS 1.5-3.0	Only 30 mg of MWCNTs as adsorbent was needed	Lopez-Feria et al., 2009
Phenols	Water	HPLC-DAD 0.9-3.8	The SPME-Pt fiber coated with SWCNTs was prepared by electrophoretic deposition Linear range of 10- 300 ng / mL	Li et al., 2009b
Oxygenated ethers	Urine	GC-MS 0.003-0.01	The SWCNT fiber exhibited higher sensitivity and longer life span (over 150 times) than CAR / PDMS fiber	Rastkari et al., 2009
Atrazine, propoxur and methidathion	Reservoir waters	HPLC-UV 2-3	At flow rate higher than 5.0 mL / min the enrichment efficiencies decreased for all pesticides Linear ranges of 5-30, 3-60 and 5-40 µg / L for atrazine, methidathion and propoxur	Al- Degs et al., 2009
Chloroacetanilide herbicides	Water	GC-ECD 0.01-0.03	The recoveries were steady in the range of 200-1000 mL sample volume Linear range of 2.5-2500 µg /L	Dong et al., 2009b
Cobalt	Water	FAAS 0.05	L-tyrosine was immobilized on CNTs and used as sorbent for SPE Adsorption capacity of 37.58 µmol Co / g CNTs	Pacheco et al., 2009
Uranium	Water	ICP-MS	CNTs were modified by heating in a mixture of HNO_3 / H_2SO_4 The Langmuir model fitted the experimental data better than the Freundlich model	Schierz et al., 2009
Arsenic	Water	FI-AFS 0.002	Carboxyl modified MWCNTs with cation surfactant CTAC were used as adsorbent The recoveries remain stable when the flow rate was below 6 mL / min	Li et al., 2009a

Analyte	Sample	Combined technique and detection limit (ng / mL)	Remarks	References
Bilirubin	Plasma apheresis	VIS spectro-photometer	MWCNTs exhibit greater adsorption for bilirubin than SWCNTs	Ando et al., 2009
Organophosphate pesticides (MP)	Garlic	SWV 5	The strong affinity of MWCNTs for phosphoric group allow extracting a large amount of MP	Du et al., 2008
Linear alkylbenzene sulfonates	Water	HPLC-UV 0.02-0.03	Carboxyl modified MWCNTs were used as adsorbents Comparison with C8 and C18	Guan et al., 2008
Pesticides	Water	HPLC 0.036-0.22	MWCNTs have better ability for the extraction than C 18 silica and activated carbon	El-Sheikh et al., 2008
Diazinon	Tap water	HPLC 0.06	Preconcentration factor of 200 was achieved for 1000 mL of sample volume Linear range of 0.3-10000 ng / mL	Katsumata et al.,2008
Organophosphorus pesticides	Fruit juices	GC-NPD 1.85-7.32	Low sample pretreatment prior to the SPE procedure Only 40 mg of MWCNTs as adsorbent was needed	Ravelo-Perez et al., 2008
Aromatic amines	Water	HPLC-UV 0.04-0.13	Automated in- tube SPME using carboxylated MWCNTs Linear range of 1.02-102 μg /mL	Liu et al., 2008
Pyrethroids	Water	HPLC – UV 1.3- 4.3	The recoveries decreased except fenpropathrin when the flow rate was over 3 mL/ min	Zhou et al., 2008
Methylene Blue Neutral Red	Water	UV-VIS spectrophoto-meter	MWCNTs filled with Fe_2O_3 nanoparticles were used as adsorbent The magnetic MWCNTs have high adsorption efficiency to dyes and can be manipulated by external magnetic field	Qu et al., 2008
Non-steroidal anti-inflammatory drugs	Urine	Capillary electrophoresis-MS 1.6-2.6	Carboxylated SWCNTs (c-SWCNT) were chemically immobilized on porous glass.High sorption capacity was related with the special orientation of c-SWCNTs	Suarez et al., 2007
Pesticides	Water	GC-MS 0.01-0.03	The recoveries were constant at the flow rate in the range of 1.5- 3 mL / min Only 100 mg MWCNTs adsorbent per extraction	Wang et al., 2007a

Analyte	Sample	Combined technique and detection limit (ng / mL)	Remarks	References
Barbiturates	Pork	GC/MS/MS 0.1-0.2	MWCNTs showed better ability for the extraction of phenobarbital than C18 Linear range 0.5-50µg / Kg	Zhao et al., 2007
Cephalosporins Sulfonamides Phenolic compounds	Water	HPLC-PDA 0.027-0.038	CNTs were much superior to C18 for the extraction of the highly polar analytesThe recoveries decreased at solution pH > 8.	Niu et al., 2007
Volatile organic compounds (VOCs)	Ambient air	GC-FID	Comparison with Tenax TA High adsorption efficiency for collecting VOCs with low boiling points and strong volatility	Jie-Min et al., 2007
Polycyclic aromatic hydro-carbons	Water	HPLC-UV 0.005-0.058	The recoveries were steady in the range of 250-1000 mL sample volume MWCNTs have better ability for the extraction than C18	Wang et al., 2007c
Fungicides Prometryn	Water	HPLC-UV 0.003-007	Sample volume up to 1500 mL Linear range of: 0.2-80 µg / L (fungicides) 0.05-20 µg /L (prometryn)	Zhou et al., 2007
Chromium	Water	FAAS 0.90	The procedure is based on SPE of the Cr(VI)-APDC chelate on MWCNTs Adsorption capacity of Cr (VI) was 9.5 mg/ g	Tuzen & Soylak, 2007
Lead	Water	ICP	CNTs were coated with Mn oxide and used as adsorbent The Langmuir equation fitted the experimental data more closely than the Freundlich model	Wang et al., 2007b
Polybrominated diphenyl ethers	Water Milk	GC-ECD 0.0036-0.0086	MWCNTs coated fibers for SPME were compared with activated carbon and PDMS-DB coated fibers	Wang et al., 2006a
Microcystins (MCs)	Water	HPLC-DAD	The size of CNTs tube pore that is fit for molecular dimension of MCs plays a dominante role Adsorption capacity of MCs was 14.8 mg / g	Yan et al., 2006
Sulfonamides	Eggs Pork	HPLC-UV 0.004-0.010	Sample loading time up to 23 min for the flow rate of 4.5 mL / min MWCNTs gave lower detection limits, higher enrichment factors and better precisions than C18 silica	Fang et al., 2006

Analyte	Sample	Combined technique and detection limit (ng / mL)	Remarks	References
Benzodiazepines	Pork	GC-MS 2-5	Static adsorption experiments 0.2 g MWCNTs were superior to 0.5g C18 for the extraction of diazepam	Wang et al., 2006b
Atrazine and simazine	Water	HPLC-DAD 0.009-0.033	The recoveries were constant at the flow rate of 2-7 mL/ min Linear range of 0.2-100 (atrazine) and 0.02-100 ng / mL (simazine)	Zhou et al., 2006b
Organochlorine pesticides	Water	HPLC-UV 0.004-0.013	The recoveries were almost constant when the flow rate was change over the range of 2-8 mL / min for sampling loading Linear range of 0.2-60 µg / L	Zhou et al., 2006a
Sulfonylurea herbicides	Water	HPLC-DAD 5.9 – 11.2	The recoveries were constant at the flow rate in the range of 2-8 mL / min Sample volume up to 2000 mL	Zhou et al., 2006c
Zinc	Water	FAAS	The Langmuir equation is more appropriate to describe the adsorption of Zn^{2+} onto CNTs than the Freundlich model.Comparison with powdered activated carbon	Lu et al., 2006
Chlorophenols	Water	HPLC-UV 0.08-0.8	The recoveries decreased slightly with the increase of sample volume higher than 200 mL Linear range of 1-200 ng/ mL	Cai et al., 2005
Volatile organic compounds	Water	GC-FID	Comparison with Carbopack B and VOCARB 3000	Li et al., 2004
Phthalate esters	Water	HPLC-DAD 0.18-0.86	Sample volume up to 3000 mL Linear range 2-100 ng / mL	Cai et al., 2003

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

extract redissolved in water was passed through 100 mg MWCNT of 2-6 nm i.d. and 0,1- 10 µm length .Dichloromethane was used for the elution of analytes. In the three types of soils satisfactory recovery values (54-91 %) were registered for several pesticides (diazinon, ethoprophos, fenitrothion, malathion and phosmet).

The comparison of MWCNTs, graphitized carbon black, fullerenes, Lichrolut EN, Oasis HLB, RP- C 18 in terms of sensitivity, selectivity and reliability has been made for the retention of amine compounds including anilines, chloroanilines, N-nitrosoamines and aliphatic amines (Jurado- Sanchez et al., 2009).The analytes were retained on a SPE sorbent column and after elution, 1 µL of the extract was analysed by gas chromatography coupled with electron impact ionization . MWCNTs are adequate to retain aromatic compounds such as aromatic N-nitrosamines and despite amine aromaticity, they only interact with trichloroanilines and 2-nitroaniline, through π- π interactions, and with some

dichloroanilines that contain chlorine atoms in accessible positions for establishing anion- π interactions, and are thus highly selective.

Simultaneous determination of three toxic pesticides (atrazine, methidathion and propoxur) in tap and reservoir waters using MWCNT as solid phase extractant was developed (Al-Degs et. al, 2009). MWCNT adsorbent showed excellent extraction/ pre-concentration of pesticides present at trace levels.The experimental factors that affect pesticides extraction by MWCNTs adsorbent such as sample volume, eluent volume, solution pH and extraction flow rate were studied and optimized. The pesticides were reproducibly detected with a detection limit of 3,2 and 3μg / L and linear ranges of 5-30, 3-60 and 5-40 μg / L for atrazine, methidathion and propoxur. In tap water, the percent recoveries for pesticides were extended from 95 to 104 % while lower recoveries were observed in reservoir water : 84-93 %.

A new kind of carbon nanotubes application to the determination of several pesticides in virgin oil samples was developed (Lopez- Feria et al., 2009). Two carbon nanotubes, MWCNT and carboxylated SWCNT were evaluated. The sorbent (30 mg) was packed in 3-mL commercial cartridge and the virgin oil samples diluted in hexane were passed through it. After a washing step with hexane to remove the sample matrix, the pesticides were eluted with ethyl acetate and analysed by GC-MS.The low limits of detection achieved (between 1.5-3.0 μg / L) afford the application of the method to control the presence of these pollutants in very restrictive samples such as the ecological virgin oil. The method involves a single preconcentration-elution step, which allows sample processing in less than 8 min.The cartridge can be reused at least 100 times without losing performance.

A new kind of solid –phase microextraction (SPME) Pt fiber coated with SWCNT was prepared by electrophoretic deposition (EPD) and applied to the assessement of phenols in aqueous samples (Li   et al., 2009b). The results revealed that EPD was a simple and reproducible technique for the preparation of SPME fibers coated with SWCNTs without the use of adhesive. The obtained SWCNT coating did not swell in organic solvents nor strip off from substrate, and possessed high mechanical strength due to the strong Van der Waals attractions between the surface of the SWCNTs. The prepared SPME fiber was conductive since both SWCNTs coating and Pt wire were conductive. Using Pt wire as substrate, the fiber was unbreakable. Owing to the presence of oxygenated groups on SWCNTs and the high surface area of SWCNTs, the SWCNT fiber was similar or superior to commercial PA fibers in extracting the studied phenols from aqueous sample. The detection limits for the phenols varied between 0.9 and 3.8 ng / mL and linear ranges were within 10 and 300 ng / mL.

A SWCNT fiber was prepared by binding the SWCNT to the surface of stainless steel wire and used as adsorbents for solid phase microextraction of several oxygenated ethers in human urine (Rastkari N. et al., 2009). SWCNTs were attached onto a stainless steel wire through organic binder. Compared with the commercial carboxen / polydimethylsiloxane (CAR / PDMS) fiber, the SWCNT fiber showed better thermal stability and longer life span (over 150 times). For all analytes the detection limits were 10 ng / L.

A sensitive method was developed using MWCNTs as SPE adsorbents followed by HPLC with UV detection for determination of six pyrethroid pesticides at trace level in environmental water samples (Zhou et al., 2009). MWCNTs showed more powerful adsorption properties than C18 in the extraction procedure, because they possess a higher

capability to extract the six pyrethroids in larger volume solutions. The detection limits for the six target compounds were in the range of 0.7-5.0 ng / L .

A novel carbon nanotubes based micro-scale phase extraction (μ - SPE) has been developed by incorporating CNTs in the needle of a syringe in packed, as well as in self assembled format (Sae-Khow & Mitra, 2009). The analytes were concentrated by drawing several milliliters of water into the syringe through the needle, and then desorbing/ concentrating them in a few microliters of solvent. The CNTs served as a high performance sorbents, where a relatively high enrichment could be achieved using small quantities of sorbent . The obtained data suggested that the applied method had a low detection limit ranging between 0.1 and 0.3 ng / mL . The enrichment on CNTs were significantly higher as compared to the amount achieved on C18 under similar conditions.

MWCNTs were used as sorbent for flow injection (FI) on-line microcolumn pre-concentration coupled with flame atomic adsorption spectrometry (FAAS) for the evaluation of trace cadmium and copper in environmental and biological samples (Liang & Han, 2009). An effective preconcentration of trace cadmium and copper was achieved in a pH range of 4.5-6.5, and 5.0-7.5, respectively.The retained cadmium and copper were efficiently eluted with 0.5 mol/ L HCl for on-line FAAS determination. The MWCNTs packed column exhibited fairly fast kinetics for the adsorption of cadmium and copper which explain the use of high sample flow rates up to at least 7.8 mL / min for the FI on line microcolumn preconcentration system without losing the retention efficiency. The detection limits were 0.30 and 0.11 μg /L for Cd and Cu, respectively.

Carboxyl modified multi-walled carbon nanotubes (CMMWCNT s) were used as SPE adsorbents to extract linear alkylbenzen sulfonates (LAS) from water samples (Guan at al., 2008). The effect of eluent and its volume, sample pH and flow rate, sample volume, the content of the electrolyte (NaCl) were investigated and optimized. The limit of detection for LAS homologues was 0.02-0.03 μg / L and the recoveries of LAS homologues in the spiked environmental water samples ranged from 84.8 to 106.1 %.A comparison study with CMMWCNTs, C8 and C18 as adsorbents for LAS was also conducted.CMMWCNTs car-tridge showed stronger retention ability than C8 and C18 cartridges for target com-pounds.

A combination of SPE using MWCNT as sorbent and square–wave voltammetric analysis resulted in a fast and selective electrochemical method for the assessement of orga-nophosphate (OP) pesticides using methyl parathion (MP) as a representative (Du at al., 2008). Due to the strong affinity of MWCNT for phosphoric group, nitroaromatic OP compounds can strongly bind to the MWCNT surface.The macroporosity and heterogeneity of MWCNTs allow the extraction of a large amount of MP in less than 5 min. The limit of detection for MP was 0.005 μg / mL. The MP assessement in garlic samples showed acceptable accuracy.

A comparison study of three different sorbents (MWCNTs, C18 silica and activated car -bon) in terms of analytical performance, application to environmental waters, cartridge re-use, adsorption capacity and cost of adsorbent has been made for propoxur, atrazine and methidathion pesticides (Sheikh at al., 2008). The adsorption capacity of MWCNTs was almost three times that of activated carbon and C 18, while activated carbon with various surface properties was often preferred to the other two adsorbents due to its low cost.

A sensitive and selective column method was proposed for the preconcentration of diazinon –one of the reprezentative compounds of organophosphorus pesticides – in water by using

MWCNTs as an adsorbent and then determined by HPLC (Katsumata et al., 2008). The obtained data showed that it is possible to have quantitative analysis when the solution pH was 6 using 200 mL of validation solution and acetonitrile as an eluent.The maximum preconcentration factor was 200 for diazinon when 1000 mL of sample solution volume was used. The limit of detection was 0.06 ng / mL.

MWCNTs have been used for the first time as SPE adsorbents for the extraction of eight organophosphorus pesticides from different fruit juices (apple, grape, orange and pine apple) (Ravelo-Perez et al., 2008).The developed method is simple and cost-effective :only 1:1 dilution with Milli- Q Water and pH adjustement to 6.0 of 10 mL of juice is necessary prior to a quick MWCNTs-SPE procedure that used only 40 mg of stationary phase (MWCNT of 10-15 nm o.d., 2-6 nm i.d. and 0.1-10 μm lenght). Mean recovery values were above 73 % for all the pesticides and fruit juices. Limits of detection ranged between 1.85 and 7.32 μg / L.

For the determination of substituted aniline compounds in water samples a simple and sensitive pretreatment technique was advanced by in-tube SPME with MWCNT-COOH adsorbent (Liu et al. 2008). High extraction capacity was achieved for the investigated analytes and great improvement of the limits of detection were obtained in comparison with other methods.The detection limit ranged from 0.04 ng /mL to 0.13 mg / mL.

A new method for the trace determination of fenpropathrin, cyhalothrin and deltametrin in environmental water was proposed using MWCNTs cartridge prior to HPLC (Zhou et al., 2008).Detailed analysis were performed concerning several parameters such as the sample pH, eluent and its volume, sample flow rate and sample volume. The linear ranges and the detection limits were in the range of 0.1-40 μg / L and 1.3-4.3 ng / L respectively. The increase of the pH value was conversely proportional to the recovery decline, requiring the adjustment to 7 of the solution pH for a better extraction based on the characteristics of analytes.

Carboxylated SWCNTs (c-SWCNTs) have shown a high sorption capacity to retain non-steroidal anti- inflammatory drugs (NSAIDs) and tetracyclines in urine (Suarez et al., 2007). Purified samples were analysed by capillary electrophoresis- mass spectrometry detection allowing the determination of 1.6 to 2.6 μg / L of NSAIDs with only 5 mL of sample.

Some factors that affect the MWCNTs enrichment efficiency in relation to some pesticides in environmental waters were investigated (El-Sheick et al., 2007). Model pesticides were selected from various common categories of pesticides, e.g. atrazine, propoxur, methidathion . The effect of MWCNTs oxidation with various oxidizing agents and the effect of length and external diameter of MWCNTs were assessed. Variables optimized included external diameter and length of the MWCNTs, oxidation of the MWCNT, mass of the MWCNT, volume and pH of water sample, composition and volume of eluting solvent and washing solvent. It was found that short –nitric acid oxidized –MWCNT exhibited higher enrichment efficiency especially for methidathion, than non-oxidized long MWCNT.

SPE with MWCNT as adsorbent was developed for determination and quantification of 12 pesticides in surface area by gas chromatography – mass spectrometry (GC-MS) (Wang et al., 2007a). Parameters that might influence the extraction efficiency such as the eluent volume, sample volume, sample flow rate and sample loading volume were optimized. The detection limits of proposed method could reach 0.01-0.03 μg / L. The experimental results showed the excellent linearity of 12 pesticides over the range of 0.04-4 μg / L. Good

recoveries achieved with spiked water samples were in the range of 82.0- 103.7 %. The advantages of this SPE method are its simplicity, speediness and the economic consumption of only 0.1 g MWCNT adsorbent per extraction.

The feasibility on the clean-up of three barbiturates (barbital, amobarbital and phenobarbital) from the complex matrix of pork utilizing MWCNTc SPE was also studied (Zhao et al., 2007). The residual barbiturates in pork were extracted by ultrasonic extrac-tion, cleaned up on a MWCNTs packed SPE cartridge and derivatized with methyl iodide under microwave irradiation. Ion trap GC/ MS/MS method eliminates the sample matrix interference . The detection limit of barbital was 0.2 μg/ kg and that of amobarbital and phenobarbital were both 0.1 μg / kg. Limit of quantification was 0.5 μg/ kg for three barbiturates.

The adsorptive potential of SWCNTs and MWCNTs for SPE of three groups of highly polar compounds (namely cefalosporin antibiotics, sulfonamides and phenolic compounds) was tested (Niu et al., 2007). It was found that the analytes were strongly retained by carbon nanotubes.Acceptable recoveries were obtained by adding ammonium acetate into the elu- ents. The performed comparative studies showed that the carbon nanotubes were superior to C18 for the extraction of the highly polar analytes . For the cephalosporins antibiotics and sulfonamides, the carbon nanotubes showed stronger retention capability than graphitized carbon blacks ; however, for some of the phenolic compounds graphitized carbon blacks seemed to be more suitable, indicating different mechanisms of these analytes. MWCNTs packed cartridge was selected to preconcentrate sulfonamide compounds from several real water samples.The detection limits of sulfonamides were in the range of 27-38 ng/ L.

A simple and efficient method was developed to determine polycyclic aromatic hydrocarbons (PAHs) in environmental waters using MWCNTs as SPE adsorbents coupled with HPLC (Wang et al., 2007c). The detection limits for the studied PAHs were 0.005-0.058 μg /L. The recoveries of PAHs spiked in environmental water samples ranged from 78.7 to 118.1 %.

Investigations were carried out to characterize the thermally treated CNTs and their adsorption properties of natural organic matter (NOM) (Lu & Su, 2007) . After the thermal treatment the structure and nature of carbon surface were changed including the increase in graphitized structure and the decrease in surface functional groups and negative charges; these properties made CNTs to adsorb more NOM. The adsorption capacity of NOM increased with initial NOM concentration and ionic strength but decreased with initial pH. A comparative analysis on the NOM adsorption capacities of CNTs and granular activated carbon (GAC) revealed that the CNTs has superior adsorption performance as compared with the GAC.

The characteristics of SWCNTs as novel adsorbent for collecting volatile organic compounds (VOCs) in ambient air have been studied (Jie-Min et al., 2007). The results reveal that SWCNTs have a large surface area and high adsorption and desorption efficiencies for collecting VOCs with low boiling points and strong volatility. The performed blank experiments show that the background of SWCNTs is very low owing to its chemical inertia. The effect of water can be neglected by increasing humidity in the sampling process because of its particular hydrophobicity. SWCNTs have large breakthrough volumes, as well as safe sampling volume.

A simple and sensitive method with MWCNT as SPE adsorbents coupled to HPLC for the determination of several fungicides and prometryn (triazine herbicide) in environmental

waters was proposed (Zhou et al., 2007). The detection limits for the studied fungicides and prometryn were in the range of 2.99- 6.94 ng /L, respectively. The results indicated that this method could be used as a reliable alternative for the environmental routine analysis.

Investigation studies were carried out regarding the trapping efficiency of MWCNTs for the analysis of several sulfonylurea herbicides (nicosulfuron, thifensulfuron- methyl and metsulfuron – methyl) in water samples (Zhou et al., 2006c).The possible parameters influencing the enrichment (eluent, sample pH, flow rate and sample volume) were optimized . The registered data showed that MWCNT has exhibited notable merits for trapping sulfonylurea herbicides at low ng / mL levels.

An on-line SPE method using MWCNT as adsorbent coupled with HPLC for simultaneous determination of 10 sulfonamides in eggs and pork was developed (Fang et al., 2006). At the level of the on-line interface SPE with HPLC, a conventional sample loop on the six-port injector valve of the HPLC was replaced by a preconcentration column packed with carbon nanotubes . The analytes in water solution were preconcentrated onto the preconcentration column and subsequently eluted with mobile phase of methanol-water.The results showed that the proposed method was simple, cost efective and sensitive.

A new procedure utilizing ultrasonic assistant extract method for the extraction, MWCNTs SPE columns for the clean–up and GC/ MS for the simultaneous determination of four benzodiazepines in pork was developed (Wang et al., 2006b).The adsorption capability of MWCNTs was proved to be obviously higher in comparison with C18. Factors that presumably affect the enrichment efficiency of MWCNT such as the volume of eluent, sample flow rate, sample pH, and volume of the water samples were optimized.The detection limits were 2 μg/kg for diazepam and 5 μg /kg for estalozam, alprazolam and triazolam in pork, respectively.

It was demonstrated that carbon nanotubes as SPE adsorbents can preconcentrate atrazine and simazine in environmental samples prior to HPLC with diode array detector (Zhou et al., 2006b).The detection limits of the atrazine and simazine were 33 and 9 ng / L, respectively.The spiked recoveries of the two analytes were over the range of 82.6- 103.7 % in most cases.

The feasibility of MWCNTs used as SPE adsorbent to enrich dichlorodiphe-nyltrichloroethane (DDT) and its metabolites at trace level in water samples was investigated (Zhou et al., 2006a). The detection limits were in the range 4-13 ng / L.

Among the newly developed procedures it must be mentioned the MWCNTs – supported micro solid phase extraction (μ- SPE) promoted by Basheer et al., 2006 . A 6 mg sample of MWCNTs was packed inside a (2cm x 1.5 cm) sheet of porous polypropylene membrane whose edges were heat-sealed to secure the contents. The μ- SPE device, which was wetted with dichlormethane, was then placed in a stirred sewage sludge sample solution to extract organophosphorous pesticides, used as a model compounds. After extraction, analytes were desorbed in hexane and analyzed using GC / MS. Since the porous membrane afforded protection of the MWCNTs no further cleanup of the extract was required. The π-π electrostatic interactions with the analytes and the large surface area of MWCNTs facilitated the adsorption of the analytes, with good selectivity and reproducibility. The comparison with hollow fiber protected (HFM-SPME) and headspace solid phase microextraction (HS-SPME) showed that this procedure is accurate and fast. μ-SPE is more sensitive in comparison with the other two procedures . The limits of detection were in the range 1-7 pg / g ; in comparison, for HFM-SPME and HS-SPME, LOD values 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 sewage sludge, sludge samples and biological fluids ,while preventing coextraction of extraneous materials.

Carbon nanotubes with the range of outside diameters from 2 to 10 mm were found to have a strong capacity in the adsorption of cyanobacterial toxins microcystins (MCs) (Yan et al., 2006). Cyanobacteria blooms in natural waters have become a growing environmental issue worldwide due to the increased discharge into rivers and lakes of wastewater containing nitrogen and phosphorus. MCs are stable in the water body and resistant to removal from drinking water by traditional water treatment technology. The adsorption amounts of MCs from lake water were about four times higher than those by activated carbon and clays tested.

A type of purified multi-walled carbon nanotubes (PMWCNTs) prepared by catalytic decomposition of methane was evaluated as an adsorbent used for trapping volatile organic compounds (VOCs) from environmental samples (Li et al., 2004). The performance in evaluation was based on breakthrough volumes (BTVs) and recoveries of selected VOCs. PMWCNTs were found to have much higher BTVs in comparison with Carbopack B, a graphitized carbon black with the same surface area as PMWCNTs. The recoveries of the tested VOCs trapped on PMWCNTs ranged from 80 to 110 %, and was not affected by the humidity of purge gas.The results indicate that PMWCNTs are a potential useful adsorbent for direct trapping VOCs from air samples.

MWCNTs possess remarkable potential for SPE of trace di-ethyl-phthalate, di-n-propyl-phthalate, di-iso-butyl-phthalate and dicyclohexyl-phthalate from tap water, river water and sea water samples. (Cai et al., 2003). The four analytes were quantitatively adsorbed on MWCNT packed cartridge, then the analytes in acetonitrile eluate were determined by HPLC. Detection limits of 0.18-0.86 ng / mL were achieved for four phthalate esters.The recoveries of SPE using MWCNT cartridge were compared with several SPE adsorbents such as C18, C8 and PS-DVB, the results showed that MWCNT were more effective than or as effective as these adsorbents for SPE of the four analytes.

4. Conclusions

SPE is an increasingly useful technique for sample concentration and clean-up in environmental applications and can be easily incorporated into automated analytical procedures. The future of SPE is closely related to improvement of sorbents that can be more effective in obtaining high enrichment efficiency of analytes. The unusual properties of CNTs, their large sorption capacity, wide surface area and the presence of a wide spectrum of surface functional groups have generated a great interest in their use as sorbent materials in a wide variety of analytical processess. The presence of the inner cavities, active sites on the surface and internanotube space can contribute to the high pollutants removal capability of CNTs. In several comparative studies the results showed that CNTs were more effective than or as effective as other commonly used adsorbents such as C 18 bonded silica, activated carbon or macroporous resins. It was reported that CNTs may be re-used more than 100 times after proper cleaning and reconditioning (Pyrzynska et al., 2008).

Carbon nanotubes have excellent adsorption ability for many kinds of substances such as inorganic and organic compounds (particularly those containing benzene rings) but lesser selectivity. It still needs to explore new chemical functionalization of CNTs to increase its

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selectivity for highly complexe samples in the future (Liu et al., 2008). Moreover, the development of new synthetic and purification procedures will contribute to the development of new microseparation methods and techniques. In a near future, it will be possible to perform chiral separation or to extract analytes selectively using chiral CNTs Another possibility will be the combination of carbon nanotubes with other new materials (e.g. quantum dots or ionic liquids) (Valcarcel et al., 2008).

Carbon nanotubes are relatively expensive and until recently, could only be obtained from a small number of suppliers. Improvements in synthesis methods and control of conditions which can develop a cost effective way of CNTs production are recommended.

Several authors suggest the need for more CNTs toxicological tests before introducing products containing CNTs into the market because these nanotubes are small enough to have the potential to enter the respiratory system and the detrimental effects are similar to those associated with asbestos. Functionalized CNTs (f-CNTs) are found to be safe while raw carbon nanotubes may possess some degree of toxicity, *in vitro* and *in vivo*. F-CNTs are employed in experimental treatment of cancer and as drug- delivery vehicles at the target without any toxic effects.

5. References

Al-Degs Y. S., Al-Ghouti M.A., El-Sheikh A.H.,(2009). Simultaneous determination of pesticides at trace levels in water using multiwalled carbon nanotubes as solid-phase extractant and multivariate calibration, *Journal of Hazardous Materials* , doi: 10.1016/ j.jhazmat.2009.03.065, in press

Ando K., Shinke K., Yamada S., Koyama T., Takai T., Nakaji S., Ogino T., (2009). Fabrication of carbon nanotube sheets and their bilirubin adsorption capacity, *Colloids and Surface B : Biointerface,* vol. 71, (2009) pp.2-29

Asensio-Ramos M., Hernandez –Borges J., Borges-Miquel T.M., Rodriguez-Delgado M.A. (2009). Evaluation of multiwalled carbon nanotubes as solid phase extraction adsorbent of pesticides from agricultural, ornamental and forestal soils, *Analytica Chimica Arta* (2009), doi: 10.1016/ j.aca.2009.06.014, in press

Basheer C., Alnedhary A.A., Rao B.S.M., Valliyaveettil S., Lee H.K., (2006). Development and application of porous membrane–protected carbon nanotube micro-solid phase extaction combined with gas-chromatography / mass spectrometry, *Analytical Chemistry*, vol. 78, (2006) pp. 2853-2858

Cai Y.Q., Jiang G.B., Liu J.F., Zhou Q.X., (2003). Multi-walled carbon nanotubes packed cartridge for the solid –phase extraction of several phthalate esters from water samples and their determination by high   performance liquid chromatography, *Analytica Chimica Acta*, vol. 494, (2003) pp 149-156

Cai Yq., Cai Yu., Mou S., LuY., (2005). Multi-walled carbon nanotubes as a solid phase extraction adsorbent for the determination of chlorophenols in environmental water samples, *Journal of Chromatography A*, vol.1081 (2005), pp. 245-247

Chen C., Hu J., Shao D., Li J., Wang X., (2009). Adsorption behavior of multiwall carbon nanotube / iron oxide magnetic composites for Ni (II) and Sr (II), *Journal of Hazardous Materials*, vol. 164, (2009) pp. 923-928

Dong M., Ma Y., Liu F., Qian C., Han L., Jiang S., (2009a). Use of multiwalled carbon nanotubes as a SPE adsorbent for analysis of carfentrazone-ethyl in water, *Chromatographia*, vol. 69, no. 1 / 2, (2009) pp 73-76

Dong M., Ma Y., ZhaoE., Qian C., Han L., Jiang S., (2009b). Using multiwalled carbon nanotubes as solid phase extraction adsorbents for determination of chloroacetanilide herbicides in water, *Microchim. Acta,* vol. 165, (2009) pp. 123-128

Du D., Wang M., Zhang J., Cai J., Tu H., Zhang A., (2008). Application of multiwalled carbon nanotubes for solid–phase extraction of organophosphate pesticides *Electrochemistry Communications*, vol. 10, (2008) pp. 85-89

El-Sheikh A.H., Insisi A.A., Sweileh J.A., (2007). Effect of oxidation and dimensions of multi-walled carbon nanotubes on solid phase extraction and enrichment of some pesticides from environmental waters prior to their simultaneous determination by high performance liquid chromatography, *Journal of Chromatography A,* vol. 1164, (2007) pp 25-32

Fang G.Z., He J.X., Wang S., (2006). Multiwalled carbon nanotubes as sorbent for on-line coupling of solid phase extraction to high –performance liquid chromatography, *Journal of Chromatography A*, vol. 1127, (2006) pp. 12-17

Guan Z., Huang Y., Wang W., (2008). Carboxyl modified multi- walled carbon nanotubes as solid phase extraction adsorbents combined with high performance liquid chromatography for analysis of linear alkylbenzene sulfonates, *Analytica Chimica Acta*, vol. 627, (2008) pp. 225-231.

Jie-Min L., Lin L., Hui-Li F., Zhan-Wu N., Peng Z., (2007). Evaluation of single –walled carbon nanotubes as novel adsorbent for volatile organic compounds, *Chinese Journal of Analytical Chemistry*, vol. 35, no. 6 ,(2007) pp 830-834

Jurado-Sanchez B., Ballesteros E., Gallego M., (2009). Comparison of several solid-phase extraction sorbents for continuous determination of amines in water by gas chromatography –mass-spectrometry, *Talanta,* doi: 10.1016/ j.talanta.2009.04.035, in press

Katsumata H., Matsumoto T., Kaneko S., Suzuki T., Ohta K., (2008). Preconcentration of diazinon using multiwalled carbon nanotubes as solid phase extraction adsorbents, *Microchemical Journal*, vol. 88, (2008) pp. 82-86.

Li L.,Huang Y., Wang Y., Wang W., (2009 a). Hemimicelle capped functionalized carbon nanotubes- based nanosized solid-phase extraction of arsenic from environmental water samples, *Analytica Chimica Acta*, vol. 631, (2009) pp. 182-188.

Li Q., Wang X., Yuan D., (2009 b). Preparation of solid-phase microextraction coated with single –walled carbon nanotubes by electrophoretic deposition and its application in extracting phenols from aqueous samples, *Journal of Chromatography A*, vol. 1216, (2009) pp. 1305-1311

Li Q.L., Yuan D.X., Lin Q.M., (2004). Evaluation of multi-walled carbon nanotubes as an adsorbent for trapping volatile organic compounds from environmental samples, *Journal of Chromatography A*, vol. 1026, (2004) pp 283-288

Liang H.D. and Han D.M., (2009). Multi-walled carbon nanotubes as sorbent for flow injection on-line microcolumn preconcentration coupled with flame atomic absorption spectrometry for determination of cadmium and copper, *Analytical Letters*, vol. 39, (2009) pp.2285-2295

Liu X.Y., Ji Y.S., Zhang H.X., Liu M.C., (2008) . Highly sensitive analysis of substituted aniline compounds in water samples by using oxidized multiwalled carbon nanotubes as an in-tube solid–phase microextraction medium, *Journal of Chromatography A*, vol. 1212, (2008), pp.10-15

Lopez-Feria S., Cardenas S., Valcarcel M., (2009). One step carbon nanotubes –based solid-phase extraction for the gas chromatographic –mass spectrometric multiclass pesticide control in virgin olive oils, *Journal of Chromatography A*, doi: 10.1016/ j.chroma.2009.02.060, in press

Lu C. & Chiu H., (2006). Adsorption of zinc (II) from water with purified carbon nanotubes, *Chemical Engineering Science*, vol.61, (2006) pp. 1138-1145.

Lu C., Chung Y.L., Chang K.F., (2005). Adsoption of trihalomethanes from water with carbon nanotubes, *Water Research*, vol. 39, (2005) pp. 1183-1189.

Lu C. & Su F., (2007) . Adsorption of natural organic matter by carbon nanotubes, *Separation and Purification Technology,* vol. 58, (2007) pp.113-121

Niu H., Cai Y., Shi Y., Wei F., Liu J., Mou S., Jiang G., (2007). Evaluation of carbon nanotubes as a solid-phase extraction of cefalosporins antibiotics, sulfonamides and phenolic compounds from aqueous solution, *Analytica Chimica Acta*, vol.594, (2007) pp 81-92

Pacheco P.H., Smichowski P., Polla G., Martinez L.D.,(2009). Solid phase extraction of Co ions using L-tyrosine immobilized on multiwall carbon nanotubes, *Talanta*, doi:10.1016/ j.talanta.2009.03.050, in press

Pyrzynska K.,(2008). Carbon nanotubes as a new solid – phase extraction material for removal and enrichment of organic pollutants in water, *Separation and Purification Review*, vol. 37, (2008) pp 372-389

Qu S., Huang F., Yu S., Chen G., Kong J., (2008). Magnetic removal of dyes from aqueous solution using multi-walled carbon nanotubes filled with Fe_2O_3 particles, *Journal of Hazardous Materials*, vol. 160, (2008) pp.634-647

Rastkari N., Ahmadkhaniha R.,Yunesian M., (2009). Single walled carbon nanotubes as an effective adsorbent in solid-phase microextraction of low level methyl tert-butyl ether, ethyl tert-butyl ether and methyl tert-amyl ether from human urine, *Journal of Chromatography B,* vol. 877, (2009) pp 1568-1574

Ravelo-Perez L.M., Hernandez-Borges J., Rodriguez- Delgado M.A., (2008). Multi-walled carbon nanotubes as efficient solid phase extraction materials of organophosphorus pesticides from apple, grape, orange and pineapple fruit juices, *Journal of Chromatography A*, vol. 1211, (2008) pp.33-42

Sae-Khow O., Mitra S., (2009). Carbon nanotubes as the sorbent for integrating μ-solid phase extraction within the needle of a syringe, *Journal of Chromatography A,* vol. 1216, (2009) pp. 2270-2274

Schierz A., Zanker H., (2009). Aqueous suspensions of carbon nanotubes : surface oxidation, colloidal stability and uranium sorption, *Environmental Pollution,* vol. 157,(2009) pp. 1088-1094

Shamspur T., Mostafavi A., (2009) .Application of modified multiwalled carbon nanotubes as a sorbent for simultaneous separation and preconcentration trace amounts of Au (III) and Mn (II), *Journal of Hazardous Materials*, doi : 10.1016/ jhazmat.2009.03.028, in press
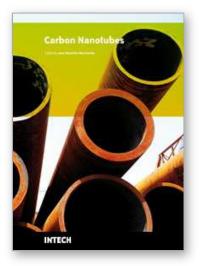
Sheikh A.H., Sweileh J.A., Al-Degs Y.S., Insisi A.A., Al-Rabady N.,(2008). Critical evaluation and comparison of enrichment efficiency of multi-walled carbon nanotubes, C18 silica and activated carbon toward some pesticides from environmental waters, *Talanta*, vol. 74, (2008) pp. 1675-1680

Suarez B., Simonet B.M., Cardenas S., Valcarcel M., (2007). Determination of non –steroidal anti-inflammatory drugs in urine by combining an immobilized carboxylated carbon nanotubes minicolumn for solid-phase extraction with capillary electrophoresis –mass spectrometry, *Journal of Chromatography A*, vol. 1159, (2007) pp. 203-207

Tuzen M, Soylak M. (2007). Multiwalled carbon nanotubes for speciation of chromium in environmental samples, *Journal of Hazardous Materials*, vol. 147 (2007), pp. 219-225

Valcarcel M., Cardenas S., Simonet B.M., Moliner- Martinez Y., Lucena R., (2008). Carbon nanostructures as sorbent materials in analytical processes, *Trends in Analytical Chemistry*, vol. 27, no. 1, (2008) pp 34-43

Wang J.X., Jiang D.Q., Gu Z.Y., Yan X.P., (2006a). Multiwalled carbon nanotubes coated fibers for solid–phase microextraction of polybrominated diphenyl ethers in water and milk samples before gas chromatography with electrone-capture detection, *Journal of Chromatography A*, vol. 1137, (2006) pp 8-14

Wang L., Zhao H., Qiu Y., Zhou Z., (2006b). Determination of four benzodiazepine residues in pork using multiwalled carbon nanotubes solid –phase extraction and gas chromatography- mass spectrometry, *Journal of Chromatography A*, vol. 1136, (2006) pp. 99-105

Wang S., Zhao P., Min G., Fang G., (2007 a). Multi-residue determination of pesticides in water using multi-walled carbon nanotubes solid –phase extraction and gas-chromatography –mass spectrometry, *Journal of Chromatography A*, vol. 1165,   (2007) pp 166-171

Wang S.G., Gong W.X., Liu X.W., Yao Y.W., Gao B.Y., Yue Q.Y., (2007b).Removal of lead (II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes, *Separation and Purification Technology*, vol.58 (2007),pp.17-23

Wang W.D., Huang Y.M., Shu W.Q., Cao J., (2007 c). Multiwalled carbon nanotubes as adsorbents for determination of polycyclic aromatic hydrocarbons in environmental waters coupled with high – performance liquid chromatography, *Journal of Chromatography A*, vol. 1173, (2007) pp 27-36

Yan H., Gong A., He H., Zhou J., Wei Y., Lv L., (2006). Adsorption of microcystins by carbon nanotubes, *Chemosphere*, vol. 62, (2006) pp. 142-148

Zhao H., Wang L., Qiu Y., Zhou Z., Zhong W., Li X., (2007). Multiwalled carbon nanotubes as a solid –phase extraction adsorbent for the determination of three barbiturates in pork by ion trap gas chromatography-tandem mass spectrometry   (GC/ MS/ MS) following microwave assisted derivatization, *Analytica Chimica Acta*, vol. 586, (2007) pp 399-406

Zhou Q., Xiao J., Ding Y.,(2007). Sensitive determination of fungicides and prometryn in environmental water samples using multiwalled carbon nanotubes solid-phase extraction cartridge, *Analytica Chimica Acta*, vol. 602, (2007) pp. 223-228

Zhou Q., Xiao J., Wang W., (2006 a). Using multi-walled carbon nanotubes as solid phase extraction adsorbents to determine dichlorodiphenyltrichloroethane and its metabolites at trace level in water samples by high performance liquid chromatography with UV detection, *Journal of Chromatography A,* vol.125, (2006)pp 152-158

Zhou Q., Xiao J., Wang W., Liu G., Shi Q., Wang J., (2006b). Determination of atrazine and simazine in environmental water samples using multiwalled carbon nanotubes as the adsorbents for preconcentration prior to high performance liquid chromatography with diode array detector, *Talanta*, vol. 68, (2006) pp.1309-1315

Zhou Q., Xiao J., Xie G., Wang W., Ding Y., Bai H., (2009). Enrichment of pyrethroid residues in environmental waters using a multiwalled carbon nanotubes cartridge, and analysis in combination with high performance liquid chromatography, *Microchim. Acta*, vol.164, (2009) pp. 419- 424

Zhou Q.,Wang W.,Xiao J., (2006c). Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron –methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography, *Analytica Chimica Acta,* vol. 559, (2006) pp.200-206

Zhou Q.X., Xie G.H., Xiao J.P., Wang W.D., Ding Y.J., (2008). Sensitive determination of fenpropathrin, cyhalothrin and deltametrin in environmental water samples using multiwalled carbon nanotubes cartridge prior to HPLC, *Chinese Chemical Letters*, vol. 19, (2008) pp. 95-98

Carbon Nanotubes

Edited by Jose Mauricio Marulanda

This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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