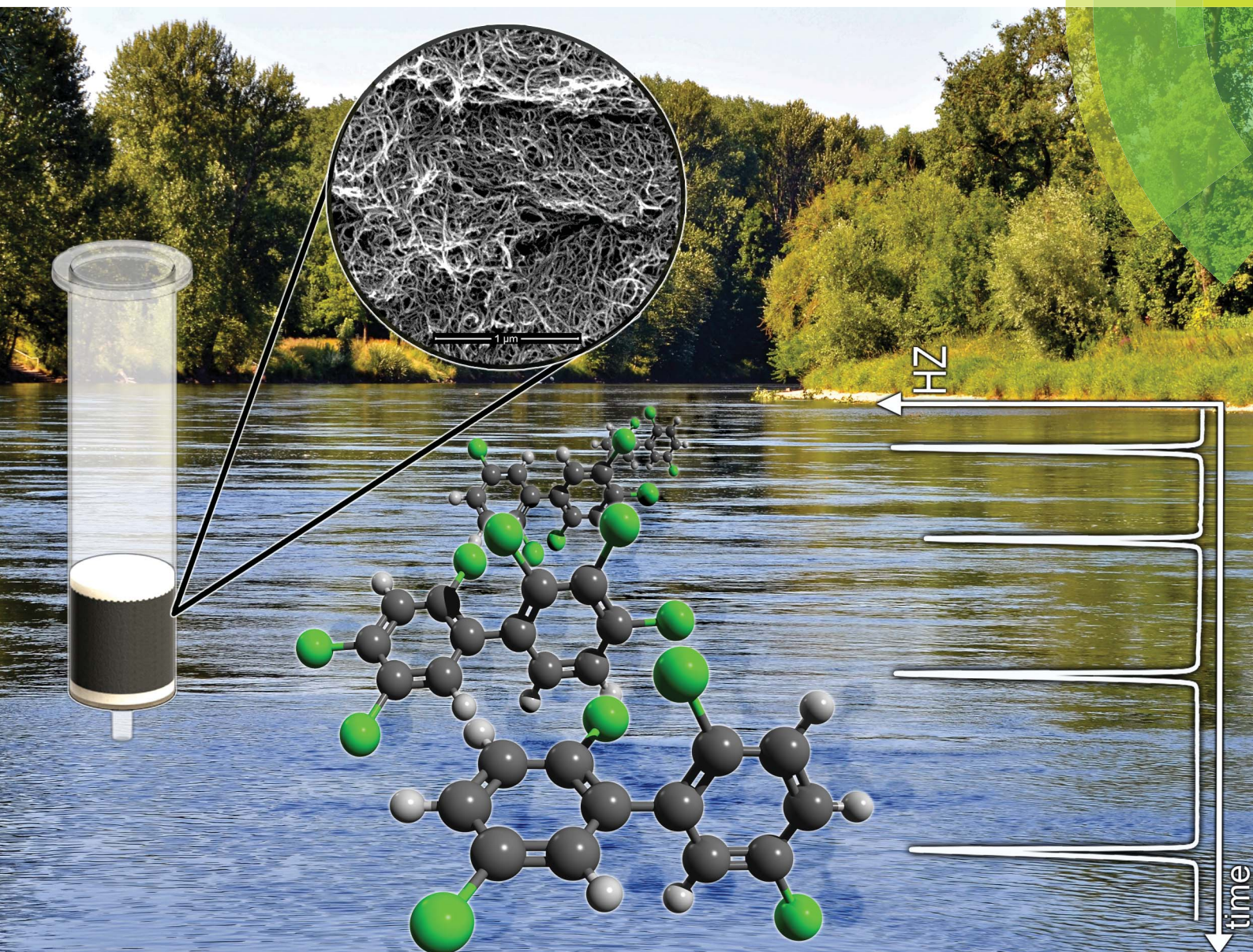


Analytical Methods

www.rsc.org/methods



ISSN 1759-9660



PAPER

Elizabeth N. Ndunda and Boris Mizaikoff

Multi-walled carbon nanotubes: innovative sorbents for pre-concentration of polychlorinated biphenyls in aqueous environments



CrossMark
click for updates

Cite this: *Anal. Methods*, 2015, 7, 8034

Multi-walled carbon nanotubes: innovative sorbents for pre-concentration of polychlorinated biphenyls in aqueous environments

Elizabeth N. Ndunda and Boris Mizaikoff*

Carbon nanotubes (CNTs) have demonstrated outstanding chemical and mechanical stability, electrical properties, and strong interactions with aromatic compounds owing to the π -electron system on the graphene sheets. Taking advantage of these unique properties, we have developed a fully validated sample pre-concentration technique for determination of polychlorinated biphenyls (PCBs) in aqueous environments using gas chromatography combined with a micro-cell electron capture detector (GC- μ ECD). The optimized method using pristine MWCNTs gave recoveries in the range of 46.0–92.5%, 51.4–91.5%, 48.7–77.8% for tap water, river water, and lake water, respectively. Compared to conventional C18 adsorbent and oxidized MWCNTs (oMWCNTs), pristine MWCNTs provided the best recoveries, thereby confirming that MWCNTs are excellent alternatives for C18, with the ability to achieve high performance. The developed protocol achieved method detection limits in the range of 0.002–0.011 $\mu\text{g L}^{-1}$ and relative standard deviation (RSD) < 15.5%.

Received 10th June 2015
Accepted 20th July 2015
DOI: 10.1039/c5ay01496d
www.rsc.org/methods

1. Introduction

Carbon nanotubes (CNTs) are materials of increasing interest since their discovery by Iijima in 1991.¹ The two forms of CNTs are the single-walled carbon nanotubes (SWCNTs) and the multi-walled carbon nanotubes (MWCNTs), which are formed from either a single roll or several cylindrical shells of graphene sheet, respectively. CNTs are characterized by their extraordinary chemical and mechanical stability, unique electrical properties,^{2–4} and strong interactions with aromatic constituents due to the delocalized π electron system.⁵

However, especially in aqueous environments their application has been limited due to their strong van der Waals forces leading to agglomeration. Past studies have indicated that surface modification *via* covalent and non-covalent interactions improves the solubility of CNTs in organic and aqueous media.^{2,3} The non-covalent modification is a physical process, which entails wrapping of polymers around the surface of the CNTs.^{6,7} In contrast, covalent modification usually involves the introduction of hydroxyl groups or carboxyl groups at the surface of the CNTs, which then provides a chemical architecture for further functionalization of the surface.²

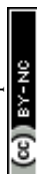
Surface-modified CNTs have therefore been used in biosensors,⁸ electrochemical sensors,⁹ diagnostics imaging,^{10,11} drug-delivery systems,¹² nanocomposites,¹³ and in general separation sciences.¹⁴ Furthermore, CNTs have been proposed as new

generation of adsorbents in solid-phase extraction (SPE), facilitating the analysis of environmental pollutants.¹⁵ Particularly, CNTs have been applied as adsorbents in SPE for quantification of polycyclic aromatic compounds,¹⁶ phthalate esters,¹⁷ poly-halogenated compounds,¹⁸ and tetracyclines.¹⁹ Since studies on the adsorption of dioxins at CNTs indicated that they are excellent materials for the removal of dioxins,²⁰ it is anticipated that CNTs should be suitable materials for pre-concentrating polychlorinated biphenyls (PCBs) from aqueous samples.

PCBs are compounds that were majorly used as dielectric fluids in capacitors and transformers during their commercial production between the 1930s and the 1970s, resulting to subsequent releases into the environment. Hence, they have been detected in soil,^{21,22} sediments,^{23–25} water,²⁶ air,²⁷ and biota;²⁸ even in areas without any commercial production, PCBs are found to date. Consequently, their wide environmental distribution is directly attributed to their stability, their long-range transport, and their persistence ranking them among the most prevalent contaminants in environmental matrices.²⁹ Therefore, monitoring of these compounds is of substantial relevance for tracking either contemporary releases or for developing appropriate strategies towards their complete remediation and elimination from the environment, as is the long term goal of the Stockholm convention on persistent organic pollutants (POPs).

However, their determination remains challenged due to their occurrence at trace-to-ultra-trace levels, and in complex matrices, thus the need for a pre-treatment step to facilitate detection at such low concentrations. Conventional sample preparation steps usually include liquid–liquid extraction (LLE)

Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany. E-mail: boris.mizaikoff@uni-ulm.de; Fax: +49-731-50-22763; Tel: +49-731-5022750



followed by a clean-up procedure or solid phase extraction (SPE) based on C18 sorbents. While LLE is demanding in terms of the volume of solvent required and the extraction time using, *e.g.*, separatory funnels, C18-SPE is limited by the non-selective enrichment of various constituents leading to co-elution, which then may interfere with the quantitative determination.

MWCNTs provide an attractive option based on their chemical properties serving as adsorbents for aromatic constituents. However, to date they are still not considered analytically or commercially viable alternatives to conventional C18 sorbents, and only few studies have reported on the pre-concentration of PCBs, *i.e.*, enriching PCBs from aqueous samples using magnetic MWCNTs grafted with a hydrophilic layer,³⁰ and clean-up of fish extracts using magnetic molecularly imprinted polymers comprising MWCNTs as support material.³¹

Though modifications are necessary especially when dealing with complex matrices, the long procedures of synthesis and grafting are not only time consuming but the need for extra reagents makes it costly for continuous monitoring as is required for PCBs. Therefore, we report herein an affordable and fully validated MWCNTs-SPE protocol for determination of 6 indicator PCBs (*i.e.*, IUPAC no. 28, 52, 101, 153, 138, 180) in aqueous environments using pristine MWCNTs. We also prove that pristine MWCNTs are excellent pre-concentration materials compared to their oxidized forms and conventional C18, thereby resulting in a ready-to-use SPE adsorbent.

2. Materials and methods

2.1 Chemicals

SPE cartridges (6 mL) and frits (20 μm porosity), pesticides grade methanol, *n*-hexane, and dichloromethane (DCM) were purchased from Carl Roth Chemicals (Karlsruhe, Germany). The two types of MWCNTs used were: MWCNTs with outer diameter 110–170 nm, length 5–9 μm , and purity > 90% carbon basis, and MWCNTs with outer diameter 10 nm, length 3–6 μm , and purity \geq 98% carbon basis synthesized *via* catalytic chemical vapour decomposition (Sigma-Aldrich, Steinheim, Germany). PCB standard mixtures (no. 28, 52, 101, 138, 153, 180), PCB 15 & 209, and SupelcleanTM LC-18 SPE cartridges (6 mL, 500 g, 51.7 μm , 490 $\text{m}^2 \text{g}^{-1}$) were purchased from Sigma-Aldrich (Steinheim, Germany). MWCNTs were dried at 120 $^{\circ}\text{C}$ for 2 h before use. Nitric acid (65%) and sulphuric acid (95–97%) were bought from Merck KGaA (Darmstadt, Germany). Water used in this study was purified using a Milli-Q filter system from Millipore (Billerica, USA). Nitrogen (99.999%) for gas chromatography was supplied by MTI IndustrieGase AG (Neu-Ulm, Germany).

2.2 Instrumentation

Gas chromatography was performed using an Agilent 6890 (Agilent Technologies) system coupled to a micro-cell electron capture detector (GC- μECD) for all the analysis discussed herein. The column used for the separation of PCBs was a ZB5-MS capillary column of dimensions 30 m \times 0.25 mm i.d. \times 0.25

μm film thickness with a 1 m silica-coated deactivated guard column (0.32 mm i.d.), which was connected to the analytical column *via* a glass capillary connector. The two temperature programs applied were: (i) initial temperature of 60 $^{\circ}\text{C}$ (hold time 2 min), ramp at 20 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$ (hold time 5 min) for PCB 15, and (ii) initial temperature of 60 $^{\circ}\text{C}$ (hold time 2 min), ramp at 15 $^{\circ}\text{C min}^{-1}$ to 210 $^{\circ}\text{C}$ (hold time 2 min), and final ramp at 15 $^{\circ}\text{C min}^{-1}$ to 275 $^{\circ}\text{C}$ (hold time 5 min) for the PCB mixtures. The detector temperature was set at 280 $^{\circ}\text{C}$.

1 μL of standards and samples was manually injected using the on-column injection mode. Nitrogen (purity > 99.999%) was used as both carrier gas at a flow rate of 2 mL min^{-1} , and as the detector make-up at 30 mL min^{-1} . Quantification was based on internal standard calibration using PCB 209, while the identification was performed by comparing the retention times with those of standards. Data was processed using the ChemStation software version A.03.08 supplied by Agilent Technologies.

2.3 Oxidation of MWCNTs

An amount of 0.5 g of pristine MWCNTs (10 nm) were placed in 100 mL flask, and 100 mL of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3 : 1; v/v) was added. The mixture was sonicated at 40 $^{\circ}\text{C}$ for 4 h (60 W, 35 kHz) and the resultant oxidized MWCNTs (oMWCNTs) were diluted with 500 mL water, filtered under vacuum, and washed with ultra-pure water until neutral pH; thereafter, they were air dried overnight.

2.4 Characterization of pristine MWCNTs and oMWCNTs

The surface morphology was investigated using a DualBeam Helios Nanolab 600 focused ion beam (FIB) – scanning electron microscopy (SEM) system (Hillsboro, OR, USA). Nitrogen adsorption-desorption experiments were performed using QuadraSorb Station SI from Quantachrome GmbH and Co. KG (Odelzhausen, Germany). Samples were degassed at 100 $^{\circ}\text{C}$ under vacuum for 3 h before data collection, and the specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Studies on the oxygen-containing functional groups at the surface of MWCNTs were done by X-ray photoelectron spectroscopy (XPS).

2.5 Validation of MWCNTs-SPE

One hundred milligrams of the MWCNTs was weighed into a 6 mL empty polypropylene cartridge with a frit (20 μm porosity) at the bottom. Aliquots of methanol were passed through the column to ensure tight packing of the adsorbent. Thereafter, a second layer of frit was added on top of the packed adsorbent. The packed column was then mounted onto the VisiprepTM SPE vacuum manifold, and conditioned with 6 mL of methanol followed by equilibration with 6 mL Milli-Q water. During these steps, the column was not allowed to dry. Spiked water samples were loaded onto the column followed by washing with 2 mL of methanol. Prior to elution, the column was dried for 15 min by drawing air through the device under full vacuum. The analytes were desorbed using 10 mL *n*-hexane : DCM (1 : 1; v/v) into round bottomed flasks, and reduced to 0.5 mL using a rotary evaporator immersed in a water bath set at 30 $^{\circ}\text{C}$. The eluate was



then transferred into a glass vial, where the volume was further reduced to near dryness under a gentle flow of argon, and reconstituted in hexane into GC autosampler vials. 4 μL of PCB 209 ($8.8 \mu\text{g mL}^{-1}$) was added before GC- μECD analysis. Conventional C18 SPE columns were subject to the same processing steps (*i.e.*, conditioning and equilibration) as the MWCNT-SPE cartridges, however, were washed with 10% methanol in water.

2.6 Collection of water samples and analysis

Tap water was collected from the laboratory (Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Germany). River water was obtained from the Danube river (Ulm), and lake water was collected from the Ludwigfelder See (Neu-Ulm). The water samples were collected into glass bottles, then filtered through $0.45 \mu\text{m}$ pore filters, and stored at 4°C until analysis following the developed method.

2.7 Adsorption capacity

Twenty milligrams of MWCNTs were packed into Eppendorf tubes, and 1 mL of $0.4 \mu\text{g mL}^{-1}$ PCB 15 in hexane was added and equilibrated for 4 h. The extent of adsorption was followed by analyzing the supernatant every 30 min. The tubes were centrifuged at 3000 rpm for 5 min, and the amount of PCB in the supernatant was determined by GC- μECD analysis. After establishing the time required to reach equilibrium, 20 mg MWCNTs were incubated with 1 mL of PCB 15 at concentrations ranging from 0.4 – $4.8 \mu\text{g mL}^{-1}$, and vortexed for 60 min. The amount of bound analyte was calculated using eqn (1) and binding characteristics determined by applying the binding data to Langmuir (2) and Freundlich (3) equations.

$$Q = \frac{(C_o - C_f)V}{m} \quad (1)$$

where Q is the binding capacity in $\mu\text{g g}^{-1}$, C_o is the initial concentration of the analyte in $\mu\text{g mL}^{-1}$, C_f is the concentration of the analyte in the supernatant in $\mu\text{g mL}^{-1}$, V is the volume of the solution in mL, and m is the mass of the MWCNTs in grams.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

q_e is the bound analyte at equilibrium ($\mu\text{g g}^{-1}$), C_e is the equilibrium concentration in $\mu\text{g mL}^{-1}$, q_m represents the monolayer coverage or maximum adsorption capacity ($\mu\text{g g}^{-1}$), and K_L is a constant related to the adsorption energy ($\text{mL } \mu\text{g}^{-1}$).

$$q_e = K_f C_e^n \quad (3)$$

K_f and n are Freundlich constants representing the adsorption capacity and heterogeneity index, and q_e and C_e are the concentrations of the bound and free analyte, respectively.

2.8 Quality control

The quality control measures included analysis of blank samples, rinsing of glassware before use, and the use of internal standards. The method performance was tested by determining

accuracy, precision, linearity, and method detection limit (MDL). Standards were prepared from $10 \mu\text{g mL}^{-1}$ of PCB mixture stock standards by dilution with *n*-hexane. Quantification was based on the internal standard method with PCB 209 added to all samples and standards. The MDL was determined following the EPA method using blank samples (Milli-Q water) spiked at low concentrations (4-times the concentration providing a signal-noise-ratio of 3), and then taken through the validated analytical procedure.³²

3. Results and discussion

3.1 Characterization of pristine MWCNTs and oMWCNTs

The SEM images revealed entangled fibres for both pristine MWCNTs and oMWCNTs. While oxidation is thought to affect both the structure and the physical properties of the MWCNTs, according to the SEM images the structure remained essentially intact, as no observable change in surface morphology were evident (Fig. 1a and b). MWCNTs (110 – 170 nm) revealed very short fibres and large diameters, as anticipated (Fig. 1c). Atomic force microscopy (AFM) studies have shown that there is an insignificant decrease in length following the oxidation process.³³ Raman spectroscopy of the oxidized MWCNTs compared to pristine MWCNTs has indicated that the graphene structure remains intact despite the curtailing of the fibre lengths.^{34,35} However, the oxidation process induces defects (*i.e.*, amorphous carbon) with the degree of deformation at the graphene sheets characterized by the I_G/I_D ratio, which is the ratio of the G-band (*i.e.*, sp^2 hybridized carbon), and D-band (*i.e.*, sp^3 hybridized carbon) intensities.^{5,36}

The increased dispersion of MWCNTs in water proved the successful oxidation of MWCNTs. Introduction of oxygen containing groups was also confirmed using XPS where increased intensity of oxygen (O1s) peak for the oMWCNTs (Fig. 2b), compared to the pristine MWCNTs (Fig. 2a) was observed. The total oxygen content is shown in Table 1. Specific surface areas determined *via* BET were 269.7 , 244.8 , and $17.4 \text{ m}^2 \text{ g}^{-1}$ for the pristine MWCNTs (10 nm), oMWCNTs, and pristine MWCNTs (110 – 170 nm), respectively. Therefore, no pronounced decrease in surface area was observed due to the oxidation process; likewise, recent studies confirm minute changes or no evident change in specific surface area after oxidation.^{37–39}

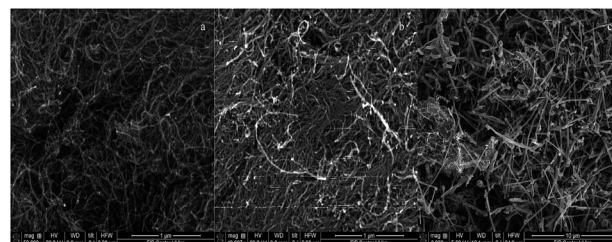


Fig. 1 SEM image of (a) pristine MWCNTs (10 nm), (b) oMWCNTs, and (c) pristine MWCNTs (110 – 170 nm).



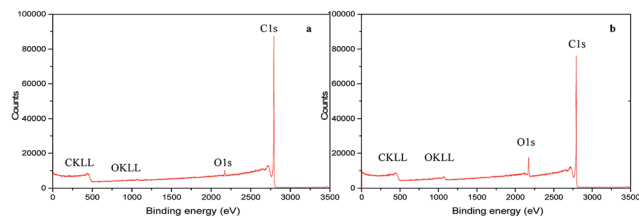


Fig. 2 XPS spectra showing change in C1s and O1s for (a) pristine MWCNTs, (b) oMWCNTs.

Table 1 Surface concentration (%) of carbon and oxygen at pristine MWCNTs and oMWCNTs

Peak	Pristine MWCNTs	oMWCNTs
C1s	98.0	91.69
O1s	2.0	8.31

3.2 Validation of MWCNTs-SPE

3.2.1 Determination of the elution solvent and volume.

Non-polar *n*-hexane and polar dichloromethane – as a mixture and as pure solvents – were tested for the elution of the PCBs after enrichment. Pure *n*-hexane was not able to desorb all constituents and gave recoveries in the range of 22.1–89.1%. While pure DCM revealed adequate recoveries (60.2–100.3%), a mixture of *n*-hexane : DCM (1 : 1) gave the best results (>70%) for all the PCBs congeners, and was therefore adopted for all further analyses using 10 mL of volume. CNTs have been reported to strongly interact with aromatic compounds;²⁰ hence, the need for a strong elution solvent, which can efficiently and effectively disrupt the interactions with the CNT surface.

3.2.2 Effect of dimension on PCBs recovery. MWCNTs that are commercially available are usually of different dimensions in terms of outside diameter (o.d.), internal diameter (i.d.), and length. Therefore, the dimension of MWCNTs should to some extent affect the retention and recovery properties for the analytes of interest. El-Sheikh *et al.*,⁴⁰ have studied the effect of dimensions on the recoveries of three pesticides at oxidized MWCNTs. Using 10–20 nm, 10–30 nm, 20–40 nm, 40–60 nm, 60–100 nm, and 40–60 nm CNTs, they found that 40–60 nm provided superior recoveries. Decreased adsorption affinity for 1,2,4,5-tetrachlorobenzene⁴¹ and dimethyl phthalate (DMP)³⁹ with increase in MWCNTs outside diameter (o.d.) has been reported before. In the present study, MWCNTs of two different dimensions were applied for pre-concentration of PCBs in Milli-Q water. MWCNTs with o.d. 110–170 nm showed decrease in recovery with increasing loading volume, while 10 nm ones maintained recoveries >80% for all loading volumes. These observations suggest that the dimension of CNTs is indeed important for adsorbents used in SPE; MWCNTs of 10 nm o.d. were applied for all further analyses herein.

3.2.3 Flow rate and breakthrough volume. The sample flow rate during the loading step is a crucial factor that affects the

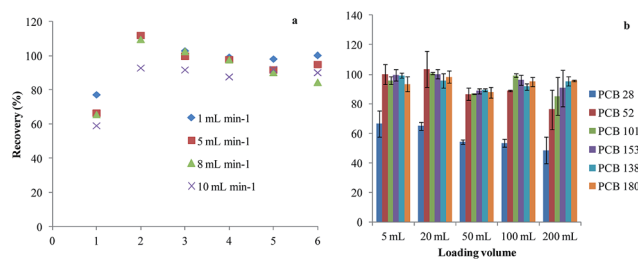


Fig. 3 (a) Recoveries of 6 indicator PCBs at different flow rates with water spiked at $1 \mu\text{g mL}^{-1}$ (i.e., 1 ppb), where 1, 2, 3, 4, 5, and 6 are PCB 28, 52, 101, 153, 138, and 180, respectively; (b) recoveries achieved for different loading volumes.

performance of SPE cartridges, as it influences the interaction time of the analytes with the adsorbent. While high flow rates are preferred, in cases where the loading volume is high they usually do not offer sufficient interaction time. On the other hand, low flow rates maximize the interaction time, yet, suffer drawbacks due to extended loading times. A compromise is therefore required to enable sufficient interaction while maintaining reasonable loading times. Flow rates of 1, 5, 8, and 10 mL min^{-1} were tested using 20 mL of spiked Milli-Q water. The recoveries were >80% for all flow rates and all PCB analytes except for PCB 28 (Fig. 3a). After optimization, a flow rate of 5 mL min^{-1} was applied for consecutive experiments. To determine the breakthrough volume, different volumes of water from 5–200 mL were loaded onto the columns following the validated method. Although a slight decrease in recoveries with increasing volume was observed, recoveries >70% were realized for all congeners in all volumes except PCB 28 (Fig. 3b). The method precision was acceptable with relative standard deviation (RSD) ranging from 2.5 to 10.7%.

3.3 Analysis of real world water samples

The pH of the water samples was determined as 7.69 ± 0.02 , 8.42 ± 0.03 , and 8.12 ± 0.00 for tap water, river water, and lake water, respectively. Water samples were analyzed before spiking to ascertain the presence or absence of any PCBs; no PCBs were detected in any of the samples. Then, the samples were spiked at a level of 0.2 ng mL^{-1} , and analyzed *via* the validated method. The recoveries ranged from 46.0–92.5% for tap water, 51.4–

Table 2 Recovery (% \pm STD^a) of 6 indicator PCBs after pre-concentration from a variety of real-world water samples

Analyte	Tap water		River water	Lake water
	MWCNTs	oMWCNTs	MWCNTs	MWCNTs
PCB 28	46.0 \pm 4.94	42.9 \pm 1.40	51.4 \pm 4.34	48.7 \pm 7.57
PCB 52	90.7 \pm 4.23	54.4 \pm 4.04	91.5 \pm 2.30	77.7 \pm 1.84
PCB 101	90.1 \pm 3.61	48.9 \pm 4.11	87.0 \pm 6.06	76.7 \pm 3.39
PCB 153	91.3 \pm 3.48	46.6 \pm 4.52	86.7 \pm 6.01	77.8 \pm 3.25
PCB 138	92.5 \pm 3.46	44.9 \pm 4.14	91.1 \pm 8.37	74.1 \pm 1.77
PCB 180	90.3 \pm 5.19	43.4 \pm 7.75	87.6 \pm 6.92	76.5 \pm 5.09

^a STD is the standard deviation of triplicate analysis.



Table 3 Adsorption isotherm parameters for pristine MWCNTs using PCB 15 as an exemplary constituent

	Langmuir				Freundlich		
	q_m ($\mu\text{g g}^{-1}$)	K_L ($\text{mL } \mu\text{g}^{-1}$)	R_L	R^2	K_f ($\mu\text{g g}^{-1}$)	n	R^2
PCB 15	555.6	0.09	0.97	0.889	54.1	0.711	0.9972

91.5% for river water, and 47.8–77.8% for lake water (Table 2). Five out of six congeners had recoveries within 70–120%, yet again, PCB 28 gave poor recoveries (<70%). PCB 28 has the lowest number of chlorine atoms and is therefore expected to be highly soluble in water in contrast to the other five PCBs studied herein.

The aqueous solubility of PCB 28 is 0.16 mg L^{-1} , compared to 0.03, 0.01, 0.001 for PCB 52, 101, and 153, respectively.⁴² It is therefore likely that PCB 28 already suffers from losses during the loading step. The same phenomenon was reported by Dahane *et al.*,⁴³ where the most soluble constituent methomyl gave recoveries in the range of 43–60%, compared to less soluble pesticides such as diazinon, whose recovery was between 58 and 106%. C18 adsorbent, which is the conventional adsorbent material used for most SPE applications recorded markedly lower recoveries (33.9–67.7%). Poor performance, *i.e.*, recoveries <60.0% for C18 cartridges, have been previously reported.^{44–46} C18 is known to retain non-polar compounds *via* hydrophobic forces; yet, MWCNTs are subject to additional π – π interactions, and therefore strongly retain aromatic constituents.⁴⁷

3.4 Effect of surface oxidation on the recovery of PCBs

To determine the effect of surface oxidation of MWCNTs on the recovery of PCBs, spiked Milli-Q water was pre-concentrated using oMWCNTs. Reduced recoveries were evident compared to pristine MWCNTs (Table 2). It should be noted that although the dispersion of functionalized MWCNTs in water increased due to the increase in hydrophilicity, the performance decreased. Similarly, a decrease in recovery of pentachlorophenol,³⁸ naphthalene,³³ phenanthrene,⁴⁸ toluene, ethylbenzene, xylene,⁴⁹ and triclosan³⁷ on oxidized MWCNTs as compared to pristine MWCNTs has been reported. The reason for the decreased performance of oxidized MWCNTs has been linked to the oxygen groups (*i.e.*, carboxyl and hydroxyl groups),

which are hypothesized to localize the electrons at the surface of the MWCNTs, thus, removing them from the π -electron system.⁵⁰ In addition, the formation of water clusters due to hydrogen bonding between the water molecules and the oxidized MWCNT surface has been argued as a possible reason for the decrease in retention pertaining non-polar molecules.³³ Therefore, the retention of water molecules rather than non-polar constituents appears highly favoured.^{33,51} Cho *et al.*,³³ suggested that oxidation could also prevent non-polar molecules from accessing the non-oxidized sites within CNT structures.

3.5 Effect of pH on the recovery of PCBs

Some studies have reported the isoelectric point of oxidized MWCNTs to be around pH 4.^{37,39} Taking this into consideration, at lower pH oxidized CNTs are protonated, and no opportunity of hydrogen bond formation with water is provided. At higher pH, CNTs are deprotonated, and therefore, chances of hydrogen bonds with surrounding water molecules increase leading to the formation of water clusters. To determine whether the recovery of PCBs is improved at lower pH, tap water was spiked at a pH of 1 (*i.e.*, pH below the reported isoelectric point for oxidized MWCNTs). The recoveries ranged from 41.4 to 50.3%, which was within the same range of recoveries as the tap water at a pH of 7.69. Therefore, it may be concluded that the introduction of polar groups (*i.e.*, surface oxygen) generally increases the polarity of MWCNTs, which in turn leads to reduced interaction with aromatic constituents, and thus, reduced adsorption capacities.⁵² These results are also backed by the earlier argument that oxygen-containing groups localize electrons at the surface of MWCNTs, thereby removing them from the π -electron system, which results in reduced adsorption.

3.6 Adsorption isotherms

The Langmuir adsorption isotherm given by eqn (2), and the Freundlich adsorption isotherm given by eqn (3) were applied for the binding characterization of the pristine MWCNTs (10 nm). Freundlich isotherms assume a heterogeneous surface with adsorption sites of different energies, while Langmuir isotherms are based on a homogeneous surface interaction. MWCNTs indicated a heterogeneous surface ($n = 0.71$) with the adsorption favouring the Freundlich isotherm, as confirmed by a correlation coefficient >0.99 (Table 3). Other studies on the adsorption of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene,

Table 4 Analytical parameters derived for the developed MWCNT-SPE method

PCB congener	Retention time (min)	Linear range (ng mL^{-1})	Regression equation	Linear response (r^2)	Method detection limit MDL ($\mu\text{g L}^{-1}$)
PCB 28	12.9	0.465–186	$y = 0.015x + 0.0217$	0.9997	0.011
PCB 52	13.6	0.465–186	$y = 0.0073x + 0.014$	0.9998	0.008
PCB 101	15.5	0.26–104	$y = 0.0102x + 0.0159$	0.9996	0.004
PCB 153	17.2	0.21–85	$y = 0.0153x + 0.0176$	0.9997	0.002
PCB 138	17.8	0.23–92	$y = 0.0254x + 0.0242$	0.9987	0.004
PCB 180	19.3	0.22–89	$y = 0.0279x + 0.0174$	0.9998	0.002



1,2,4,5-tetrachlorobenzene, and trihalomethanes on CNTs have reported *n*-values of 0.52–0.65, 0.64, 0.75, and 0.58–0.75, respectively.^{41,53,54}

3.7 Analytical performance of the proposed method

The obtained MDL values ranged from 0.002–0.011 $\mu\text{g L}^{-1}$ with PCB 180 and PCB 138 providing the lowest MDL value, and PCB 28 the highest (Table 4). The RSD of replicate analyses ranged from 2.21–14.6%. The obtained calibrations were linear across the investigated concentration range of 0.465–186 ng mL^{-1} for lower chlorinated PCBs, and 0.21–104 ng mL^{-1} for the higher chlorinated ones at coefficients of linearity >0.99 (Table 4).

4. Conclusions

A fully validated MWCNT-SPE protocol for the pre-concentration of PCBs in aqueous environments has been presented. Pristine MWCNTs revealed higher recoveries for the investigated PCBs compared to conventional C18 adsorbents and oMWCNTs, confirming that pristine MWCNTs can be applied for studies of PCBs in aqueous media. In addition, only 100 mg of MWCNTs were necessary compared to 500 mg for conventional sorbent, thereby suggesting not only more reliable, but potentially also more affordable method for SPE. Compared to C18, the cost of MWCNTs – at this small quantity – is already now slightly less, thus offering an excellent alternative to conventional sorbent matrices. The developed method shows detection limits way below the maximum contamination level of 0.5 $\mu\text{g L}^{-1}$ for PCBs in drinking water (as set by US environmental protection agency (EPA)), therefore suggesting that the established analytical method may be readily implemented for monitoring of drinking water quality and safety, which is of substantial societal relevance. However, despite the results achieved herein, the developed protocol may only be applicable for pre-concentrating sufficiently chlorinated constituents, as more soluble (*i.e.*, less chlorinated) constituents may be retained less due to the reduced interaction with MWCNTs.

Acknowledgements

The authors thank G. Neusser and the *Focused Ion Beam Center UUl*m (Institute of Analytical and Bioanalytical Chemistry, University of Ulm) for the SEM images, C. Egger (Institute of Inorganic Chemistry II, University of Ulm) for the BET studies, and T. Diemant (Institute of Surface Chemistry and Catalysis, University of Ulm) for the XPS measurements. S. Gienger is appreciated for assistance with the gas chromatography experiments. E. Ndunda is grateful to the Ministry of Higher Education, Science and Technology (MOHEST) of Kenya in conjunction with the Deutscher Akademischer Austauschdienst (DAAD) for financial support.

References

1 S. Iijima, *Nature*, 1991, **354**, 56–58.

- K. Balasubramanian and M. Burghard, *Small*, 2005, **1**, 180–192.
- M. Valcárcel, B. M. Simonet, S. Cárdenas and B. Suárez, *Anal. Bioanal. Chem.*, 2005, **382**, 1783–1790.
- N. B. Singh and S. Agrawal, *J. Sci. Med. Chem.*, 2013, **1**, 1–8.
- R. Amade, S. Hussain, I. R. Ocaña and E. Bertran, *J. Environ. Eng. Ecol. Sci.*, 2014, **3**, 1–7.
- A.-E. Hsiao, S.-Y. Tsai, M.-W. Hsu and S.-J. Chang, *Nanoscale Res. Lett.*, 2012, **7**, 2–5.
- A. Liu, I. Honma, M. Ichihara and H. Zhou, *Nanotechnology*, 2006, **17**, 2845–2849.
- C. Han, A. Doepeke, W. Cho, V. Likodimos, A. A. de la Cruz, T. Back, W. R. Heineman, H. B. Halsall, V. N. Shanov, M. J. Schulz, P. Falaras and D. D. Dionysiou, *Adv. Funct. Mater.*, 2013, **23**, 1807–1816.
- W. Guo, M. Geng, L. Zhou, S. Chao, R. Yang, H. An and H. Liu, *Int. J. Electrochem. Sci.*, 2013, **8**, 5369–5381.
- L. Gemma, G. Vidili, E. Venturelli, C. Ménard-moyon and M. Antonietta, *PNAS*, 2012, **109**, 16612–16617.
- X. Shi, S. H. Wang, M. Shen, M. E. Antwerp, X. Chen, C. Li, E. J. Petersen, Q. Huang, W. J. Weber and J. R. Baker, *Biomacromolecules*, 2009, **10**, 1744–1750.
- A. M. A. Elhissi, W. Ahmed, I. U. Hassan, V. R. Dhanak and A. D'Emanuele, *J. Drug Delivery*, 2012, **2012**, 1–10.
- A. May-Pat, F. Aviles, P. Toro, M. Yazdani-Pedram and J. Cauich-Rodriguez, *EXPRESS Polym. Lett.*, 2011, **6**, 96–106.
- Y. Chang, B. Bai, L. Du, T. Pang and Y. Fu, *J. Chil. Chem. Soc.*, 2013, **58**, 2209–2212.
- B. Constantin, in *Carbon Nanotubes*, ed. J. M. Marulanda, InTech, Shanghai, 1st edn, 2010, pp. 524–542.
- W.-D. Wang, Y.-M. Huang, W.-Q. Shu and J. Cao, *J. Chromatogr. A*, 2007, **1173**, 27–36.
- Y.-Q. Cai, G.-B. Jiang, J.-F. Liu and Q.-X. Zhou, *Anal. Chim. Acta*, 2003, **494**, 149–156.
- M. Abdel Salam and R. Burk, *Anal. Bioanal. Chem.*, 2008, **390**, 2159–2170.
- B. Suárez, B. Santos, B. M. Simonet, S. Cárdenas and M. Valcárcel, *J. Chromatogr. A*, 2007, **1175**, 127–132.
- R. Q. Long and R. T. Yang, *J. Am. Chem. Soc.*, 2001, **123**, 2058–2059.
- M. A.-E. Abdallah, D. Drage and S. Harrad, *Environ. Sci.: Processes Impacts*, 2013, **15**, 2279–2287.
- J. O. Grimalt, B. L. van Drooge, A. Ribes, R. M. Vilanova, P. Fernandez and P. Appleby, *Chemosphere*, 2004, **54**, 1549–1561.
- S. Afful, J. Awudza, S. Twumasi and S. Osae, *Chemosphere*, 2013, **93**, 1556–1560.
- W. Ameer, S. Trabelsi, B. El Bedoui and M. Driss, *Bull. Environ. Contam. Toxicol.*, 2011, **86**, 539–544.
- A. Covaci, A. Gheorghe, S. Voorspoels, J. Maervoet, E. Steen Redeker, R. Blust and P. Schepens, *Environ. Int.*, 2005, **31**, 367–375.
- R. Barra, P. Popp, R. Quiroz, C. Bauer, H. Cid and W. Tümpling, *Chemosphere*, 2005, **58**, 905–915.
- M. E. Aydin, S. Ozcan and A. Tor, *Clean: Soil, Air, Water*, 2007, **35**, 660–668.



- 28 T. Brázová, V. Hanzelová and D. Miklisová, *Parasitol. Res.*, 2012, **111**, 779–786.
- 29 UNEP, *Stockholm convention on persistent organic pollutants (POPs)*, Secretariat of the Stockholm Convention on Persistent Organic Pollutants, Geneva, Switzerland, 2009.
- 30 S. Zeng, Y. Cao, W. Sang, T. Li, N. Gan and L. Zheng, *Int. J. Mol. Sci.*, 2012, **13**, 6382–6398.
- 31 X. Du, S. Lin, N. Gan, X. Chen, Y. Cao, T. Li and P. Zhan, *J. Sep. Sci.*, 2014, **37**, 1591–1600.
- 32 K. Gomez-Taylor, M. Kahn, H. D. Telliard, W. A. Ditthavong, K. Kopylev, L. McCarty, H. Riddick, L. Miller, K. Cuddeback, J. Rushneck, D. Dedah and S. Stralka, *Technical support document for the assessment of detection and quantitation approaches*, US Environmental Protection Agency, Washington, DC, 2003.
- 33 H.-H. Cho, B. A. Smith, J. D. Wnuk, D. H. Fairbrother and W. P. Ball, *Environ. Sci. Technol.*, 2008, **42**, 2899–2905.
- 34 K. Goh, L. Setiawan, L. Wei, W. Jiang, R. Wang and Y. Chen, *J. Membr. Sci.*, 2013, **446**, 244–254.
- 35 D. W. Seo, W. J. Yoon, S. J. Park, M. C. Jo and J. S. Kim, *Carbon: Sci. Technol.*, 2006, **7**, 266–270.
- 36 S. T. Kim, H. J. Choi and S. M. Hong, *Colloid Polym. Sci.*, 2006, **285**, 593–598.
- 37 H.-H. Cho, H. Huang and K. Schwab, *Langmuir*, 2011, **27**, 12960–12967.
- 38 M. Abdel Salam, *Arabian J. Chem.*, 2012, **5**, 291–296.
- 39 W. Den, H. Liu, S. Chan, K. T. Kin and C. Huang, *J. Environ. Eng. Manage.*, 2006, **16**, 275–282.
- 40 A. H. El-Sheikh, A. A. Insisi and J. A. Sweileh, *J. Chromatogr. A*, 2007, **1164**, 25–32.
- 41 W. Chen, L. Duan and D. Zhu, *Environ. Sci. Technol.*, 2007, **41**, 8295–8300.
- 42 Y. W. Shiu and D. Mackay, *J. Phys. Chem. Ref. Data*, 1986, **15**, 911–928.
- 43 S. Dahane, M. D. Gil García, A. Uclés Moreno, M. Martínez Galera, M. D. M. Socías Viciano and A. Derdour, *Microchim. Acta*, 2015, **182**, 95–103.
- 44 C. Sun, Y. Dong, S. Xu, S. Yao, J. Dai, S. Han and L. Wang, *Environ. Pollut.*, 2002, **117**, 9–14.
- 45 W.-L. Ho, Y.-Y. Liu and T.-C. Lin, *Environ. Eng. Sci.*, 2011, **28**, 421–434.
- 46 J. Lai, R. Niessner and D. Knopp, *Anal. Chim. Acta*, 2004, **522**, 137–144.
- 47 M. Kragulj, J. Tričković, B. Dalmacija, Á. Kukovecz, Z. Kónya, J. Molnar and S. Rončević, *Chem. Eng. J.*, 2013, **225**, 144–152.
- 48 S. Gotovac, Y. Hattori, D. Noguchi, J. Miyamoto, M. Kanamaru, S. Utsumi, H. Kanoh and K. Kaneko, *J. Phys. Chem. B*, 2006, **110**, 16219–16224.
- 49 F. Yu, J. Ma and Y. Wu, *J. Hazard. Mater.*, 2011, **192**, 1370–1379.
- 50 R. W. Coughlin and F. S. Ezra, *Environ. Sci. Technol.*, 1968, **2**, 291–297.
- 51 F. Yu, J. Ma and S. Han, *Sci. Rep.*, 2014, **4**, 1–8.
- 52 F. Ahnert, H. A. Arafat and N. G. Pinto, *Adsorption*, 2003, **9**, 311–319.
- 53 X. Peng, Y. Li, Z. Luan, Z. Di, H. Wang, B. Tian and Z. Jia, *Chem. Phys. Lett.*, 2003, **376**, 154–158.
- 54 C. Lu, Y.-L. Chung and K.-F. Chang, *Water Res.*, 2005, **39**, 1183–1189.

