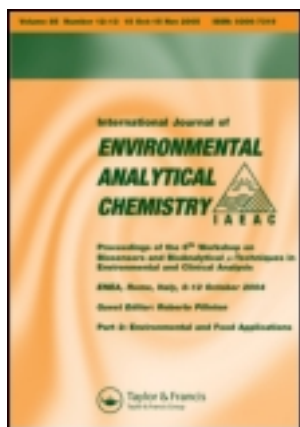


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Solid phase extraction and uptake properties of multi-walled carbon nanotubes of different dimensions towards some nitro-phenols and chloro-phenols from water

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Solid phase extraction and uptake properties of multi-walled carbon nanotubes of different dimensions towards some nitro-phenols and chloro-phenols from water

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Equilibrium sorption studies and solid phase extraction (SPE) of various phenols (Phenol (Ph), 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP)) on oxidized and raw multi-walled carbon nanotubes (MWCNTs) of various external diameters (10–20, 10–30, 20–40, 40–60 and 60–100 nm) and various lengths (short: 1–2 μm and long: 5–15 μm) were tested. Equilibrium sorption studies showed that 2-NP fits the Langmuir isotherm model (LIM), while the other phenolic compounds fit the Freundlich isotherm model (FIM). There was generally an inverse relation between external diameter of MWCNT and its sorption capacity towards phenolic compounds. Long MWCNT showed higher sorption capacity than short MWCNT. Thus dimensions of MWCNT play a role in retaining the sorbed molecules. Oxidation of MWCNT caused a decrease in sorption capacity of phenolic compounds of lower acidity where hydrophobic interaction is predominant, while it caused an increase in sorption capacity of phenolic compounds of higher acidity where H-bonding is predominant. The dependence of sorption on the acidity of phenols (pK_a values) indicates that the basic groups (pyrone-like groups) on the MWCNT surface play a role in the sorption process. In SPE experiments, it was found that hydrogen peroxide-oxidized MWCNT of external diameter 40–60 nm and length 5–15 μm was the best extractant at pH 6.5 using acetonitrile as eluting solvent. The optimized SPE procedure gave detection limits range: 0.027–0.202 ng mL^{-1} within the studied concentration range (10–100 ng mL^{-1}). Application of the optimum SPE method on spiked tap water, reservoir water and stream water gave recovery range of 84.3–100% for 2-CP, 3-CP and 4-CP (%RSD range 2.8–9.2%); while Ph, 2-NP, 4-NP, and 2,4-DNP gave recoveries <67.6%.

Keywords: multi-walled carbon nanotubes; solid phase extraction; adsorption models; phenols; preconcentration; water samples; oxidized carbon nanotubes

1. Introduction

Phenolic compounds are discharged into environmental waters causing unpleasant taste and odor [1]. The EU legislation requirement is that the maximum permissible concentration of phenols in drinking water should not exceed $0.5 \mu\text{g L}^{-1}$ for the total content and $0.1 \mu\text{g L}^{-1}$ for the individual one. Therefore methods with low detection limits

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are required [2]. Some analytical instruments, such as high-performance liquid chromatography (HPLC), cannot determine phenols at the prescribed levels. This is a major problem associated with analysis of phenols beside other problems such as matrix interferences. For this reason, it is important to develop a simple and efficient method for detection and accurate determination of these pollutants in water samples. In this case, sample preconcentration is essential to achieve these limits. Solid phase extraction (SPE) is one of the most common techniques that are used for preconcentration of analytes in environmental waters [3–9]. The choice of sorbent is the most important factor for obtaining higher enrichment efficiency of analytes. Simultaneously, it is important to study the sorption behavior of the sorbent towards the analyte, since this will provide the researcher with important information regarding the sorption capacity, sorption favourability and surface heterogeneity.

Various sorbents have been used in the literatures for SPE and preconcentration of phenols, including C18 [10], activated carbon [11], molecularly imprinted polymers [12]; in addition to many other sorbents that have been reviewed [6–9,13].

Multi-walled carbon nanotubes (MWCNT) have been used to sorb different pollutants from various aqueous samples. This is due to strong interaction between the MWCNT surface and the pollutants. Different mechanisms have been proposed for this interaction, such as hydrophobic interactions, π - π interaction, electrostatic interactions, and hydrogen bonding [14]. Each mechanism works differently depending on the environmental conditions. For example, when H-bonds are predominant, increased oxygen-containing functional groups on CNT would increase sorption. In contrast, for sorption controlled by hydrophobic interactions, the increased functional groups would decrease the accessibility and affinity of CNTs for organic chemicals.

The applicability of MWCNT's as packing adsorbent for SPE of some phenols was reported. Cai *et al.* [15] have used MWCNT for SPE of bisphenol A, 4-n-nonylphenol, and 4-tert-octylphenol. They [16] have also used MWCNTs for preconcentration of chlorophenols 4-Chlorophenol, 3-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol. Niu *et al.* [17] reported the use of single-walled carbon nanotubes (0.5–1.6 nm external diameter) and MWCNT (30–60 nm external diameter) for SPE of phenol, hydroxyquinonen, 1,3,5-trihydroxybenzene, 3,5-dihydroxybenzoic acid and guaiacol. Liu *et al.* [18] reported the use of oxidized MWCNT (10–20 nm external diameter and 5–15 μ m length) as a SPE fibre for determination of phenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol, 2,4-dimethylphenol and 2,4,6-trichlorophenol. Abdel Salam and Burk [19] reported the modification of MWCNT with octadecylamine and with poly ethylene glycol for SPE and determination of pentachlorophenol and 2,4,5-trichlorophenol. In another publication [20] the authors reported the adsorption of pentachlorophenol by oxidized MWCNT; the data were fitted with Langmuir, Freundlich, Radke and Prausnitz, and Fritz–Schlunder models. Yang *et al.* [21] studied the sorption of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol and 4-methylphenol on MWCNT; the results were fitted with Dubinin-Ashtakhov model. Lin and Xing [22] reported the adsorption of phenol, catechol, pyrogallol, 2-phenylphenol, 1-naphthol and naphthalene; the Freundlich equation was employed to fit the sorption data. Another adsorption study for 2,4-dichlorophenol and 2-naphthol on SWCNTs was reported by Chen *et al.* [23] and the data were fitted with the Freundlich isotherm. Pan *et al.* [24] reported the adsorption of Bisphenol A and 17 α -Ethinyl Estradiol on both single-walled CNTs and MWCNTs;

the results were fitted using Polanyi-Mane and Langmuir models while Freundlich model generally failed to describe their results.

It is thought that the dimensions and surface chemistry of MWCNTs will affect the sorptive properties of CNTs. Studying the effect of dimensions and surface chemistry of MWCNTs on the sorption behaviour of phenols may shed some light on the nature of this sorption behaviour. Surface chemistry of CNTs may be altered by chemical oxidation of the surface.

Although many authors have used MWCNTs for preconcentration and sorption of some phenols, none of the studies was dedicated to observe the effect of dimensions and oxidation of the MWCNT on preconcentration and sorption behaviour of phenols. This is the main objective of this study. Surface chemistry of MWCNTs may be altered by chemical oxidation. This will cause functionalization of the MWCNT surface with some acidic (carboxylic acid, phenolic, lactonic groups) and basic (pyrone-like groups) surface functional groups [25]. These groups may significantly affect the sorption process.

2. Experimental

Two types of experiments were conducted in this work: batch equilibrium sorption isotherm experiments (Section 3.1) and solid phase extraction experiments (column 'cartridge' experiments (Section 3.2)). The first part was conducted to study the effect of dimensions and oxidation of MWCNTs on its sorption characteristics towards the targeted phenolic compounds, while the second part was conducted to study the effect of dimensions and oxidation of MWCNT on its SPE and preconcentration characteristics of the targeted phenolic compounds.

2.1 Chemicals and materials

Chemicals were purchased from the following sources: 3-chlorophenol (3-CP), 2,4-dinitrophenol (2,4-DNP) from ACROS (Belgium); phenol (Ph) from POCH (Poland); 2-chlorophenol (2-CP), hydrogen peroxide (HP), ammonium persulfate (APS), hydrochloric acid and diethyl ether from Scharlau (Spain); 4-chlorophenol (4-CP) from Fluka (Italy); 2-nitrophenol (2-NP) from Aldrich (Germany); 4-nitrophenol (4-NP) and methanol from Merck (Germany); acetonitrile (ACN), nitric acid (NA), tetrahydrofuran (THF), glacial acetic acid (AA), ammonium hydroxide (NH₄OH), and dichloromethane (DCM) from TEDIA (USA). All solvents were of HPLC grade.

Multi-walled carbon nanotubes (MWCNTs) of different dimensions (length and external diameters) were purchased from Shenzhen Nanotech port Co. Ltd., Shenzhen, China. Six different MWCNTs samples of various dimensions were used in this study, abbreviated as: L-MWCNT-1020 (external diameter range: 10–20 nm, length: 5–15 μm); L-MWCNT-1030 (external diameter range: 10–30 nm, length: 5–15 μm); L-MWCNT-2040 (external diameter range: 20–40 nm, length: 5–15 μm); L-MWCNT-4060 (external diameter range: 40–60 nm, length: 5–15 μm); L-MWCNT-60100 (external diameter range: 60–100 nm, length: 5–15 μm); S-MWCNT-4060 (external diameter range: 40–60 nm, length: 1–2 μm). Some characteristics of the MWCNTs as provided by the manufacturer are as follows: purity >95%; ash ≤0.2 wt%; amorphous carbon 2%; specific surface area 40–300 m² g⁻¹. All MWCNTs were dried before use at 70–80°C for 2 hours. Oxidation of L-MWCNT-4060 with various oxidizing agents was performed using either concentrated

HNO₃ solution at room temperature for 24 hours; or using a saturated solution of (NH₄)₂S₂O₈ in 1.0 M H₂SO₄ at room temperature for 18 h; or using a mixture of 50 mL H₂O₂ and 50 mL of 1.0 M H₂SO₄ at 50°C for 1 h. Adsorbents were then washed with water to remove excess oxidizing agent and other water soluble species. The produced adsorbents were labelled L-MWCNT-4060-NA, L-MWCNT-4060-HP and L-MWCNT-4060-APS, respectively, where NA, HP and APS refers to nitric acid oxidation, hydrogen peroxide oxidation and ammonium persulphate oxidation, respectively. The same procedures were used as necessary to oxidize other MWCNTs of different dimensions.

2.2 Instruments and equipment

The quantitative determination of phenols was carried out using an HPLC instrument. A Perkin Elmer (USA) HPLC instrument consisted of a model 785A programmable absorbance detector and a series 200 LC pump with 20 µL sample loop. Separation was performed using a Thermo electron Corporation, ODS HYPERSIL (150 × 4.6 mm, 5 µm) column. The mobile phase consisted of methanol and water and glacial acetic acid glacial (25/74/1, v/v/v) respectively, and the flow rate of the mobile phase was set at 1.5 mL min⁻¹. Chromatographic data were acquired and processed by UV detection at 280 nm using a Perkin Elmer integrator model 1022 LC, Plus system, PE NELSON, USA, using the peak area mode for quantification. All measurements were carried out at room temperature (22 ± 2°C). Solid phase extraction (SPE) was performed using a visiprep-12-port vacuum manifold from Supelco, Germany. The outlet tip of the manifold was connected to a vacuum pump (Heidolph, Germany) to control the flow rate. MWCNTs cartridge was prepared by placing MWCNT's in an empty 6 mL polypropylene SPE-tube (Supelco, Germany). Polyethylene frits were used to hold the sorbent packing in the cartridge. A Nicolet evolution 100 UV-Visible spectrophotometer, Thermo electron Corporation, was used for determination of the remaining concentrations of phenols in aqueous medium in the phenols adsorption experiments. All pH-measurements of water samples were measured using a Weilheim (Germany) pH meter with a combination glass electrode.

2.3 General SPE procedure: column (cartridge) experiments

100 mg of L-MWCNT-4060-HP adsorbent was packed into the SPE cartridge and pre-conditioned by washing with 5 mL acetonitrile (ACN) then with 5 mL distilled water ahead of the preconcentration procedure. 70 mL of water sample (spiked with 100 µg L⁻¹ of each phenol simultaneously at pH 6.5) was then passed under the force of gravity through the cartridge. Then, the cartridge was washed with 5 mL of 5% ACN aqueous solution to remove co-adsorbed matrix materials. Next, the retained phenols were eluted with 3 mL ACN. 20 µL of the eluate was injected into HPLC system for quantitative determination of phenols as described in Section 2.2.

2.4 Environmental water samples

Three types of environmental waters were used for evaluation of the proposed SPE method; tap water, reservoir water and stream water. Tap water samples were taken after flowing for 10 min from various water taps in our school in different days, and then pooled and used to generate a composite tap water sample. Reservoir water composite sample was

generated by collecting several samples from local household reservoirs. Stream water composite sample was generated by collecting several samples from Al-Zarqa stream. Before use, all the environmental water samples were filtered through 0.45 μm micropore membranes and stored in glass bottles at 4°C.

The optimum SPE procedure was applied on water samples before and after spiking with the targeted phenols. SPE procedures were applied in five replicates ($n=5$), after which each extract was analysed for phenols as separate sample.

2.5 Sorption isotherms: equilibrium (batch) studies

Adsorption isotherms of various oxidized and non-oxidized MWCNTs towards the seven phenols were estimated in separate experiments. For that purpose: 50 mL aqueous solutions containing 10, 20, 30, 40, 50, 60, 70, 80 and 90 mg L^{-1} of the targeted phenol were transferred separately into 100 mL conical flasks each containing 25 mg of the MWCNT sorbent. pH of the mixtures were adjusted to 6.5 by adding dilute acid or dilute base. The flasks were closed and equilibrated using thermo-stated shaker (GFL, Germany) at 25°C (± 1) for 24 hours. Blank solutions (containing no sorbent) were also included. For each solution, a sample from the supernatant was withdrawn and the absorbance of the phenolic compound was measured spectrophotometrically. Ph was measured at 270 nm; 2-CP and 3-CP at 276 nm; 2-NP at 278 nm; 4-CP at 282 nm; 4-NP at 316 nm; 2,4-DNP at 354 nm. The equilibrium concentrations of phenols (C_e) were then estimated (mg L^{-1}) using a daily prepared calibration graph. The measured concentrations were used to calculate q_e (mg g^{-1}), which is milligram of sorbed phenolic compound per gram sorbent. Plots of q_e against C_e were then drawn to get the sorption isotherms.

Two of the most commonly used isotherm theories have been adopted in this part, namely, the Langmuir isotherm model (LIM) and Freundlich isotherm model (FIM).

LIM model assumes that the surface has a limited number of active sites and the sorption of the solute continues until the surface sites are occupied and the interaction between sorbed molecules is negligible. The form of Langmuir equation can be represented by the following linear equation [26]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}$$

where C_e is the equilibrium concentration of remaining phenolic compound in the solution (mg L^{-1}). q_e is the amount of phenolic compound sorbed per unit mass of sorbent at equilibrium (mg g^{-1}). Q_{\max} is the amount of sorbate at complete monolayer coverage (mg g^{-1}). b is a constant that is related to the heat of sorption. It also represents the equilibrium adsorption constant (L mg^{-1}), which is the ratio of sorption and desorption rate constants. Higher values of b indicate that the solute favourably transfers from the solution to attach to the sorbent surface.

Freundlich isotherm model can be represented by the following linear equation [27]:

$$\log q_e = \log K_F + n \log C_e$$

K_F ($\text{mg}^{1-n} \text{g}^{-1} \text{L}^n$) represents the sorption capacity when equilibrium concentration equals to 1, and n represents the degree of dependence of sorption on equilibrium concentration.

K_F is an indicator of sorption capacity and n is an indicator of sorption intensity. Additionally n is an indicator of surface heterogeneity and sorption favourability [28,29].

Lower values of n reflect the high heterogeneity of the sorbent surface and that the energies of active sites are highly variable [29,30]. A relatively slight slope ($n < 1$) indicates that sorption is favourable over the entire studied concentrations range, while a steep slope ($n > 1$) means that sorption is favourable at high concentrations but much less so at lower concentrations [28,31].

In addition to LIM and FIM, linear sorption isotherm (LinIM) (which is a special case of Freundlich isotherm when n equals unity) was also applied. LinIM has the form:

$$K_D(L/g) = q_e/C_e$$

where K_D is the distribution coefficient, which measures the extraction power of the sorbent toward the sorbate. Higher K_D values ($\gg 1$) indicates higher extraction power of the sorbent from solution.

3. Results and discussion

3.1 Sorption characteristics of phenols

Sorption isotherms (q_e vs. C_e) of 2-CP (as an example of constant partition isotherm 'C-1 isotherm') and 2-NP (which is the only Langmuir type isotherm 'L-2 isotherm' in this study) on various MWCNT sorbents are shown in Figure 1 (a and b).

The sorption data were treated using LIM, FIM and LinIM. The results of these treatments using linear regression procedure showed that sorption of Ph, 2-CP, 3-CP, 4-CP, 4-NP and 2,4-DNP followed FIM and LinIM. Freundlich constants and K_D values of the six phenolic compounds on various sorbents are shown in Tables 1 and 2. On the other hand, sorption of 2-NP followed LIM. Langmuir constants and values of K_D at selected C_i values are shown in Table 3.

3.1.1 Types of sorption isotherms

All the phenolic compounds studied in this work (except 2-NP) were of constant partition type (C-1 type) isotherms, which means that the sorbate always distribute itself between the sorbent and the solution in constant ratio. Figure 1(a) shows the sorption isotherms of 2-CP on various MWCNTs (as an example). In this type, it is expected that linear sorption isotherm is obeyed. Other phenolic compounds (Ph, 3-CP, 4-CP, 4-NP, and 2,4-DNP) exhibited similar isotherm type. 2-NP was the only phenolic compound that obeyed LIM. This is probably attributable to negligible interaction between the adsorbed 2-NP molecules owing to intra-molecular H-bonding in the 2-NP molecule rather than inter-molecular H-bonding. Negligible interaction between the sorbed molecules is necessary for LIM to be obeyed [26]. The shapes of isotherms presented in Figure 1(b) indicate that the sorbent effectively removes 2-NP at low initial concentrations; at higher concentrations the isotherms reached a maximum sorption capacity as indicated by the plateau. The shape of 2-NP uptake is 'L2' type according to Giles classification for isotherms [32]. Many sorption isotherms from aqueous solution have L-shape (Langmuir shape), which indicate that sorption process is 'favourable' [31,32]. Figure 1(b) indicates that the LinIM was not obeyed. However, some K_D values were calculated at certain initial concentrations (C_i) (10, 40, 70 mg L⁻¹ of each phenol) as shown in Table 3. It is noted that K_D values generally decreased with increasing C_i , which is attributed to limited number of active sites. LIM failed to represent other phenols probably owing to inter-molecular interaction between

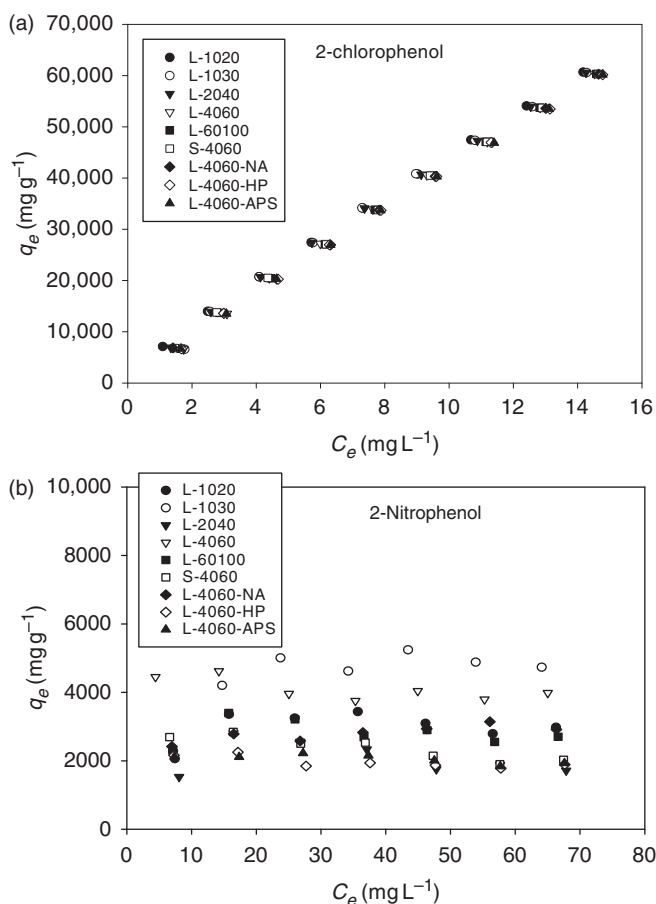


Figure 1. Sorption isotherms of (a) 2-CP (type C-1) isotherm, and (b) 2-NP (type L-2 isotherm) on various MWCNT sorbents.

the sorbed molecules. They exhibited almost linear relationships between q_e and C_e , which indicates multi-layer sorption.

Values of n were generally close to unity except for those of 4-NP and 2,4-DNP. The values of n for 4-NP were generally <1 , which indicate that the sorption of 4-NP is favourable over the entire studied concentration range. Oppositely, 2,4-DNP gave n values >1 , which indicate favourable sorption at high concentration. Sorption here is more intensive [28,31].

3.1.2 Effect of oxidation of MWCNT on sorption capacity

Among the three oxidants used in this study, hydrogen peroxide seems to be the most effective in modifying the sorptive surface properties of MWCNTs. Sorption of 4-NP and 4-NP were more than doubled, while that of 2,4-DNP was more than tripled upon oxidation with HP (Table 4). Sorption of chlorophenols was also improved dramatically. Performance of other oxidants is far less dramatic and inconsistent for the sorption

Table 1. Freundlich constants and distribution coefficients (K_D) for sorption of Ph, 2-CP, 3-CP and 4-CP on various MWCNT sorbents.

	FIM			LinIM	
	R^2	K_F	n	K_D (L/g)	R^2
sorbate: Ph					
L-MWCNT-1020	0.9926	723	0.83	352	0.9896
L-MWCNT-1030	0.9937	476	0.95	371	0.9944
L-MWCNT-2040	0.9828	470	0.95	354	0.9933
L-MWCNT-4060	0.9965	589	0.87	338	0.9957
L-MWCNT-60100	0.9933	345	1.00	331	0.9854
S-MWCNT-4060	0.9849	244	1.10	359	0.9890
L-MWCNT-4060-NA	0.9901	532	0.86	299	0.9965
L-MWCNT-4060-HP	0.9934	197	1.11	300	0.9940
L-MWCNT-4060-APS	0.9873	381	0.94	296	0.9916
sorbate: 2-CP					
L-MWCNT-1020	0.9996	6490	0.83	4046	0.9990
L-MWCNT-1030	0.9770	4682	0.98	4115	0.9929
L-MWCNT-2040	0.9982	5581	0.90	4052	0.9979
L-MWCNT-4060	0.9936	4143	1.02	4104	0.9965
L-MWCNT-60100	0.9950	4489	0.98	4059	0.9981
S-MWCNT-4060	0.9981	5038	0.93	3981	0.9988
L-MWCNT-4060-NA	0.9998	4901	0.93	3999	0.9997
L-MWCNT-4060-HP	0.9972	4294	0.99	4003	0.9987
L-MWCNT-4060-APS	0.9981	4297	0.99	4003	0.9989
sorbate: 3-CP					
L-MWCNT-1020	0.9993	3967	0.86	2547	0.9991
L-MWCNT-1030	0.9980	3162	0.95	2568	0.9981
L-MWCNT-2040	0.9932	2895	0.98	2610	0.9968
L-MWCNT-4060	0.9985	2371	1.02	2501	0.9990
L-MWCNT-60100	0.9931	1943	1.09	2522	0.9986
S-MWCNT-4060	0.9922	1952	1.09	2527	0.9982
L-MWCNT-4060-NA	0.9809	2029	1.09	2578	0.9973
L-MWCNT-4060-HP	0.9976	2556	1.01	2545	0.9981
L-MWCNT-4060-APS	0.9887	2061	1.08	2591	0.9978
sorbate: 4-CP					
L-MWCNT-1020	0.9999	3446	0.86	2094	0.9975
L-MWCNT-1030	0.9976	2866	0.92	2118	0.9981
L-MWCNT-2040	0.9974	2811	0.93	2129	0.9970
L-MWCNT-4060	0.9974	3374	0.85	2060	0.9989
L-MWCNT-60100	0.9899	2232	1.00	2109	0.9965
S-MWCNT-4060	0.9918	2269	0.99	2090	0.9962
L-MWCNT-4060-NA	0.9784	3011	0.87	2172	0.9802
L-MWCNT-4060-HP	0.9989	2478	0.96	2122	0.9982
L-MWCNT-4060-APS	0.9937	2317	0.99	2093	0.9950

of different phenols. Generally, APS oxidation procedure seems to be more efficient than that of NA.

From Tables 1 to 3, it is generally noted that the effect of oxidation of the MWCNT on sorption capacity depends on the acidity of the sorbate. For example, while 4-NP (pK_a 7.15) and 2-NP (pK_a 7.17) gave lower K_F values upon oxidation of MWCNT;

Table 2. Freundlich constants and distribution coefficients (K_D) for sorption of 4-NP, 2,4-DNP on various MWCNT sorbents.

	FIM			LinIM	
	R^2	K_F	n	K_D (L/g)	R^2
sorbate: 4-NP					
L-MWCNT-1020	0.9845	2834	0.58	666	0.9826
L-MWCNT-1030	0.9829	3379	0.52	498	0.8845
L-MWCNT-2040	0.9891	1668	0.77	705	0.9600
L-MWCNT-4060	0.9901	1714	0.71	640	0.9890
L-MWCNT-60100	0.9626	842	0.94	628	0.9758
S-MWCNT-4060	0.9940	1361	0.79	653	0.9931
L-MWCNT-4060-NA	0.9918	1211	0.78	580	0.9886
L-MWCNT-4060-HP	0.9896	904	0.89	642	0.9690
L-MWCNT-4060-APS	0.9889	695	0.95	591	0.9830
sorbate: 2,4-DNP					
L-MWCNT-1020	0.9926	2350	0.88	1658	0.9937
L-MWCNT-1030	0.9822	694	1.13	1113	0.9622
L-MWCNT-2040	0.9749	1203	1.10	1570	0.9672
L-MWCNT-4060	0.9966	379	1.36	1483	0.9790
L-MWCNT-60100	0.9737	521	1.27	1402	0.9307
S-MWCNT-4060	0.9835	195	1.26	1389	0.9651
L-MWCNT-4060-NA	0.9971	920	1.23	1547	0.9953
L-MWCNT-4060-HP	0.9852	719	1.30	1588	0.9958
L-MWCNT-4060-APS	0.9984	4092	0.84	2447	0.9966

Table 3. Langmuir constants and distribution coefficients (K_D) at various concentration levels for sorption of 2-NP on various MWCNT sorbents.

MWCNT type	LIM			K_D ($L g^{-1}$)		
	R^2	b ($L mg^{-1}$)	Q_{max} ($mg g^{-1}$)	$C_i = 10 mg L^{-1}$	$C_i = 40 mg L^{-1}$	$C_i = 70 mg L^{-1}$
L MWCNT-1020	0.9801	1.00	3333	278	96	45
L-MWCNT-1030	0.9765	0.20	5000	319	135	73
L-MWCNT-2040	0.9649	0.19	1667	228	63	25
L-MWCNT-4060	0.9960	1.50	3333	1011	106	61
L-MWCNT-60100	0.9868	0.50	2500	324	73	41
S-MWCNT-4060	0.9828	0.18	2000	408	69	30
NA-L-MWCNT-4060	0.9914	0.33	3333	345	77	44
HP-L-MWCNT-4060	0.9955	0.55	1667	296	52	28
APS-L-MWCNT-4060	0.9918	0.33	2000	289	58	29

2,4-DNP (pK_a 4.96) gave higher K_F values after oxidation of MWCNT. A similar trend was observed for chlorophenols. i.e. while 4-CP (pK_a 9.2) and 3-CP (pK_a 8.8) gave lower K_F values upon oxidation, 2-CP (pK_a 8.5) gave higher K_F values after oxidation. Phenol (pK_a 9.89) showed lower values of K_F upon oxidation. Pan and Xing [14] reported that when H-bonds are predominant, increased oxygen-containing functional groups on CNT would increase the sorption. This may be attributed to the fact that oxidation introduces

Table 4. Optimization of some parameters of the SPE procedure of phenols from aqueous medium using column (cartridge) experiments. Sorbed phenols were washed with 5 mL of 5% ACN then eluted with 5 mL can.

	Recovery, % (\pm %RSD)						
	Ph	4-NP	2-NP	2,4-DNP	2-CP	4-CP	3-CP
Oxidation of MWCNT ¹							
L-MWCNT-4060	47.2 \pm 3.9	6.2 \pm 0.2	17.8 \pm 0.4	<5	42.7 \pm 1.2	61.7 \pm 7.1	56.6 \pm 5.2
L-MWCNT-4060-APS	34.9 \pm 0.7	17.1 \pm 1.2	45.3 \pm 0.3	<5	51.6 \pm 1.2	78.1 \pm 4.4	78.7 \pm 1.3
L-MWCNT-4060-HP	50.1 \pm 1.3	13.3 \pm 0.9	37.7 \pm 1.2	<20	63.0 \pm 2.9	100.0 \pm 1.4	79.6 \pm 4.1
L-MWCNT-4060-NA	48.7 \pm 0.1	6.6 \pm 0.4	20.7 \pm 0.1	<5	38.5 \pm 0.2	50.1 \pm 0.1	50.6 \pm 0.4
Dimensions of MWCNT ²							
L-MWCNT-1020-HP	38.0 \pm 3.2	5.5 \pm 0.4	18.7 \pm 1.4	<5	52.9 \pm 0.6	41.7 \pm 1.7	69.7 \pm 2.4
L-MWCNT-1030-HP	56.0 \pm 2.0	7.4 \pm 0.7	18.8 \pm 2.6	<5	58.1 \pm 2.7	61.9 \pm 2.4	79.6 \pm 2.9
L-MWCNT-2040-HP	53.4 \pm 3.6	4.6 \pm 0.1	15.7 \pm 1.7	<5	64.6 \pm 2.9	58.7 \pm 2.2	71.6 \pm 2.8
L-MWCNT-4060-HP	50.1 \pm 2.1	27.7 \pm 1.3	64.3 \pm 1.9	<20	78.5 \pm 3.8	91.7 \pm 3.9	106.1 \pm 3.9
L-MWCNT-60100-HP	17.8 \pm 2.0	9.4 \pm 1.0	18.6 \pm 1.1	<5	28.8 \pm 1.8	44.4 \pm 4.5	56.1 \pm 2.4
S-MWCNT-4060-HP	29.7 \pm 1.3	<5	7.7 \pm 0.6	<5	17.2 \pm 1.1	<5	<5
pH of water sample ³							
1	50.2 \pm 2.3	20.8 \pm 1.0	35.9 \pm 0.5	5.7 \pm 0.6	54.7 \pm 1.2	56.1 \pm 2.1	52.3 \pm 2.2
3	52.2 \pm 0.6	15.5 \pm 1.6	42.5 \pm 1.4	<5	60.6 \pm 1.1	62.1 \pm 2.2	59.4 \pm 2.0
5	53.5 \pm 2.4	12.2 \pm 1.0	34.0 \pm 0.9	<5	67.6 \pm 1.3	65.6 \pm 1.8	72.3 \pm 1.8
6.5	63.9 \pm 3.9	11.7 \pm 1.0	63.9 \pm 0.7	<20	90.6 \pm 2.4	91.7 \pm 2.1	84.1 \pm 0.7
9	52.8 \pm 3.9	19.2 \pm 0.2	52.2 \pm 1.6	<5	76.0 \pm 5.9	87.5 \pm 3.7	84.8 \pm 3.1
Flow rate ⁴							
Low	75.5 \pm 3.1	17.9 \pm 1.7	58.5 \pm 2.9	<20	63.0 \pm 2.9	90.9 \pm 6.4	91.8 \pm 6.8
Moderate	50.6 \pm 2.7	24.2 \pm 1.4	65.5 \pm 1.0	<5	47.5 \pm 4.4	78.5 \pm 3.4	77.9 \pm 6.3
High	45.0 \pm 4.2	16.6 \pm 0.3	24.2 \pm 1.5	<5	29.1 \pm 1.5	36.7 \pm 0.4	50.7 \pm 3.4
Mass of adsorbent ⁵ , mg							
100	21.7 \pm 2.4	46.8 \pm 3.5	76.0 \pm 1.6	22.4 \pm 0.4	45.8 \pm 2.2	89.0 \pm 8.6	81.3 \pm 2.9
200	63.3 \pm 4.7	12.3 \pm 1.2	30.8 \pm 1.9	17.8 \pm 1.3	45.0 \pm 1.1	81.2 \pm 7.1	73.2 \pm 2.5
300	78.9 \pm 1.6	7.4 \pm 0.8	11.3 \pm 1.2	<5	37.6 \pm 2.0	66.2 \pm 7.4	41.4 \pm 3.2

¹200 mg sorbent; loading 50 mL water sample (pH = 6.5, 100 $\mu\text{g L}^{-1}$ of each phenol simultaneously) at low flow rate.²200 mg sorbent; loading 50 mL water sample (pH = 6.5, 100 $\mu\text{g L}^{-1}$ of each phenol simultaneously) at low flow rate.³200 mg of L-MWCNT-4060-HP as sorbent; loading 50 mL of water sample (pH = 6.5, 100 $\mu\text{g L}^{-1}$ of each phenol simultaneously) at low flow rate.⁴200 mg of L-MWCNT-4060-HP as sorbent; loading 50 mL of water sample (pH = 6.5, 100 $\mu\text{g L}^{-1}$ of each phenol simultaneously).⁵L-MWCNT-4060-HP sorbent; loading 50 mL of water sample (pH = 6.5, 100 $\mu\text{g L}^{-1}$ of each phenol simultaneously) at low flow rate.

more polar surface oxides, which offer more polar-polar and ion exchange type interaction with phenols. This will enhance sorption of more polar phenolic compounds. On the other hand, for sorption controlled by hydrophobic interactions, the increased functional groups would decrease the accessibility and affinity of CNTs for organic chemicals, due to formation of water clusters on the formed surface oxides. Thus equilibrium sorption of 2-CP and 2,4-DNP may be mainly governed by H-bonding, while equilibrium sorption of 3-CP, 4-CP, Ph, 2-NP and 4-NP may be mainly governed by hydrophobic interaction.

3.1.3 Effect of dimensions of the MWCNTs on sorption capacity

From Tables 1 to 3, with some exceptions, a general decrease in the sorption capacity was observed with increasing external diameter of MWCNT. This may indicate that the sorption of the phenolic compounds occurs mainly on the external graphene sheets since more external surface area is available with smaller external diameter. Thus MWCNTs of larger external diameter will provide smaller surface area and thus adsorption decrease. Furthermore, almost all the phenolic compounds exhibited higher sorption capacity towards L-MWCNT-4060 than that towards S-MWCNT-4060. This is probably attributed to more grooves and interstitial adsorption sites with long MWCNT. This indicates that although the surface chemistry of MWCNT plays an important role in the sorption process of phenols, dimensions also play an important role in retention of the sorbed molecules.

3.1.4 Effect of sorbate acidity (K_a) on sorption

From Table 1, it is clear that the extraction power (K_D) and sorption capacity (K_F) of the MWCNT sorbents towards various chlorinated phenols are in the order: Ph < 4-CP < 3-CP < 2-CP. This is exactly the same order of increasing acidity of the respective phenols (pK_a : 9.89, 9.20, 8.80, 8.50, respectively). A similar trend of increasing K_D values with increasing acidity of nitrophenols is evident too; order of K_D (Ph \approx 2-NP < 4-NP < 2,4-DNP) is the same order of increasing acidity (pK_a values are 9.89, 7.17, 7.15, 4.96, respectively). Phenols of higher acidity are attracted more to the MWCNT surface which may indicate that their oxidation generated more polar carboxylic, phenolic and lactonic functional groups that play a significant role in the sorption of the more hydrophilic nitro derivatives of phenol. 2-NP gave the lowest values of K_D probably due to the intramolecular hydrogen bonding between the phenolic hydrogen and the oxygen of the nitro substituent in the ortho position. This makes the phenolic proton of 2-NP less available for interaction with the functional groups of the MWCNT surface.

It is noted that K_D values of nitrophenols are lower than those of chlorophenols, probably because hydrophobic interaction of the benzene ring in these phenols with the MWCNTs is more pronounced than the hydrophilic dipole-dipole interaction or hydrogen bonding typical with nitrophenols.

3.2 SPE of phenols from water: Column (cartridge) experiments

While the study in 'Section 3.1' was an equilibrium sorption process, the study in this section is a kinetic sorption process. Furthermore the sorption process (loading the water sample) in SPE is followed by an elution (desorption) step. Another note is that while equilibrium sorption experiments use high analyte concentrations (10–90 mg L⁻¹),

kinetically controlled SPE experiments uses much lower concentrations ($100 \mu\text{g L}^{-1}$). Therefore some of the results from both sections may not be consistent with each other, while other results may support each other.

3.2.1 Effect of sorbent oxidation

Three types of oxidized MWCNTs (L-MWCNT-4060-NA, L-MWCNT-4060-APS, and L-MWCNT-4060-HP) were used as solid extractants of the targeted phenols from water and compared with non-oxidized sorbent. The results are shown in Table 4. It is noted that oxidation of the MWCNT has generally enhanced the recovery of most phenols. The highest recoveries of most phenols was achieved by using hydrogen peroxide oxidized MWCNT (sorbent L-MWCNT-4060-HP). It is worth mentioning that this sorbent did not give the highest sorption capacity in the equilibrium sorption experiments (Section 3.1), but the process here is limited by kinetic factors, which may indicate that sorption reaches equilibrium very fast at low levels of concentrations. The highest recoveries were recorded for chloro-phenols while phenol and nitro-phenols gave low-to-moderate recoveries even with oxidized MWCNTs. This is in agreement with lower values of K_D and K_F of nitro-phenols relative to chloro-phenols (see Section 3.1 and Tables 1 to 3). Therefore, L-MWCNT-4060-HP was selected as the optimum oxidized sorbent in the proposed SPE optimum procedure. It seems that at low concentration of phenols, since oxidation of MWCNT increased the recovery, therefore the predominant retention force is H-bonding rather than hydrophobic interaction [14]. Another potential reason for the increased recovery of phenols could be that oxidation of MWCNT may lead to an increase in the sorptive area owing to dispersion of the agglomerated nanoparticles. Aggregates pores play an important role in the adsorption [33,34]. On the other hand, in the equilibrium sorption experiments (where high concentrations were used), hydrophobic interaction was predominant sorption mechanism in the compounds where oxidation of the MWCNT decreased K_F , while H-bonding was predominant in the compounds where oxidation of the MWCNT increased K_F .

3.2.2 Effect of dimensions of the MWCNTs

MWCNTs of specific dimensions (external diameter and length) may be more capable of capturing sorbate molecules inside the central tube or in the inter-layer-graphite sheets than MWCNT of other dimensions. In this section, SPE of phenols was applied using different MWCNTs (all oxidized with hydrogen peroxide) of various external diameters and length. Sorbents involved were: L-MWCNT-1020-HP, L-MWCNT-1030-HP, L-MWCNT-2040-HP, L-MWCNT-4060-HP, L-MWCNT-60100-HP and S-MWCNT-4060-HP. The results are shown in Table 4. It is noted that the highest recoveries for all the nitro-phenols and chloro-phenols were achieved with L-MWCNT-4060-HP. The highest recovery for Ph was achieved with L-MWCNT-1030-HP, which gave very close result to L-MWCNT-4060-HP. In the equilibrium sorption experiments (Section 3.1), there was an inverse proportionate between the external diameter and values of K_F , which indicated that sorption occurs on the central tube. This relationship was not observed here. Probably L-MWCNT-4060-HP is the most kinetically favoured sorbent which gave the fastest sorption of phenols. Otherwise oxidation of MWCNT with HP may have probably a synergetic effect with this MWCNT dimension, and thus the highest recovery was achieved. Low recoveries were recorded for short MWCNT (sorbent S-MWCNT-4060-HP). This agrees with the equilibrium sorption

experiments (Section 3.1). In a previous work [25], it was reported that S-MWCNT-4060-NA was the best sorbent for preconcentration of pesticides (propoxur, atrazine and methidathion). In another work [35], L-MWCNT-1030 was reported as the best preconcentration sorbent for metals. In this work, L-MWCNT-4060-HP was selected as the MWCNT sorbent of optimum dimensions in the proposed SPE method. This sorbent may have the optimum dimensions that suits well the molecular dimensions of the studied phenols. However the situation is not that easy because sorption may take place inside the inner-graphite sheets of the CNT or on the outer surface the CNT. Furthermore the surface chemistry has an important role in the sorption process.

3.2.3 *Effect of water sample pH*

The pH of water sample is an important parameter that affects SPE of phenols because these phenols are weak acids. Based on pK_a values of phenols, changing the pH of the sample may cause deprotonation of the phenolic groups and the functional groups on the MWCNT surface. Therefore changing the pH of the sample solution may affect the extraction efficiency of phenols. Since these phenols have different pK_a , therefore different effects of pH of the sample may be observed for different phenols.

A set of experiments were carried out to investigate the influence of sample pH over the pH range of 1.0 to 9.0. The results are shown in Table 4. It is clear that highest recoveries of most of the phenols were achieved at pH 6.5 where the phenols and the surface functional groups are present in the protonated form. This will facilitate H-bonding between the surface and the neutral phenols.

Slightly lower recoveries were obtained in solutions adjusted to pH 9.0, owing to repulsion between negatively charged phenolate anion and the deprotonated surface functional groups at this pH. Low recoveries were recorded for pH values 1.0–5.0 due to more competition by hydronium ions for the active surface sites. Therefore pH 6.5 was selected as the optimum pH in the proposed SPE method.

3.2.4 *Optimization of other SPE parameters*

Effect of sample flow rate

Flow rate of sample solution is an important parameter in SPE system, mainly to improve the analytical speed without a decrease in recovery. Therefore, the effect of the flow rate of sample solution was examined as described in Section 2.2, where low flow rate was 3 mL min^{-1} ; moderate flow rate was 20 mL min^{-1} ; and high flow rate was 60 mL min^{-1} . The results are shown in Table 4. The highest recoveries for phenol and chloro-phenols were recorded when low sample flow rate was used; this is obviously due to the longer contact time between the phenols and the sorbent. Nitro-phenols gave low recoveries even at low flow rates. Therefore it was decided to select the low flow rate in the proposed SPE optimum method.

Effect of mass of sorbent

In SPE, it is preferred to use the minimum mass of adsorbent that is sufficient to completely sorb the analytes, and to allow desorption of the retained analytes with the minimum volume of eluent. For this reason, SPE experiments with various sorbent masses were executed to find the optimum mass. The results are shown in Table 4. It is noted that the highest recovery was achieved when 100 mg of sorbent. For phenol, recovery is directly proportional to the mass of adsorbent. This is probably owing to easier elution of Ph with

Table 5. Optimization of other parameters of the SPE procedure of phenols from aqueous medium using column (cartridge) experiments. Loading, at low flow rate, 50 mL of water sample (however see note 5) of pH 5.6, spiked with 100 μg of each phenol (simultaneously) through 100 mg of L-MWCNT-4060-HP sorbent.

	Recovery, % ($\pm\%$ RSD)						
	Ph	4-NP	2-NP	2,4-DNP	2-CP	4-CP	3-CP
Washing solvent type ¹ , %ACN in water							
5	50.7 \pm 1.0	26.1 \pm 1.9	42.0 \pm 2.1	22.4 \pm 0.1	61.5 \pm 2.1	70.5 \pm 3.2	91.3 \pm 6.2
10	65.0 \pm 4.2	40.5 \pm 2.8	72.5 \pm 5.1	25.4 \pm 1.2	99.6 \pm 3.4	99.9 \pm 2.4	100.4 \pm 1.6
15	46.4 \pm 3.6	25.9 \pm 0.5	55.9 \pm 2.2	9.3 \pm 1.3	56.9 \pm 3.2	56.3 \pm 2.4	84.8 \pm 3.1
Washing solvent volume ² , mL of 5% ACN in water							
5	69.4 \pm 6.5	36.6 \pm 6.1	61.8 \pm 1.1	22.4 \pm 1.3	99.0 \pm 2.3	101.3 \pm 8.8	96.5 \pm 7.4
10	31.3 \pm 2.1	34.1 \pm 1.5	33.1 \pm 2.9	9.5 \pm 2.0	55.2 \pm 4.3	65.6 \pm 2.7	72.2 \pm 2.5
15	15.4 \pm 0.8	16.2 \pm 1.3	30.2 \pm 2.2	11.2 \pm 0.9	57.7 \pm 2.2	65.3 \pm 2.7	64.4 \pm 2.5
Eluting solvent type ³							
Acetonitrile (ACN)	62.0 \pm 2.3	24.6 \pm 0.7	33.5 \pm 2.5	25.4 \pm 1.1	77.4 \pm 5.5	96.2 \pm 1.1	85.3 \pm 2.8
Methanol	54.1 \pm 4.3	13.6 \pm 2.3	12.9 \pm 0.6	7.8 \pm 0.6	46.7 \pm 3.1	54.7 \pm 2.2	51.7 \pm 3.4
Eluting solvent volume ⁴ , mL							
1	7.1 \pm 0.8	7.9 \pm 1.5	9.7 \pm 1.9	7.5 \pm 0.6	18.3 \pm 1.1	23.6 \pm 1.0	19.0 \pm 0.7
2	22.0 \pm 2.2	8.3 \pm 0.1	10.7 \pm 0.5	7.1 \pm 0.7	55.7 \pm 7.4	64.0 \pm 2.7	72.9 \pm 3.2
3	51.5 \pm 4.6	21.3 \pm 1.8	34.2 \pm 1.3	27.0 \pm 0.5	91.7 \pm 1.7	96.9 \pm 1.7	94.4 \pm 1.3
4	56.3 \pm 5.5	21.8 \pm 1.1	31.4 \pm 1.4	7.9 \pm 0.7	98.7 \pm 1.0	98.3 \pm 4.0	96.5 \pm 8.4
5	62.8 \pm 3.4	24.9 \pm 1.3	55.9 \pm 3.7	25.4 \pm 0.2	92.5 \pm 5.3	99.1 \pm 6.3	94.7 \pm 7.4
6	62.0 \pm 2.1	24.4 \pm 1.2	35.5 \pm 1.5	5.9 \pm 0.4	89.0 \pm 2.2	92.9 \pm 3.4	101.8 \pm 5.2
Water sample volume ⁵ , mL							
20	60.2 \pm 1.1	61.6 \pm 1.4	63.1 \pm 3.1	25.0 \pm 2.2	102.6 \pm 4.6	102.0 \pm 2.1	101.7 \pm 4.1
30	61.6 \pm 2.0	57.1 \pm 3.7	70.4 \pm 1.6	26.4 \pm 2.3	99.7 \pm 1.2	97.8 \pm 4.6	93.1 \pm 3.9
50	49.5 \pm 1.0	50.5 \pm 4.5	72.3 \pm 1.8	27.0 \pm 0.2	96.2 \pm 1.0	95.5 \pm 1.1	100.3 \pm 1.5
70	52.8 \pm 3.4	55.1 \pm 2.2	72.0 \pm 5.4	25.3 \pm 0.8	94.1 \pm 5.8	91.1 \pm 6.8	90.2 \pm 5.0
90	13.9 \pm 1.4	18.9 \pm 1.3	26.7 \pm 0.1	11.3 \pm 0.6	32.3 \pm 1.4	43.8 \pm 1.8	43.5 \pm 3.4

¹washing with 5 mL of washing solvent; elution with 5 mL of ACN.

²washing with 5% ACN aqueous solution; elution with 5 mL of ACN.

³washing with 5 mL of 10% ACN aqueous solution; elution with 5 mL eluting solvent.

⁴washing with 5 mL of 10% ACN aqueous solution.

⁵Variable loading water sample volume washing with 5 mL of 10% ACN aqueous solution; elution with 3 mL of ACN.

limited amount of acetonitrile, while more strongly sorbed chloro- and nitro- phenols need more acetonitrile to be eluted with increasing mass of sorbent. It was decided to select 100 mg sorbent as the optimum mass of the sorbent in the proposed SPE procedure.

Effect of washing solvent

Washing solvent is applied in SPE procedure to remove co-adsorbed matrix materials from the adsorbent without affecting analytes recovery. Washing solvents of various compositions (5, 10 and 15% acetonitrile aqueous solutions) were tested. From Table 5, it was found that 10% acetonitrile in water gave the highest recovery; at higher percentages of acetonitrile, the recovery started to decline due to elution of phenols with the washing solvent. Thus it was decided to select 5 mL of 10% acetonitrile aqueous solution as the optimum washing solvent in the proposed SPE procedure.

Effect of eluting solvent

Different elution efficiencies would be obtained when different eluting solvents are used because of the physical and chemical properties of the involved organic solvents and the characteristics of the sorbents and analytes in the cartridge. The effect of eluting solvent type (acetonitrile or methanol) is shown in Table 5. It is evident that acetonitrile gave better elution performance for the seven phenols than methanol. Therefore, it was selected for subsequent optimization steps.

In the elution step, it is necessary to elute all the retained analytes with minimum volume to get the highest enrichment factor. A series of experiments were executed to obtain the proper volume without loss of extraction efficiency: 1, 2, 3, 4, 5, and 6 mL of acetonitrile were tested. The effect of eluting solvent volume is shown in Table 5. It is noted that 3 mL of acetonitrile was enough to maintain high recovery for most phenols. So that it was considered the optimum volume of eluate.

Effect of water sample volume: Breakthrough volume

Volume of the loaded sample has a proportional effect on enrichment factor. Various volumes of samples were tested. The results are shown in Table 5. Taking into consideration that we want high recovery and high enrichment factor; 70 mL was selected as an appropriate water sample volume above which the recovery of phenols was significantly decreased.

3.2.5 Analytical performance of the method

In order to evaluate the analytical performance of the method, analytical parameters such as linear range, detection limit, accuracy, and precision should be evaluated. For that purpose, purified distilled water was spiked with the seven targeted phenols simultaneously with the following concentrations: 10, 25, 37.5, 50, 62.5, 75, 87.5, and 100 $\mu\text{g L}^{-1}$; the proposed SPE procedure was then applied ($n=4$). The linearity of the calibration curve of each phenol was determined by plotting the average peak area against the concentration of each phenol. The linearity was estimated based on R^2 value of the calibration curve. The detection limits were estimated as three times the standard deviation of the blank signal. Accuracy of the methods was estimated based on the % relative error and the precision of the method was estimated based on the %RSD of replicate samples.

A typical chromatogram from the SPE of spiked distilled water is shown in Figure 2(a). The analytical figures of merit of the method are shown in Table 6. The method was linear within the studied range (10-100 $\mu\text{g L}^{-1}$) for 2-CP, 3-CP and 4-CP; but it was linear up to 75 $\mu\text{g L}^{-1}$ for Ph and 4-NP; and up to 62.5 $\mu\text{g L}^{-1}$ for 2-NP and 2,4-DNP. The method showed high relative errors for Ph, 2-NP, 4-NP and 2,4-DNP; but it showed an excellent accuracy towards 2-CP, 3-CP and 4-CP confirmed by a low relative error range (-15.5 to +6.2%) for the three chloro-phenols. Detection limits for all the studied phenols ranged between 27.4-202.2 ng L^{-1} . Some detection limits reported in other works are presented in Table 6. It is noted that the detection limits for 3-CP and 4-CP reported in our work are slightly lower than those reported by Cai *et al.* [16]. On the other hand, our method gave detection limits for Ph, 2-NP, 4-NP and 2,4-DNP much lower than those reported by Liu *et al.* [18] and Penalver *et al.* [36]. The precision of the method was acceptable as indicated by the %RSD range (0.4-11.0%) for all the studied phenols; while the %RSD range for chloro-phenols was 0.4 to 8.1%.

Table 6. Analytical performance of the proposed SPE optimum method for the determination of phenols ($n=4$) and comparison with other methods.

	Limit of linearity ($\mu\text{g L}^{-1}$)	R^2	LOD (ng mL^{-1})	%RSD range, %	Sensitivity, (peak are/ ($\mu\text{g L}^{-1}$))	LOD [18]* (ng mL^{-1})	LOD [35]* (ng mL^{-1})	LOD [16]* (ng mL^{-1})
<i>Ph</i>	75	0.9964	0.202	3.0–11	850	3.67	23	–
<i>2-CP</i>	100	0.9911	0.048	0.4–7.4	3607	–	–	–
<i>3-CP</i>	100	0.9966	0.066	0.5–8.1	2606	–	–	0.10
<i>4-CP</i>	100	0.9911	0.089	1.3–4.7	1930	–	–	0.08
<i>2-NP</i>	62.5	0.9927	0.027	1.9–7.5	6269	0.67	1.6	–
<i>4-NP</i>	75	0.9812	0.073	1.8–9.5	2369	0.25	3.6	–
<i>2,4-DNP</i>	62.5	0.9858	0.095	2.3–6.8	1806	0.65	4.1	–

*from previous studies.

Based on the above discussion, it is clear that the proposed SPE method is capable of accurate determination of chloro-phenols; but less accurate for the determination of nitro-phenols and Ph. Improving the recovery of Ph may be achieved if higher mass of sorbent is used (see 'Effect of the mass of the adsorbent' (Section 3.2.4)). On the other hand, improvement of the recovery of 2-NP and 4-NP may be achieved by moderation of sample flow rate. The use of higher sorbent mass and higher sample flow rate was not considered since this would decrease the recovery of chloro-phenols (2-CP, 3-CP and 4-CP).

3.2.6 Application of the method on real water samples

To validate the applicability and reliability of the proposed method for environmental use, the optimum method was applied on three unspiked environmental water samples (tap water, reservoir water and stream water). None of the phenols were found. Therefore, real water samples were spiked with two different concentrations: 10 and 25 ng mL^{-1} . All experiments were performed in five replicates ($n=5$). Typical chromatograms are shown in Figures 2(b) to 2(g). The obtained recoveries are shown in Table 7. The recovery range for 2-CP, 3-CP and 4-CP was 84.3–100%; while the %RSD was in the range 2.8–9.2%. The recovery of Ph and nitro-phenols was in the range 28.4–67.6%. This clearly proves the suitability of the method for accurate determination of chloro-phenols, while the method was less accurate for determination of Ph and nitro-phenols.

The validity of the proposed method was checked by determination of the three chlorophenols using 500 mg/3 mL Hypersep C-18 cartridges (Thermo electron corporation) for SPE. The percent recoveries (\pm RSD) were 94.3(\pm 0.9) for 2-CP, 88.4(\pm 1.2) for 3-CP and 87.3(\pm 1.9) for 4-CP. These results compare favourably with those of the proposed method (Table 7).

4. Conclusions

Dimensions and oxidation of MWCNTs have a touchable effect on SPE and adsorption of organic pollutants from water samples. By proper optimization of these two parameters, some pollutants rather than others may be selectively extracted from water.

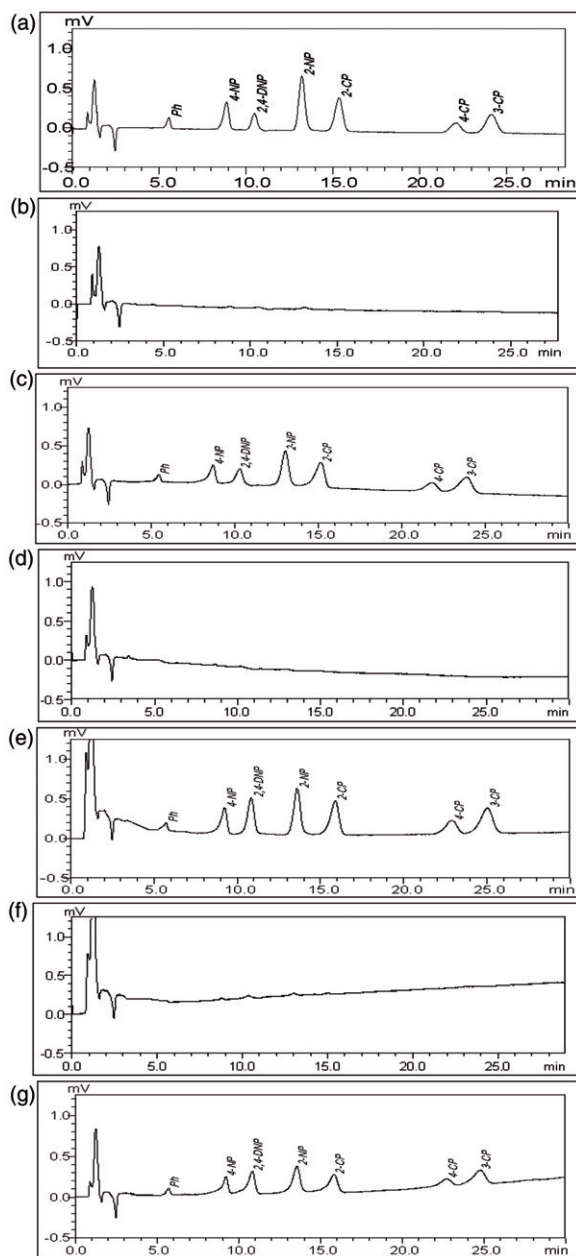


Figure 2. Chromatograms for phenols using L-MWCNT-4060-HP sorbent according to the proposed SPE method. (a) spiked distilled water ($50 \mu\text{g L}^{-1}$), (b) unspiked tap water, (c) spiked tap water ($25 \mu\text{g L}^{-1}$), (d) unspiked reservoir water, (e) spiked reservoir water ($25 \mu\text{g L}^{-1}$), (f) unspiked stream water, (g) spiked stream water ($25 \mu\text{g L}^{-1}$).

Table 7. Recovery of the seven targeted phenols from real water samples after application of the proposed optimum method ($n = 5$).

Added concentration, $\mu\text{g L}^{-1}$	Recovery, % ($\pm\%$ RSD)		
	Tap water	Reservoir water	Stream water
Ph			
10	40.75 ± 9.7	45.05 ± 6.7	29.6 ± 10.9
25	42.00 ± 9.9	48.55 ± 6.4	29.3 ± 8.7
2-CP			
10	94.5 ± 5.8	94.2 ± 3.8	84.3 ± 9.2
25	96.8 ± 4.4	89.2 ± 4.1	95.3 ± 2.8
3-CP			
10	97.5 ± 6.9	98.4 ± 4.0	92.2 ± 3.2
25	97.3 ± 3.5	93.4 ± 2.8	92.9 ± 3.4
4-CP			
10	100.0 ± 4.4	93.7 ± 2.9	90.1 ± 3.1
25	95.1 ± 4.6	87.8 ± 7.1	89.4 ± 3.9
2-NP			
10	49.7 ± 6.9	63.5 ± 3.9	43.7 ± 6.2
25	67.6 ± 3.9	60.1 ± 3.6	41.4 ± 3.5
4-NP			
10	55.8 ± 8.2	57.4 ± 5.3	43.5 ± 5.2
25	53.7 ± 6.5	52.3 ± 5.4	43.5 ± 4.7
2,4-DNP			
10	28.5 ± 11.5	31.5 ± 5.9	28.4 ± 9.3
25	33.9 ± 9.8	26.9 ± 8.8	34.9 ± 3.5

The following conclusions may be drawn from our results:

- (1) There is a general inverse relation between the external diameter of MWCNTs and their sorption capacity for phenolic compounds. Furthermore, long MWCNTs showed higher sorption capacity than short MWCNTs.
- (2) Oxidation of MWCNTs caused a decrease in sorption capacity of phenolic compounds of lower acidity, but an increase in sorption capacity for phenolic compounds with relatively higher acidity. This shows the important role of oxidation-generated functional groups in the sorption process.
- (3) Equilibrium sorption data (distribution isotherms) of the targeted phenols on MWCNTs of various dimensions (raw or oxidized) indicated that Freundlich Isotherm Model is generally obeyed except for 2-nitrophenol where Langmuir Isotherm Model was obeyed. This is probably attributable to the presence of intra-hydrogen bonding in this phenol derivative.
- (4) Oxidation of MWCNTs (5–15 μm long, 40–60 nm external diameter) with hydrogen peroxide increased recoveries in SPE of phenols from water as compared with un-oxidized MWCNTs. Hydrogen bonding seems to be a predominant mechanism for SPE of trace level phenolic compounds.

- (5) Optimization of different variables in SPE of phenolic compounds from water revealed that oxidized MWCNTs could be used for accurate and precise determination of 2, 3 and 4-chloro phenols in real water samples with a low LOD of 0.027-0.202 ng mL⁻¹. SPE of phenol and nitrophenols are less quantitative with recoveries in the range of 20 to 67%

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