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Evaluation of different carbon materials in adsorption and solid-phase microextraction of 2,4,6-trichlorophenol from water

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ABSTRACT

The adsorption process of 2,4,6-trichlorophenol (TCP) by carbonaceous materials, such as Carbopack B graphitized carbon black, Vulcan XC72 carbon black and two kinds of multi-walled carbon nanotubes, have been studied. The adsorption kinetics was best represented by the pseudo-second order kinetic model. Adsorption took place in accordance with the Freundlich equation. The materials were used to prepare novel, solid-phase microextraction (SPME) fibers. The efficiency of the fibers was evaluated using a gas chromatograph with an atomic emission detector for the extraction of TCP from the headspace of aqueous samples. Both the carbon nanotubes and carbon blacks coated fibers were of higher quality than commercially available fibers prepared from polydimethylsiloxane and polyacrylate. The results proved the ability of the proposed SPME fibers to detect TCP in water.

Keywords: Adsorption; Solid-phase microextraction (SPME); Multi-walled carbon nanotubes (MWCNT); Carbon black; 2,4,6-Trichlorophenol

1. Introduction

Phenols, as well as their chlorinated derivatives – chlorophenols, are common water contaminants generated by inter alia petrochemical, pharmaceutical, paper and pesticide producing industries [1]. In general, they are persistent pollutants and are proven to do great harm to the environment. Their typical representative is 2,4,6-trichlorophenol (TCP), which has been recognized as a toxic, mutagenic and carcinogenic compound. It is also very harmful to aquatic life if it is discharged into rivers, lakes and seas. Thus, the detection, determination and removal of TCP from the environment are very crucial [2].

Many techniques (physical and chemical) have been used for the removal of organic contaminants, including chlorophenols, in water treatment. Among them, adsorption has proved to be one of the most attractive and most popular techniques. Adsorption is favored for its flexibility, simplicity of design, universal application, high efficiency and remediation of organic and inorganic compounds, even at low concentrations. The most popular and widely used adsorptive material is activated carbon [3–6]. In recent years, as an adsorbent for the removal of chlorophenols from water, carbon nanotubes (CNTs) [7–13] have also been studied.

The adsorption process plays a very important role not only in the removal of organic compounds from water but also in the preparation of real samples for quantitative analysis, for example, in solid phase extraction (SPE). SPE is a cost-effective sample preparation technique used for analyte concentration and sample cleanup (removal of interferences from complex matrices). Quite a specific type of SPE is solid phase microextraction (SPME), a solvent-free sample preparation technique [14] in which the extracting phase is usually a solid adsorbent, typically of a high porosity, to increase the surface area available for adsorption. The analytes are

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adsorbed and/or absorbed (depending on the nature of the coating) by the fiber phase until an equilibrium is reached in the system. In comparison to standard sample preparation techniques, SPME provides many advantages, including its speed, simplicity and ease of operation; moreover, it combines sampling and sample preparation into one step and can be coupled with separation techniques (e.g., gas chromatography) [15]. Commercially available fibers seem to be responsible for some drawbacks, such as low thermal and chemical stability, the stripping of coating and short lifetime [16]. Carbon materials have long been used as adsorbents for trapping or separation of organic compounds [17–20]. In SPME, carbon materials, such as polycrystalline graphite [21], glassy carbon [22], activated carbon [23,24], fullerene [25], graphene [26,27], carbon black [24] and CNTs [28–31], have been successfully used as SPME fibers.

In this study, the adsorption of TCP from aqueous solutions on various carbonaceous materials was studied. New SPME fibers coated with these carbon materials and their efficiencies for the extraction of TCP from water were also evaluated. The Carbopack B graphitized carbon black, Vulcan XC72 carbon black and two kinds of multi-walled CNTs (non-modified and OH functionalized) were chosen because of their similar specific surface area.

2. Experimental

2.1. Chemicals and apparatus

All the chemicals used were of analytical grade, and deionized water (18.2 MΩ/cm) was used for the preparation of the aqueous solution.

The short, MWCNT and short, hydroxyl multi-walled carbon nanotubes (MWCNT-OH) were obtained from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences (Chengdu, China). The Vulcan XC72 carbon black was purchased from Cabot Corporation (Boston, USA), while the Carbopack B graphitized carbon black was from Sigma-Aldrich (Steinheim, Germany). Commercial 100 µm polydimethylsiloxane (PDMS) and 85 µm polyacrylate (PA) fiber for comparative purpose and SPME holder were purchased from Supelco (Bellefonte, USA).

The morphology of the prepared SPME sorptive coatings was examined by scanning electron microscopy (SEM). A Quanta 3D FEG Dual Beam SEM (DB FEI Company, Hillsboro, USA) was used for the analyses. Nitrogen adsorption–desorption isotherms were obtained using ASAP 2010 (Micromeritics, Norcross, USA) at 77.4 K. The Brunauer–Emmett–Teller (BET) equation was used to calculate specific surface areas of the materials. Water adsorption isotherms at 25°C were determined gravimetrically using a dynamic vapor sorption apparatus (DVS Advantage Surface Measurement Systems Ltd., London, UK).

2.2. Analytical methods

In the adsorption experiments, for determination of TCP, a high-performance liquid chromatography method with ultraviolet detection at 294 nm was used. The chromatographic measurements were carried out under isocratic conditions on a Phenomenex Luna C_{18}, 1.0 × 100 mm, 3 µm column (Torrance, USA). The mobile phase was a mixture of acetonitrile and water adjusted to pH 3.0 with acetic acid (50/50, v/v), and the flow rate was set at 0.15 mL/min.

An HP 6890 series gas chromatograph with an AED – atomic emission detector (Hewlett Packard, USA), equipped with a ZB 5 column (30 m × 0.32, 0.5 µm film thickness), was used to evaluate the SPME fibers. The carrier gas (helium) flow rate was set at 1 mL/min, the column was held at 70°C for 2 min and increased to 250°C at a rate of 10°C/min. The injector temperature (250°C) was carried out on a split ratio mode of 50:1. The GC-AED interface was maintained at 270°C.

2.3. Adsorption

All of the adsorption experiments were carried out in batch mode. For each experiment, 0.03 g of adsorbents and 20 mL of TCP solution were mixed in an Erlenmeyer flask, which was then shaken at 25°C at 200 rpm. After mixing, the solutions were filtered and analyzed by liquid chromatography.

The kinetic studies were conducted for initial concentration of TCP 0.2 mmol/L. The amount of compound adsorbed at time t, q_t (mmol/g) was calculated using the following equation:

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

where C_0 and C_t are the initial TCP concentration and concentration at time t (mmol/L), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

In adsorption isotherm studies, solutions with different initial TCP concentrations (0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 mmol/L) were prepared. The equilibrium time was set at 6 h. The uptake of the TCP at equilibrium, q_e (mmol/g), was calculated using the equation:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

where C_e is the equilibrium concentration of TCP (mmol/L) in the solution.

2.4. Solid phase microextraction

The SPME fibers were prepared with the use of sol-gel technology, as described elsewhere [24]. The coating process was repeated six times by using a freshly prepared sol solution each time. The prepared fibers were placed in a desiccator at room temperature for 24 h. Prior to use, the fibers were conditioned in a GC injection port at 250°C for 1 h. The extraction was done by exposing the fiber to the headspace over the sample (TCP concentration = 0.2 mmol/L) for a period of time at 25°C. After extraction, the fiber was withdrawn into the needle and subsequently inserted into the GC injector for desorption (10 min) and final analysis. A detailed headspace procedure has been described in a previously published paper [24]. All the experiments with prepared CNT and carbon black coated fibers were repeated by using commercial PDMS and PA fibers in order to compare the results.

3. Results and discussion

3.1. Characteristics of the carbon materials

The quality of the MWCNT, MWCNT-OH, Vulcan XC72 and Carbopack B samples used in this study was examined by N_2 adsorption-desorption analysis (Fig. 1). The specific surface areas (S_{BET}), as well as the total pore volumes (V_t) of the materials, were calculated and are presented in Table 1.

The water vapor adsorption isotherms of the carbonaceous materials are shown in Fig. 2. For estimation of the primary adsorption centers of the adsorbents, the Dubinin–Serpinsky equation [32] was used:

$$a = \frac{a_0 ch}{1 - ch} \tag{3}$$

which can be linearized to the form:

$$\frac{h}{a} = \frac{1}{a_0 c} - \frac{1}{a_0} h \tag{4}$$

where h is the equilibrium relative pressure (p/p_0), a is the adsorption (mmol/g), c is the equation constant equal to the ratio of the kinetic constants, and a_0 is the number of primary adsorption centers (mmol/g). The equation expresses the concave, steeply rising branch of the water adsorption isotherm. The plot of $h/a = f(h)$ should be linear in a range of 0.2–0.5 mmol/g, and the a_0 value can be determined from the slope of the curve. The calculated values of primary adsorption sites of the Carbopack B, Vulcan XC72, MWCNT and MWCNT-OH were 0, 0.546, 0.178 and 3.98 mmol/g, respectively. A higher value of the a_0 constant indicates a greater hydrophilicity of the surface.

Table 1
Textural properties of the carbon materials

Carbon material	S_{BET} (m^2/g)	V_t (cm^3/g)
Vulcan XC72	230	0.249
Carbopack B	98	0.583
MWCNT	181	0.703
MWCNT-OH	162	0.654

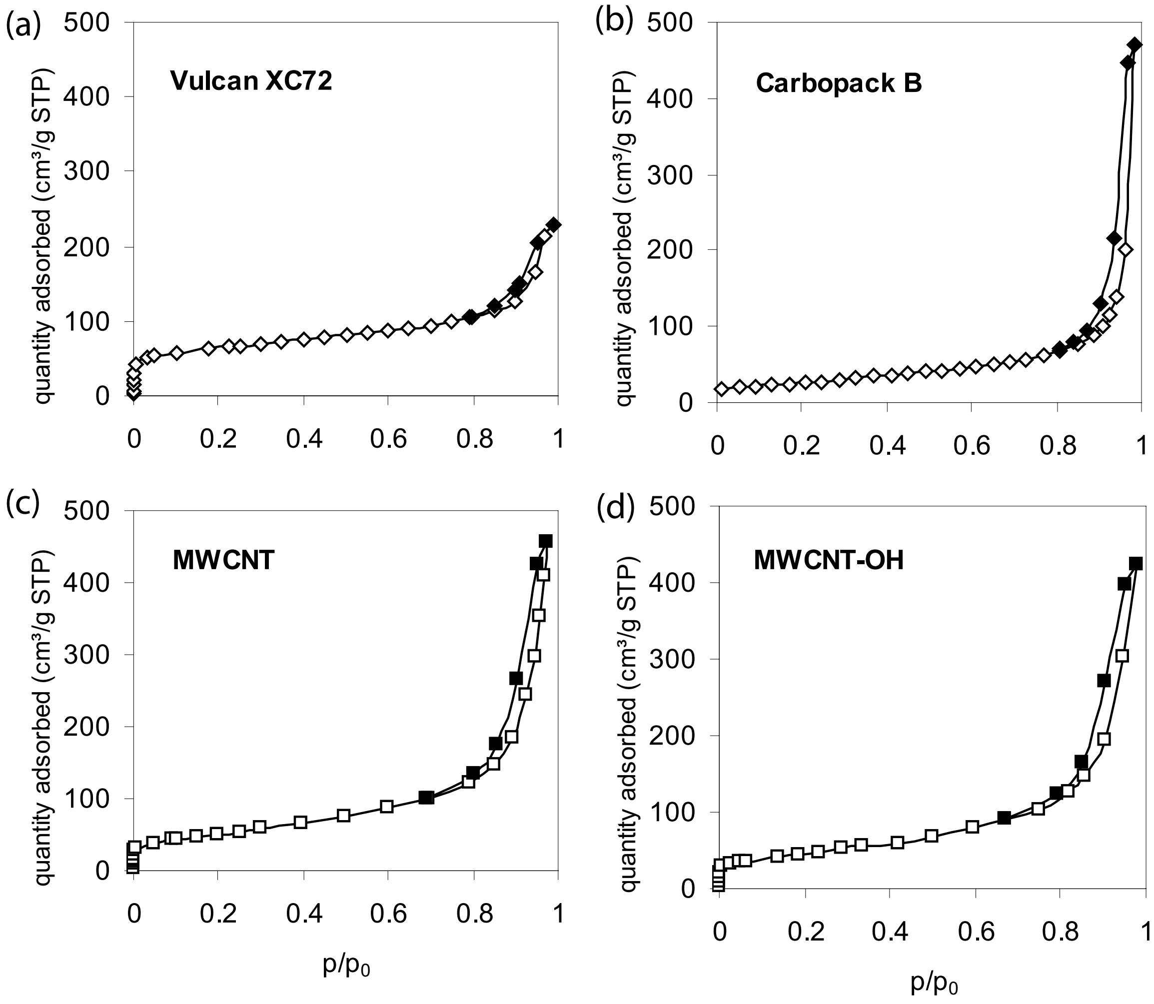

Fig. 1. Nitrogen adsorption–desorption isotherms for (a) Vulcan XC72, (b) Carbopack B, (c) MWCNT and (d) MWCNT-OH at 77.4 K.

The morphological structure of the new fibers was investigated using the scanning electron micrograph technique. Fig. 3 shows that the surface of the prepared coatings possessed a rough and porous structure. Moreover, it managed to obtain uniform coatings, which can provide a good binder between the coating and the surface of the fiber.

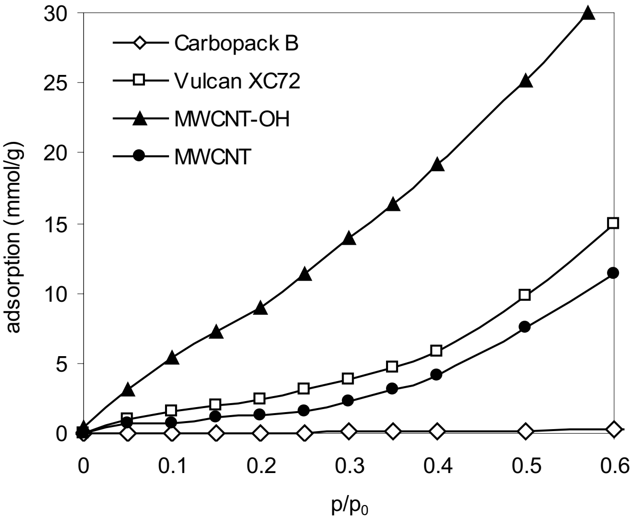

Fig. 2. Isotherms of water vapor adsorption on the carbonaceous materials.

3.2. Adsorption studies

3.2.1. Adsorption kinetics

Fig. 4 presents the adsorption kinetic curves of the TCP (plots of q_t as a function of time). Adsorption equilibriums were achieved after about 2–3 h for carbon blacks and after 1 h for CNTs. The kinetics of TCP adsorption on selected adsorbents was investigated using the pseudo-first order [33] (Eq. (5)) and the pseudo-second order [34] (Eq. (6)) model equations:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

where q_e and q_t are the amounts of adsorption at equilibrium and at time t, respectively, k_1 is the pseudo-first order rate constant (1/min), and k_2 is the pseudo-second order rate constant (g/mmol min).

The results are shown in Table 2. As can be seen, the pseudo-second order model provides a better fitting with

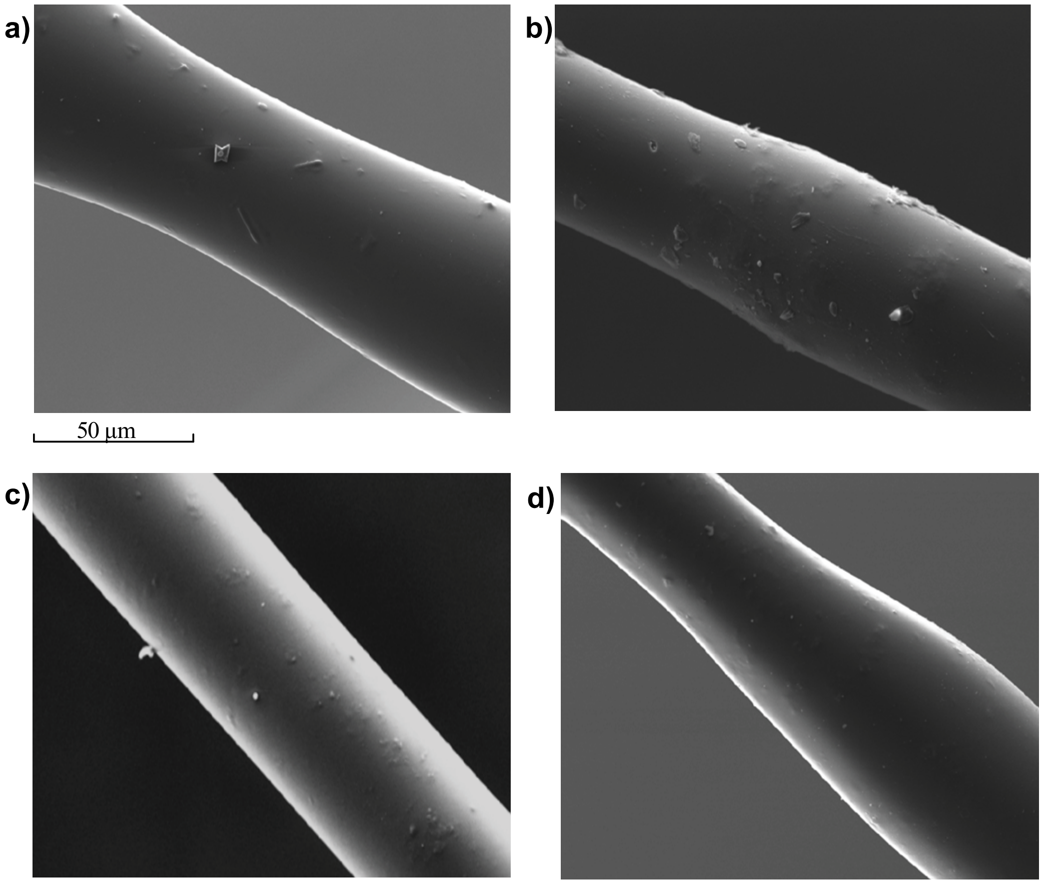

Fig. 3. SEM images of SPME fibers with coatings containing (a) Vulcan XC72, (b) Carbopack B, (c) MWCNT and (d) MWCNT-OH.

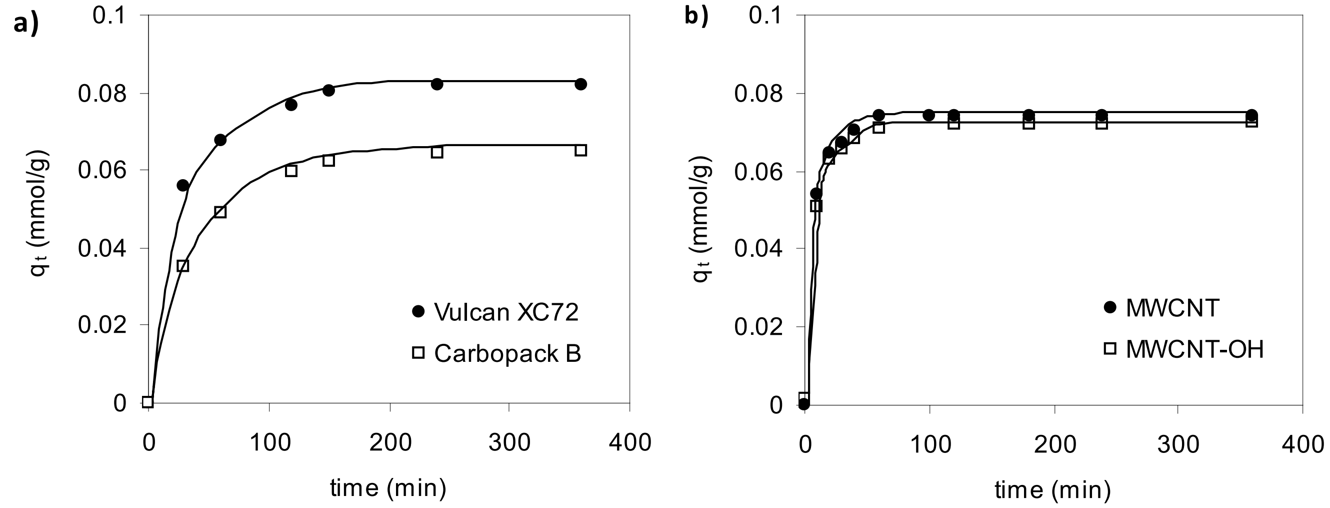

Fig. 4. Adsorption kinetics of TCP on (a) Vulcan XC72, Carbopack B, and (b) MWCNT, MWCNT-OH.

Table 2
Kinetic study of 2,4,6-TCP adsorption onto Vulcan XC72, Carbopack B, MWCNT and MWCNT-OH

Carbon material	Pseudo-first order		Pseudo-second order	
	k_1 (1/min)	R^2	k_2 (g/mmol min)	R^2
Vulcan XC72	0.0076	0.919	1.333	0.998
Carbopack B	0.0047	0.982	1.065	0.995
MWCNT	0.0123	0.925	6.812	0.999
MWCNT-OH	0.0155	0.966	6.323	0.999

high R^2 values (>0.99). This indicates that the adsorption system belongs to the second order kinetic model.

In order to gain insight into the mechanisms and rate controlling the steps affecting the kinetics of adsorption, the kinetic experimental results were fit to the Weber–Morris intra-particle diffusion model [35]:

$$q_t = k_i t^{0.5} + C_i \tag{7}$$

where k_i is the intra-particle diffusion rate constant (mmol/g min$^{-0.5}$), and C_i is the thickness of the boundary layer (mmol/g).

Fig. 5 shows the plot of q_t vs. $t^{0.5}$ for the TCP on all of the carbon materials. None of the lines passed through the origin; moreover, the plots were not linear over the entire time range. This indicates that the intra-particle diffusion was not the only rate-controlling step and that more than one process affected the adsorption of the TCP on all four of the carbon materials.

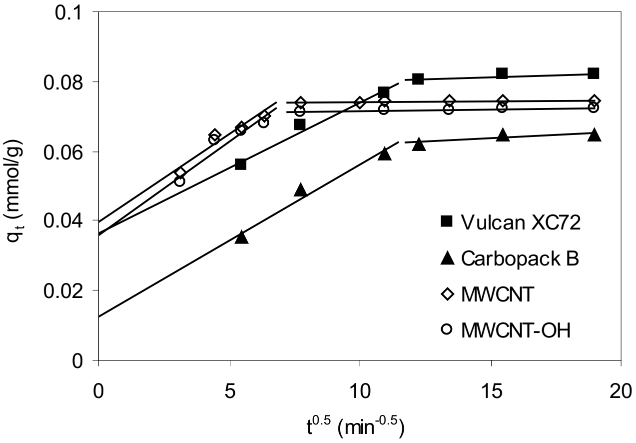

Fig. 5. Intra-particle diffusion plots for the TCP adsorption onto Vulcan XC72, Carbopack B, MWCNT and MWCNT-OH.

3.2.2. Adsorption isotherms

The experimental adsorption isotherms ($q_e = f(C_e)$) of TCP on Vulcan XC72, Carbopack B, MWCNT and MWCNT-OH from aqueous solutions are presented in Fig. 6. The Freundlich [36] and Langmuir [37] isotherm models were used to test the fitting of the experimental data. The linear form of the Freundlich isotherm is expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{8}$$

where K_F ((mmol/g) (L/mmol)$^{1/n}$) and n are the Freundlich constants related to sorption capacity and sorption intensity of the adsorbent, respectively. These constants were calculated from the intercept and slope of lnq_e vs. lnC_e plot.

The linear form of the Langmuir isotherm is described by the formula:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{9}$$

where q_m (mmol/g) is the maximum adsorption capacity, and b (L/mmol) is the constant related to the free energy of adsorption. In order to obtain the rate constants and

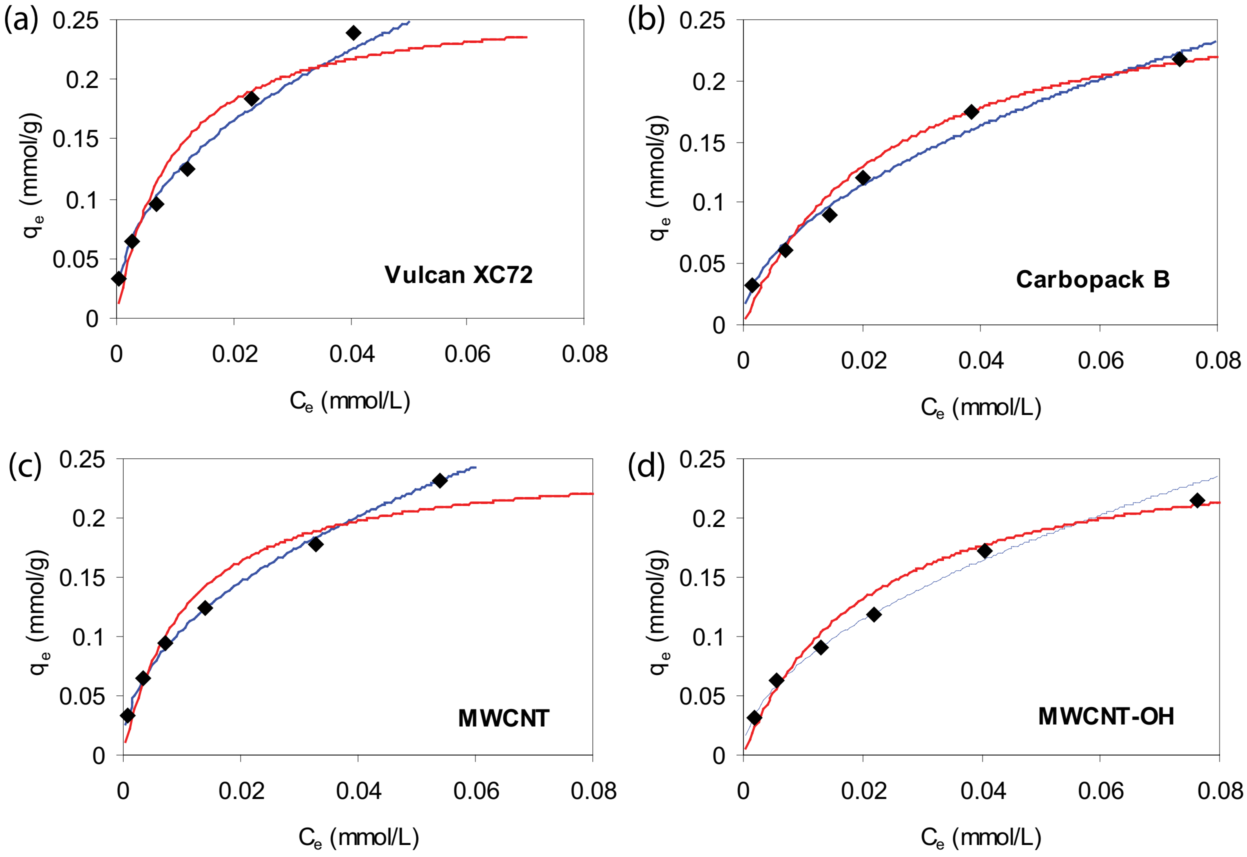

Fig. 6. Adsorption isotherms of TCP onto (a) Vulcan XC72, (b) Carbopack B, (c) MWCNT and (d) MWCNT-OH (blue line – Freundlich isotherm, red line – Langmuir isotherm).

correlation coefficients, the straight-line plots of C_e/q_e vs. C_e were tested, and the results are shown in Table 3.

A comparison of the R^2 values for the two mathematical models indicates that the Freundlich isotherm equation provides a better correlation of the experimental data for the adsorption of TCP than the Langmuir equation. The Langmuir model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies with no transmigration of adsorbate in the plane of the surface. The Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with a non-uniform distribution of energy level. The Freundlich equation describes reversible adsorption and is not restricted to the formation of a monolayer. The good fit obtained with the Freundlich model suggests that the adsorption of TCP onto all of the tested materials may involve multi-layer adsorption with interactions between the TCP molecules and the heterogeneous nature of the adsorbents' surface. The K_F values increased in the order Carbopack B < MWCNT-OH < MWCNT < Vulcan XC72. This suggests that the adsorption of chlorophenol is correlated with the specific surface area of the carbon materials. Adsorption of the TCP increases with increasing the adsorbent surface area S_{BET}. The mechanisms of adsorption TCP on the carbon materials used in this work have never been clearly defined. For example, some mechanisms have been proposed to interpret the adsorption of TCP on CNTs:

Table 3
Freundlich and Langmuir isotherm equation parameters and correlation coefficients R^2 for adsorption of 2,4,6-TCP onto Vulcan XC 72, Carbopack B, MWCNT and MWCNT-OH

Carbon material	Freundlich			Langmuir		
	K_F	n	R^2	q_m	b	R^2
Vulcan XC 72	0.940	2.247	0.985	0.271	9.08	0.946
Carbopack B	0.847	1.953	0.994	0.246	4.19	0.950
MWCNT	0.903	2.146	0.983	0.265	9.40	0.990
MWCNT-OH	0.881	1.912	0.993	0.259	4.76	0.968

- hydrogen-bonding interaction between –OH group of TCP and oxygen-containing groups on MWCNT;
- direct anion-π interaction between –OH and $–O^-$ (*n*-electron donor) groups of TCP and electron-depleted sites (π-electron acceptor) of CNTs;
- π–π electron donor–acceptor interaction between aromatic ring of chlorophenol and CNTs surface [38].

3.3. SPME studies

3.3.1. Determination of the extraction time

The objective of the SPME experiments, in principle, is to reach distribution equilibrium in the system. At this condition, the system is stationary, and therefore a variation of mass transfer does not affect the final results. The equilibration time is defined as the time after which the amount of extracted analyte remains constant and corresponds within the experimental error to the amount extracted at infinite extraction time [15]. Headspace sampling is commonly chosen to minimize the exposure of SPME fiber to the sample matrix and prolong the life of the fiber. Headspace SPME is an equilibrium process that involves the partitioning of analytes through a three-phase system: aqueous matrix, headspace and fiber coating [39]. Optimization of extraction time, which influences the partition of analytes, is extremely essential.

Fig. 7 shows extraction time dependence for TCP and six different SPME coatings (four prepared in this work and two commercial coatings for comparison). It is apparent that the extraction time profile depends on the individual stationary phase of coating. For the MWCNT and MWCNT-OH fiber, an equilibrium for the selected compound is already reached after 60 min. Much longer equilibrium times are necessary if the Vulcan XC72 and Carbopack B fibers are used.

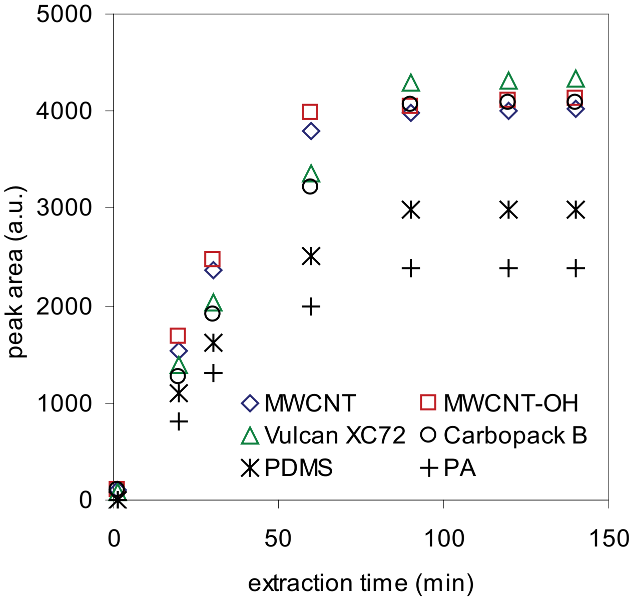

Fig. 7. Extraction time profile for TCP. Conditions: extraction temperature – 25°C; salt concentration – 0.05 mol/L Na_2SO_4; desorption temperature – 250°C; desorption time – 10 min.

3.3.2. Comparison of new fibers with PDMS and PA fibers

Commercial PDMS and PA fibers were selected for comparison with all new fibers developed in this study. The comparison of the extraction quantities of fiber under the optimal SPME conditions of each fiber is represented in Fig. 7. The results revealed that all the fibers prepared in this work have higher extraction efficiency than the commercial fibers. Fig. 8 shows a typical chromatogram obtained after HS-SPME-GC-AED determination of analyte in water under optimized extraction conditions. The fibers made from Vulcan XC72 and Carbopack B have the highest extraction efficiency. The surface area of the first material is the highest and results in a greater adsorption capacity than the other carbon materials. The properties of Carbopack B make it a slightly better SPME modifier, although it has less surface area than CNTs. The adsorption capacity of TCP onto MWCNT-OH and raw MWCNT is very similar. This is probably due to the fact that there were many oxygen-containing groups attached to the surface of MWCNT-OH, which made them become more hydrophilic and suitable for adsorption of relatively polar molecules. The CNTs are also insoluble in any organic solvent because of the pure carbon element and their stable structure, which limits its usage in the sol-gel preparation. To improve the solubility (dispersion) of CNTs in an organic solution, functionalized CNTs are used

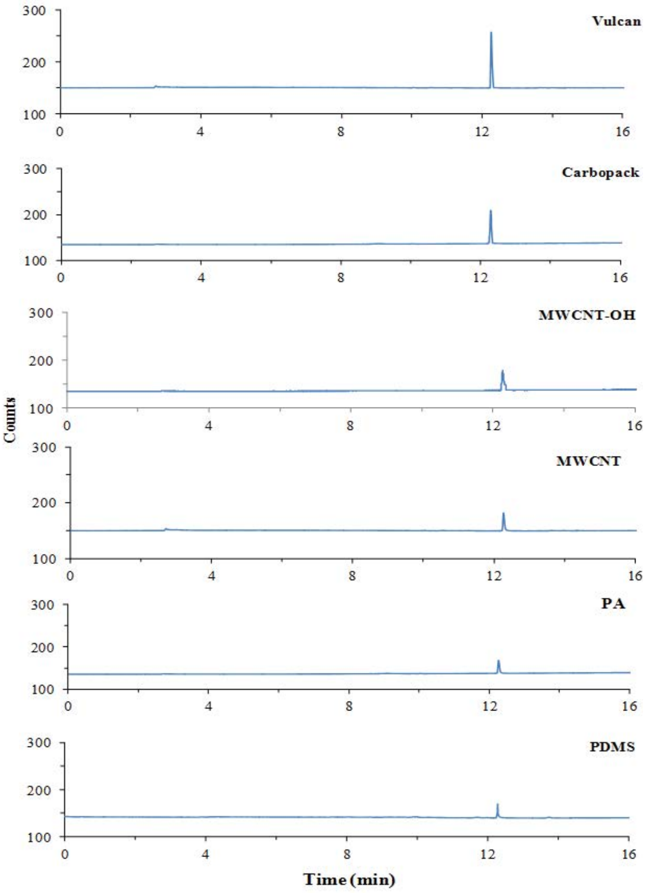

Fig. 8. GC/AED chromatograms of TCP showing the carbon 179 channel.

[40]. Therefore, the fiber made from modified CNTs can probably extract a slightly larger amount of analytes than unmodified CNTs.

4. Conclusions

In this study, the kinetics and equilibria of TCP adsorption onto multi-walled carbon nanotubes (MWCNT and MWCNT-OH) and carbon blacks (Vulcan XC72 and Carbopack B) were investigated. The results show that these materials can be used as adsorbents for the removal of TCP (and other chlorophenols) from aqueous solutions. Adsorption takes place in accordance with the Freundlich equation, as well as in accordance with the kinetics of the pseudo-second order model. Adsorption was very fast, while equilibrium was fixed at 60 min for CNT adsorbents and approximately 2–3 h for carbon blacks. New SPME fibers prepared from these carbon materials are a promising alternative to the commercial fibers due to their robustness, high porosity, low cost and ease of preparation. Among the different materials used for fabrication of the fibers, the Vulcan XC72 and Carbopack B fibers showed superior extraction properties. The fibers made from MWCNT and MWCNT-OH can also be successfully used for extraction of TCP from water samples. Moreover, for the MWCNT and MWCNT-OH coated fiber, equilibrium times are already reached after approximately 60 min. Much longer equilibrium times are necessary if the Vulcan XC72 and Carbopack B containing fibers are used. Both the CNT and carbon black coated fibers described in this paper were of higher quality than commercially available fibers.

References

[1] M. Czaplicka, Sources and transformations of chlorophenols in the natural environment, Sci. Total Environ., 322 (2004) 21–39.

[2] E.O. Igbinosa, E.E. Odjadjare, V.N. Chigor, I.H. Igbinosa, A.O. Emoghene, F.O. Ekhaise, N.O. Igiehon, O.G. Idemudia, Toxicological profile of chlorophenols and their derivatives in the environment: the public health perspective, Sci. World J., 2013 (2013) 1–11.

[3] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon, 42 (2004) 83–94.

[4] A. Dąbrowski, P. Podkościelny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon - a critical review, Chemosphere, 58 (2005) 1049–1070.

[5] K.Y. Foo, B.H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, J. Hazard. Mater., 175 (2010) 1–11.

[6] M.L. Soto, A. Moure, H. Dominguez, J.C. Parajo, Recovery, concentration and purification of phenolic compounds by adsorption: a review, J. Food Eng., 105 (2011) 1–27.

[7] Q. Liao, J. Sun, L. Gao, Adsorption of chlorophenols by multi-walled carbon nanotubes treated with HNO_3 and NH_3, Carbon, 46 (2008) 544–561.

[8] G.C. Chen, X.Q. Shan, Y.S. Wang, B. Wen, Z.G. Pei, Y.N. Xie, T. Liu, J.J. Pignatello, Adsorption of 2,4,6-trichlorophenol by multi-walled carbon nanotubes as affected by Cu(II), Water Res., 43 (2009) 2409–2418.

[9] M. Abdel Salam, M. Mokhtar, S.N. Basahel, S.A. Al-Thabaiti, A.Y. Obaid, Removal of chlorophenol from aqueous solutions by multi-walled carbon nanotubes: kinetic and thermodynamic studies, J. Alloys Compd., 500 (2010) 87–92.

[10] V.A. Tóth, A. Törocsik, E. Tombácz, K. László, Competitive adsorption of phenol and 3-chlorophenol on purified MWCNTs, J. Colloid Interface Sci., 387 (2012) 244–249.

[11] S. Biniak, A. Świątkowski, M. Pakuła, M. Sankowska, K. Kuśmierek, G. Trykowski, Cyclic voltammetric and FTIR studies of powdered carbon electrodes in the electrosorption of 4-chlorophenols from aqueous electrolytes, Carbon, 51 (2013) 301–312.

[12] K. Kuśmierek, A. Świątkowski, The influence of an electrolyte on the adsorption of 4-chlorophenol onto activated carbon and multi-walled carbon nanotubes, Desal. Wat. Treat., 56 (2015) 2807–2816.

[13] H. Ding, X. Li, J. Wang, X. Zhang, C. Chen, Adsorption of chlorophenols from aqueous solutions by pristine and surface functionalized single-walled carbon nanotubes, J. Environ. Sci., 43 (2016) 187–198.

[14] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem., 62 (1990) 2145–2148.

[15] J. Pawliszyn, Applications of Solid Phase Microextraction, The Royal Society of Chemistry, Cambridge, 1999.

[16] A. Kumar, A.K. Malik, D.K. Tewary, B. Singh, A review on development of solid phase microextraction fibers by sol-gel methods and their applications, Anal. Chim. Acta, 610 (2008) 1–14.

[17] F. Augusto, E. Carasek, R.G.C. Silva, S.R. Rivellino, A.D. Batista, E. Martendal, New sorbents for extraction and microextraction techniques, J. Chromatogr. A, 1217 (2010) 2533–2542.

[18] A.V. Herrera-Herrera, M.A. Gonzalez-Curbelo, J. Hernandez-Borges, M.A. Rodriguez-Delgado, Carbon nanotubes applications in separation science: a review, Anal. Chim. Acta, 734 (2012) 1–30.

[19] B. Pérez-López, A. Merkoçi, Carbon nanotubes and graphene in analytical sciences, Microchim. Acta, 179 (2012) 1–16.

[20] B.T. Zhang, X. Zheng, H.F. Li, J.M. Lin, Application of carbon-based nanomaterials in sample preparation: a review, Anal. Chim. Acta, 784 (2013) 1–17.

[21] R. Aranda, P. Kruus, R.C. Burk, Assessment of polycrystalline graphites as sorbents for solid-phase microextraction of nonionic surfactants, J. Chromatogr. A, 888 (2000) 35–41.

[22] M. Giardina, S.V. Olesik, Application of low-temperature glassy carbon-coated macrofibers for solid-phase microextraction analysis of simulated breath volatiles, Anal. Chem., 75 (2003) 1604–1614.

[23] T. Sun, J. Jia, N. Fang, Y. Wang, Application of novel activated carbon fiber solid-phase, microextraction to the analysis of chlorinated hydrocarbons in water by gas chromatography-mass spectrometry, Anal. Chim. Acta, 530 (2005) 33–40.

[24] K. Kuśmierek, M. Sankowska, K. Skrzypczyńska, A. Świątkowski, The adsorptive properties of powdered carbon materials with a strongly differentiated porosity and their applications in electroanalysis and SPME-GC, J. Colloid Interface. Sci., 446 (2015) 91–97.

[25] J. Yu, L. Dong, C. Wu, L. Wu, J. Xing, Hydroxyfullerene as a novel coating for solid-phase microextraction fiber with sol-gel technology, J. Chromatogr. A, 978 (2002) 37–48.

[26] Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai, G. Jiang, Evaluation of graphene as an advantageous adsorbent for solid-phase extraction with chlorophenols as model analytes, J. Chromatogr. A, 1218 (2011) 197–204.

[27] Z. Pei, L. Li, L. Sun, S. Zhang, X.Q. Shan, S. Yang, B. Wen, Adsorption characteristics of 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, 2-naphthol and naphthalene on graphene and graphene oxide, Carbon, 51 (2013) 156–163.

[28] X. Liu, Y. Ji, Y. Zhang, H. Zhang, M. Liu, Oxidized multiwalled carbon nanotubes as a novel solid-phase microextraction fiber for determination of phenols in aqueous samples, J. Chromatogr. A, 1165 (2007) 10–17.

[29] H. Liu, J. Li, X. Liu, S. Jiang, A novel multiwalled carbon nanotubes bonded fused-silica fiber for solid phase microextraction-gas chromatographic analysis of phenols in water samples, Talanta, 78 (2009) 929–935.

[30] W. Du, F. Zhao, B. Zeng, Novel multiwalled carbon nanotubes-polyaniline composite film coated platinum wire for headspace solid-phase microextraction and gas chromatographic deter-

mination of phenolic compounds, J. Chromatogr. A, 1216 (2009) 3751–3757.

[31] P. Kueseng, J. Pawliszyn, Carboxylated multiwalled carbon nanotubes/polydimethylsiloxane, a new coating for 96-blade solid-phase microextraction for determination of phenolic compounds in water, J. Chromatogr. A, 1317 (2013) 199–20.

[32] M.M. Dubinin, E.D. Zaverina, V.V. Serpinsky, The sorption of water vapour by active carbon, J. Chem. Soc., (1955) 1760–1766.

[33] S. Lagergren, Theorie der sogenannten adsorption geloester stoffe, Vetenskapsakad. Handl., 24 (1898) 1–39.

[34] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[35] W. Weber Jr., J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., 18 (1963) 31–42.

[36] H.M.F. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem., 57 (1906) 385–470.

[37] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc., 38 (1916) 2221–2295.

[38] B. Pan, B. Xing, Adsorption mechanisms of organic chemicals on carbon nanotubes, Environ. Sci. Technol., 42 (2008) 9005–9013.

[39] W. Wardencki, M. Michulec, J. Curyło, A review of theoretical and practical aspects of solid-phase microextraction in food analysis, Int. J. Food Sci. Technol., 39 (2004) 703–717.

[40] N. Zhang, J. Xie, M. Guers, V.K. Varadan, Chemical bonding of multiwalled carbon nanotubes to polydimethylsiloxanes and modification of the photoinitiator system for microstereolithography processing, Smart Mater. Struct., 13 (2004) N1–N4.