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Original Paper

Sorption behavior of acidic herbicides on carbon nanotubes

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Abstract. Carbon nanotubes and graphitized carbon are investigated as adsorbents for solid phase extraction of dicamba and 2,4,5-T, two phenoxyalkanoic acid herbicides. These adsorbents have much greater adsorption capability than that of C_{18} bonded silica, which was also tested for comparison studies. The adsorption capacity increases remarkably at lower pH of the sample solution. Freundlich isotherms were applied to analyze the data. Our studies suggest that carbon nanotubes have great potential applications in environmental analysis.

Key words: Carbon nanotubes; graphitic carbon; adsorption; herbicides; water samples.

Carbonaceous sorbents, including activated charcoal, graphitized carbon black and carbon molecular sieves have been proven to be effective adsorbents for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media [1, 2]. The widespread use of carbon materials in solid-phase extraction technique stems mainly from their high versality in texture properties and surface chemistry as well as from their chemical stability in many conditions. Their surface could act as a Lewis base toward polar solutes and is also involved in π–π interactions as well as dispersive interactions with aromatic analytes [2]. Compounds are retained by hydrophobic and electronic interaction, so that apolar and also very polar compounds can be highly retained from aqueous solutions.

Carbon nanotubes (CNTs) are novel materials which possessing many unique electronic, mechanical and chemical properties, high surface and excellent strength. Large efforts have been devoted to improving their syntheses, determining their structures, measuring their properties and finding applications [3]. CNTs, including single-walled nanotubes and multiwalled nanotubes, have attracted great attention in recent years also in analytical chemistry as a target analyte and as an analytical tool [4, 5]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interactions with other molecules, which make them a promising adsorbent material. Carbon nanotubes have been applied for solid-phase extraction of bisphenol A, 4-n-nonylphenol and 4-tert-octylphenol [6], several phtalate esters [7], chlorobenzenes [8, 9], volatile organic compounds [10], fluoride [11] as well as some metal ions [12, 13].

In this study, sorption behavior of some acidic herbicides on carbon nanotubes was tested. The results were compared with that obtained on graphitized carbon black (GCB) and on bonded silica (C_{18}), being the most widely applied for isolation and enrichment of phenoxyalkanoic acids [14–16]. These herbicides are widely used in agriculture to control the growth of broad-leaf weeds in crops. Due to their persistence,

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large scale of application, polar nature and water solubility, they are present in several environmental compartments like water, soil and food products. By a adsorption–desorption process, contaminants in water can be recycled. To meet the objectives for the monitoring of these compounds in environmental samples at trace levels, the selection of appropriate adsorbent is therefore important. The potential of carbon nanotubes for extraction of dicamba was evaluated in the previous paper [17]. This work presented more detailed studies including also 2,4,5 herbicide.

Experimental

Reagents and apparatus

Multiwalled carbon nanotubes (produced by catalytic vapor decomposition) were purchased from Aldrich, with average outer diameter of 10–30 nm, surface area of 40–600 $m^2 g^{-1}$ and purity above 95%. Nonporous, homogeneous graphitized carbon (Xpertek) with a surface area of 100 $m^2 g^{-1}$ were obtained from Cobert Associates Inc. (www.cobertassoc.com) C_{18} silica (ENVI) from Supelco has surface area of 475 $m^2 g^{-1}$.

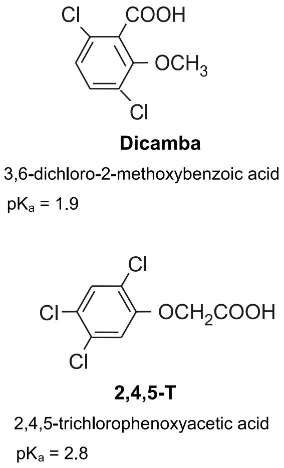

Fig. 1. Names, structural formulae and pK_a values of tested acidic herbicides

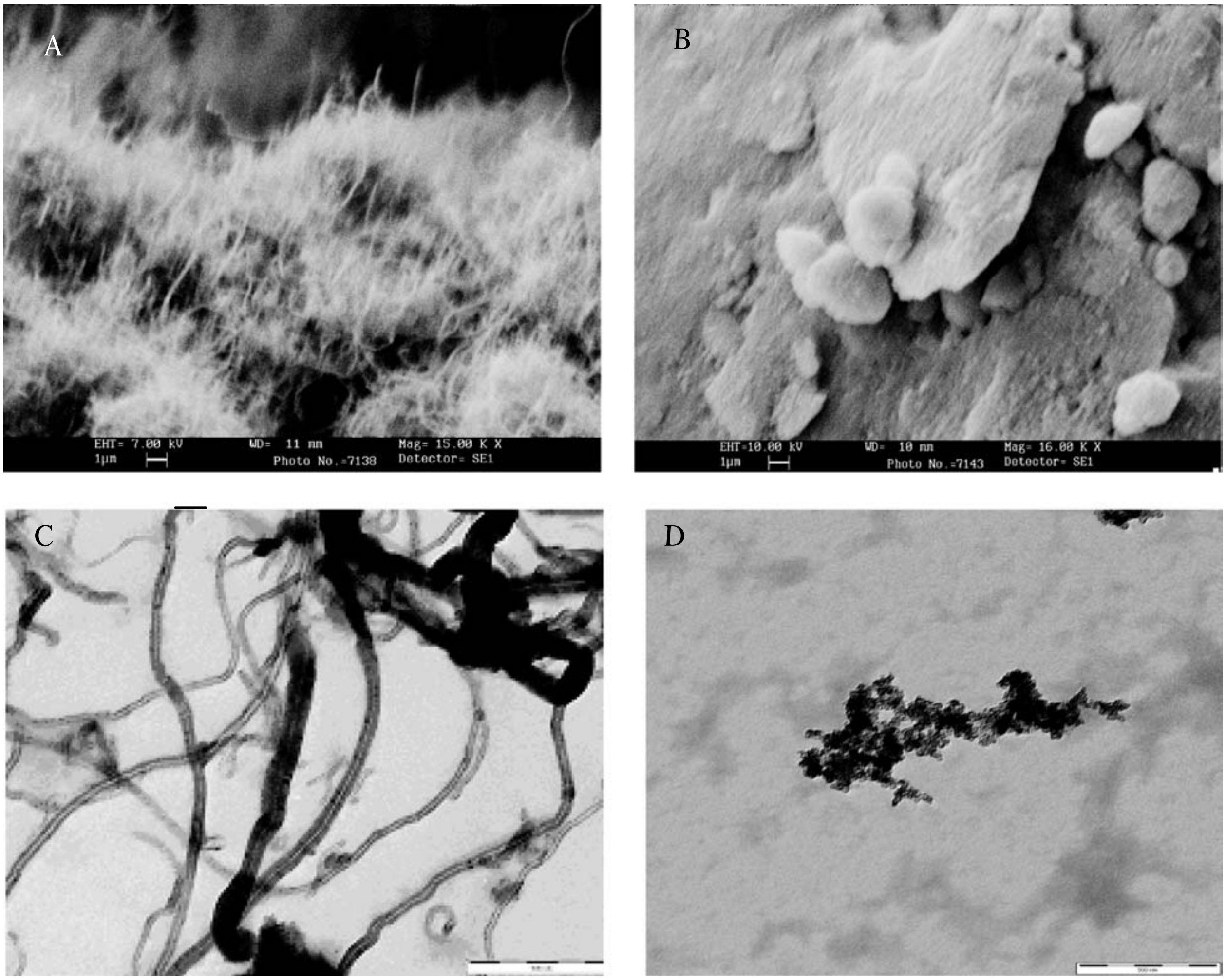

Fig. 2. SEM (A, B) and TEM (C, D) images of examined carbon nanotubes (A, C) and graphitized carbon (B, D)

The surface morphology of the carbon sorbents were examined by a Leo 912 Zeiss transmission electron microscopy (TEM) with an acceleration voltage of 80 kV and a Leo scanning electron microscopy (SEM). The SEM and TEM images of the CNTs at high magnification is shown in Fig. 1. The content of acidic and basic surface groups were obtained by titration [18].

The acidic herbicides including 2,4,5-T and dicamba (see Fig. 2 for names and structural formulae) were obtained as individual standards from Sigma-Aldrich and used for preparing the stock standard solutions. Their determination was carried out an HPLC system from Merck with a 40 µL sample loop. The analytical column was a Phenomenex C18(2) Luna 5 µm (250 × 4.6 mm i.d.). The mobile phase consisted of 26.2 mmol L^{-1} acetic acid at pH 2.5 with 45% (v/v) acetonitrile. It was delivered isocratically at 1 mL min^{-1}. UV detection was performed at 225 nm.

Sorption experiments

Adsorption of herbicides on examined sorbents were examined at their concentration ranging from 0.25 to 50 mg L^{-1} at different pH and 25 °C. In each adsorption experiment 100 mL of the analytes solutions were contacted with 200–500 mg of tested adsorbent. The supernatant was analysed by HPLC. The amount of adsorbed analyte was calculating as the difference between initial and final concentration.

Analysis of water sample

250 mL of collected lake water (from Zalew Zegrzynski, close to Warsaw, Poland) sample was filtered through a 0.45 µm filter, adjusted to pH 1, spiked with appropriate amount of both compounds and passed through the microcolumns containing 200 mg of CNTs or 500 mg of C_{18} silica. Elution was done with 3 mL of acetonitrile/NH_3 (80:20, v/v) solution or 2 mL of methanol, respectively.

Results and discussion

Sorption studies

To evaluate the analytical potential of carbon nanotubes and graphitized carbon black as solid-phase extraction adsorbents for enrichment of acidic herbicides, dicamba and 2,4,5-T were used as model compounds due to their different chemical structure and hydrophobicity (Fig. 2). Adsorption experiments were carried out at different pH values as solution pH determines the dissociation and ionization of the adsorbates through their pKa values as well as the surface charge of a carbon surface. For comparison the study were conducted also with C_{18} silica, frequently used for isolation and preconcentration of organic compounds. Adsorption isotherms for dicamba and 2,4, 5-T are shown in Fig. 3.

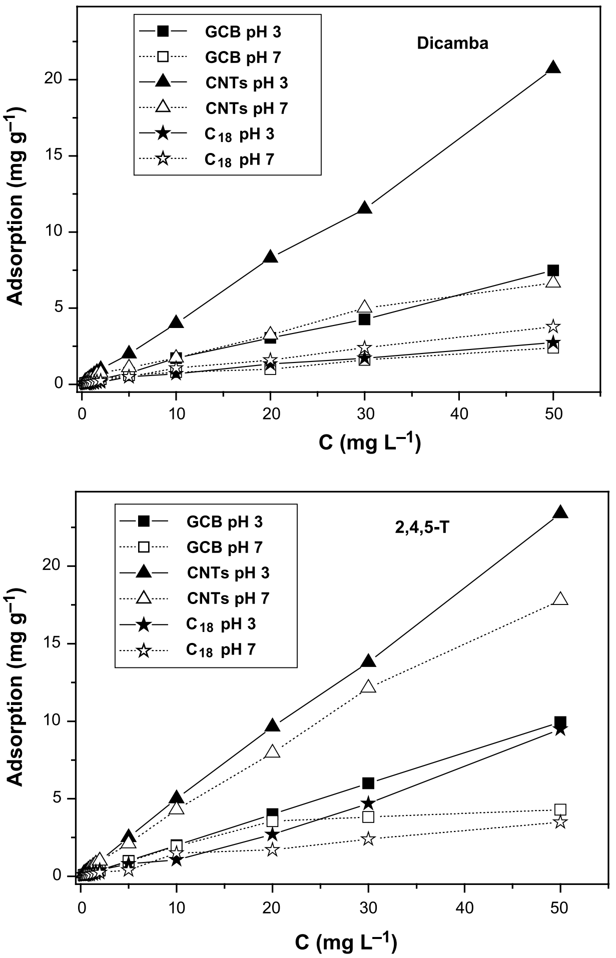

Fig. 3. Adsorption isotherms of dicamba and 2,4,5-T herbicides onto GCB, CNTs and C_{18} adsorbents

CNTs have much greater herbicides adsorption capability than that of GCB and C_{18} adsorbents. The absorption capacity increases remarkably at lower pH of sample solution. The decrease of pH leads to decrease in ionization of the analytes and simultaneously to neutralization of the surface charge of carbon sorbents. At pH 3 herbicides are present in both neutral and negatively charged forms, therefore, both electrostatic and hydrophobic sorption mechanisms could be anticipated, although it was not possible to distinguish between them in this work. The shape of obtained isotherms, particularly at pH 7, indicates that as more sites in the substrate are filled, it becomes increasingly difficult for the analyte molecules to find an available vacant site [19]. This could be either because the adsorbate molecules are more likely to be adsorbed flat or because there is no strong competition from the solvent. The adsorption capacities of 20.7, 7.5 and 2.7 mg g^{-1} were obtained for CNTs, GCB and C_{18} adsorbents, respectively, at dicamba equilibrium concentration of 50 mg L^{-1} and pH 3. The higher values of adsorption capacity determined for 2,4,5-T herbicide on CNTs under these experimental conditions (23.4, 9.9 and 9.5 mg g^{-1} for CNTs, GCB and C_{18} adsorbents, respectively) could be explained by its different chemical structure and higher lipophilicity. The change in sample solution pH from 3 to 7, does not influence remarkably the adsorption of 2,4,5-T on CNTs, as it was observed for dicamba, due to its lower degree of ionization.

As can be seen from Fig. 3 pH have a remarkable effect on the sorption properties of CNTs for dicamba, which is a relatively strong acid. To increase its retention capacity, pH of the sample should be lower than pK_a of the analyte. A series of experiments showed that at pH 1 the adsorption capacity of CNTs reached the value of $24.1\,mg\,g^{-1}$ at its equilibrium concentration of $50\,mg\,L^{-1}$. Under these conditions, the surface charge of CNTs is positive and dicamba exists mostly in its unionized state.

The acidic surface properties of carbon sorbents are caused by the presence of carboxyl groups or lactols and hydroxyl groups of phenolic character [18]. The acidity of a given group depends on its chemical environment, such as size and shape of the polyaromatic layers, the presence and position of other substituents and the charge of neighboring dissociated groups. While the nature of the acidic surface sites is quite well understood, the origin of surface basicity is still under discussion. One of the possibly explanation is the existence of pyrone-type structures on the edges of the polyaromatic layers. Graphitized carbon adsorbent has higher amount of acidic ($3.315\,mmol\,g^{-1}$) and basic ($0.470\,mmol\,g^{-1}$) functional groups in comparison with carbon nanotubes (2.365 and $0.032\,mmol\,g^{-1}$, respectively) as was determined by Boehm titration. The pH of both carbon sorbents is very similar (4.98 and 5.02). The results showed that the adsorption of tested phenoxyalkanoic acids on GCB is strongly influenced by surface chemistry of graphitized carbon adsorbent and by its reduced porosity (Fig. 1B).

In the case of C_{18} silica, adsorption of organic molecules is governed only by non-electrostatic interactions, such as π–π dispersion or hydrophobic interactions. The adsorbent efficiency decreases as compound polarity increases. For dicamba the change in sample solution pH does not influence remarkably the adsorption capacity of C_{18} material (Fig. 3A). This adsorbent could not be applied in strong acidic conditions due to its low chemical stability.

According to literature reports [8, 9], the Freundlich and Langmuir adsorption isotherms have been useful for describing the adsorption behavior of CNTs, thus, both these models were applied to analyze obtained data. From the linear form of the Freundlich adsorption isotherm, which represents the relationship between the amount of herbicide adsorbed by per unit mass of adsorbent (q_e) and its concentration at equilibrium (C_e), equation can be written as follows:

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

where K_f and n are constants representing the adsorption capacity and the intensity of the adsorption, respectively. Constants of Freudlich adsorption isotherm models according to the above equation are presented in Table 1. In general, all isotherms were fit very well by linear regression analysis as it is confirmed by the comparison of r^2 values, which are mostly >0.98. K_f is decreasing with an increase in pH value for both carbon sorbents, which is consistent with the experimental observations. The parameter K_f can be used to indicate the relative sorption capacity of the system and the reported in Table 1 values show the same trend as the sorption capacity for the herbicides studied.

Table 1. Parameters of Freundlich adsorption isotherm for dicamba and 2,4,5-T

Adsorbent	Analyte	pH	K_f	n	r^2
CNTs	2,4,5-T	1	0.49	0.98	0.994
		3	0.47	0.98	0.997
		7	0.48	0.93	0.996
	Dicamba	1	0.48	0.92	0.998
		3	0.48	0.94	0.989
		7	0.37	0.72	0.995
GCB	2,4,5-T	1	0.49	0.98	0.998
		3	0.20	0.99	0.996
		7	0.19	0.97	0.998
	Dicamba	1	0.49	0.98	0.998
		3	0.19	0.92	0.989
		7	0.17	0.71	0.985
C_{18}	2,4,5-T	3	0.14	0.81	0.994
		7	0.19	1.00	0.995
	Dicamba	3	0.07	0.95	0.997
		7	0.14	0.81	0.995

The strong interactions between herbicide molecules and carbon nanotubes may be attributed to the unique structure and electronic properties of CNTs. GCB sorbent has a nonporous structure with a planar graphite surface, while CNTs are open-ended, with adsorption sites on both internal and external surfaces. Strong interactions between the benzene rings and the surface of nanotubes could occur with all surfaces on the walls. More homogeneous systems will have a n value approaching unity and a value greater than 2 is typical of hindered adsorption [20]. The obtained results prove that all three adsorbents would be appropriate for the preconcentration of acidic herbicides,

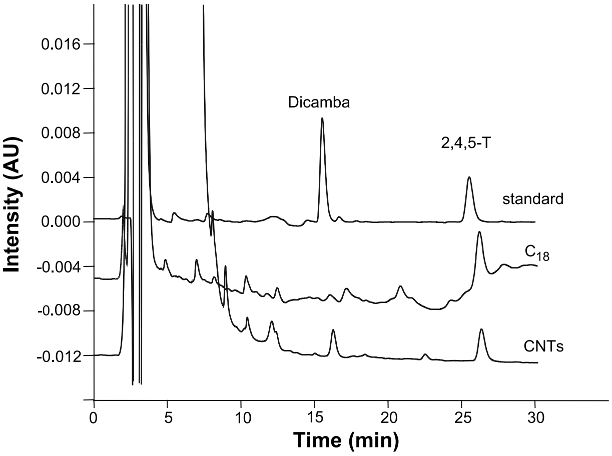

Fig. 4. Solid-phase extraction/HPLC chromatograms of river water samples (250 mL) spiked with 0.04 mg mL^{-1} of dicamba and 2,4,5-T and preconcentrated on C_{18} and CNTs microcolumns. See text for the experimental conditions

although with different adsorption ability and CNTs exhibit the highest adsorption capacity for both tested compounds. The obtained experimental data for adsorption of dicamba and 2,4,5-T on tested adsorbents could not be approximated by the isotherm model of Langmuir as its linear form of equation gives very poor presentation for herbicide sorption behavior ($r^2 < 0.80$).

Enrichment of herbicides on CNTs

Retention behavior of dicamba and 2,4,5-T on CNTs was investigated using batch equilibrium technique in the function of pH (Fig. 4). As it was expected, dicamba exhibits the highest affinity toward carbon nanotubes at the lowest pH value. Under these conditions, the surface charge of CNTs is positive and dicamba exists mostly in its unionized state. At pH $\geq$4 cannot be sorbed by Van der Waals forces because it is mainly present in anionic form. While the changes in acidity of the sample do not influence essentially the adsorption of 2,4,5-T.

With the aim to determine the breakthrough of CNTs microcolumn, different volumes of sample in the 25–1000 mL range containing 0.1 mg L^{-1} of both analytes at pH 1 were passed through the sorption material. The complete adsorption was observed up to 250 mL, that shows very strong retention of studied compounds.

In a solid phase extraction column system, the flow rate of sample solution not only affects the recoveries of analytes, but also controls the analysis time. It was found that flow rates up to 2.5 mL min^{-1} for water sample loading on the microcolumn packed with 200 mg of CNTs has no effect on the quantitative adsorption of the two tested analytes.

Several types of eluents including methanol, ethanol, acetone, acetonitrile and dimethylformamide were tested for the desorption of herbicides. However, these compounds demonstrate also high retention in pure organic solvents as mobile phase. The prediction of the elution conditions for carbon sorbents is not as straightforward as on C_{18} silicas, when the elution strength of common organic solvents is well known and follows the solubility parameter order of the solvents. For this reason dichloromethane with methanol was recommended for many organic pollutants [21]. Special care had to be taken when using this elution mixture due to problems with double layers during the subsequent evaporation if water was not well removed before elution. Additionally, when the microcolumn is washing with small volume of methanol before applying the dichloromethane-methanol mixture, some weakly retained compounds could be loss. Our experiments showed that acetonitrile/NH_3 (80:20, v/v) solution was the most effective eluent for desorption of dicamba and 2,4,5-T herbicides. Moreover, the backflush desorption (in the opposite way to loading) permits to use only 3 mL of eluent with a 0.2 g SPE microcolumn. Although complete desorption made carryover be very minor, to obtain quantitative analytical results for the next extraction, the microcolumn was washed further with another 2 mL acetonitrile with ammonia preparing it immediately for the next preconcentration step.

For GCB adsorbent, even though breakthrough of analytes does nor occur during the loading of samples, the recoveries were low, owing to the desorption problems.

Table 2. Recoveries of dicamba and 2,4,5-T herbicides in lake water

Dicamba			2,4,5-T		
Added (μg mL^{-1})	Detected (μg mL^{-1})	Recovery (%)	Added (μg mL^{-1})	Detected (μg mL^{-1})	Recovery (%)
0.01	0.008	83.2 ± 4.9	0.01	0.009	95.3 ± 3.6
0.04	0.034	85.5 ± 3.2	0.04	0.039	96.9 ± 2.8

Mean and standard deviation for four determination.

Application to real water samples

Based on above selected parameters a novel method for determination of these two herbicides at trace level was developed. Relevant performance of the proposed method was validated with a series of designed experiments with spiked lake water solutions. 250 mL of collected lake water was filtered through a 0.45 μm, adjusted to pH 1, spiked with 0.04 μg mL^{-1} and 0.01 μg mL^{-1} of both compounds and passed through the microcolumns containing 200 mg of CNTs. After elution HPLC analysis was done. The results are shown in Table 2.

The detection limits of these two analytes were obtained based on the signal as three-fold the baseline noise ($S/N = 3$) for an extraction of 250 mL water sample, and the favorable detection limits of dicamba and 2,4,5-T were 3.6 and 2.8 μg L^{-1}, respectively.

As an important parameter of robust method, reproducibility was also investigated by fortifying herbicides into the 250 mL lake water solution with the final concentration of 0.04 μg mL^{-1}. The results indicated that precision, expressed as relative standard deviation (RSD), for six replicate measurements were equivalent to 2.5 and 3.3% for 2,4,5-T and dicamba, respectively.

For comparison the lake water sample with herbicides was preconcentrated also on C_{18} silica cartridge (500 mg) and elution was done with 2 mL of methanol. The chromatograms of these samples after preconcentration step are presented in Fig. 4. The obtained results showed that CNTs were more effective than C_{18} (dicamba recovery was only 13%) for the solid phase extraction of tested herbicides.

The results showed that CNTs are the most effective sorbents for the preconcentration of these compounds of the three sorbent materials examined. Their adsorption properties depend significantly on the pH value of the solution, being the highest at strong acidic media. These conditions are very suitable for natural water samples, which have to be acidified after sampling.

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