

# ADSORPTION ON MWCNTS FROM AQUEOUS SOLUTIONS IN ENVIRONMENTALLY RELEVANT CONDITIONS

Ajna Tóth<sup>1</sup>, Erik Geissler<sup>2</sup>, Erwin Klumpp<sup>3</sup>, Erzsébet Oláh<sup>4</sup>,  
Krisztina László<sup>1</sup>

<sup>1</sup>Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

<sup>2</sup>Laboratoire de Spectrométrie Physique CNRS UMR 5588, Université J. Fourier de Grenoble, BP 87, 38402 St Martin d'Hères cedex, France

<sup>3</sup>Institut Agrosphäre (ICG 4) Institut für Chemie und Dynamik der Geosphäre, Forschungszentrum Jülich, 52425 Jülich, Germany

<sup>4</sup>Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary

## Introduction

Owing to expanding large-scale production of the nanoindustry, incomplete combustion of fossil fuels and continuously growing motorization, carbon nanotubes (CNTs) are increasingly emitted into the environment. They are mobile, either air- or waterborne. CNTs raise concerns about their possible fate in nature, as they have been detected in air, water and soil phases even as far from any motorization as the Polar areas [1-2].

In spite of the widespread occurrence of CNTs in nature, their effect on the environment is poorly known. Their potential for exerting such effects is high, due to their specific physical and chemical features. CNTs have a high light absorption capacity, they have a relatively large surface area, porosity, high aspect ratio, etc. They have the potential to influence the energy balance of Earth, and may act as catalysts in various chemical reactions in air, water or soil [2]. Due to their small size, they can easily be incorporated into living systems. CNTs may be deposited in the airways of mammals, causing severe lung problems as their shape is very similar to asbestos. Interactions with the environment may also result in the modification of their characteristics [3-6]. Having a relatively large surface area (180-220 m<sup>2</sup>/g), they can adsorb pollutants and act as a vector and potential source either of these harmful compounds or their intermediates. In the soil CNTs can be deposited, concentrated, stored and – when the conditions change – move on again and/or immobilize the pollutants.

The behaviour of CNTs in the environment and their influence on it is therefore complex and remains to be discovered. We focus on their properties in aqueous media. This work reports the sorption properties of various aromatic pollutants, namely phenol, dopamine and sulfadiazine, on the

surface of CNT and oxidized CNT from non-buffered solution and from solutions of initial pH= 3 and 10, respectively.

## Experimental

### Materials

Multiwall carbon nanotubes, one pristine (CNT) and the other oxidized (CNTOX), were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences (Chengdu, China). They were used as received for the experiments.

### Methods

#### SAXS

The CNTs were investigated by small and wide angle X-ray scattering (SAXS and WAXS) at incident energy 19.8 keV with a synchrotron source on the BM2 small angle camera at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, spanning the transfer momentum range  $0.005 < q < 6 \text{ \AA}^{-1}$ .

#### Nitrogen adsorption

Nitrogen adsorption/desorption isotherms were measured at 77 K, using a Quantachrome Nova computer-controlled apparatus. Samples were previously evacuated at 473 K for 24 hours.

#### Water vapour adsorption

Water vapour adsorption/desorption isotherms were measured at 293 K, using a Quantachrome Hydrosorb computer-controlled apparatus. The initial slope of the adsorption branch was used to characterize the hydrophobicity of the surface.

#### Sorption from dilute aqueous solutions

The CNTs were shaken with the aqueous solution of the corresponding pollutant at 20 °C until reaching equilibrium. Contact times needed to reach equilibrium were deduced from preliminary kinetic measurements. The initial concentrations were set according to the solubility of the aromatic molecule. Phenol was dissolved in distilled water and the pH was set to 3 and 10 with HCl and NaOH solutions, respectively. The concentration  $c_e$  was determined by UPLC method.

## Results and Discussion

### Porosity and surface chemical characterization of the CNTs

SAXS studies indicate that the pristine nanotubes possess a distribution of outer diameters centred on 240 Å and a broader range of inner diameters with an average of approximately 40 Å. The density of the graphite decreases towards the outer layers, and the surface of the tubes is rough. The average thickness of the walls is about 85 Å, i.e., the walls are built up of ca. 25 graphene layers. The surface derived from SAXS measurements is 235 m<sup>2</sup>/g is in good agreement with  $S_{\text{BET}}$ . When immersed in water, it penetrates both into the inner bore of the tubes, and into the defects on the rough outer surface. Table 1 shows the porosity data obtained from nitrogen adsorption.

**Table 1. Results derived from N<sub>2</sub>-adsorption isotherm\***

	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{tot}}$ (cm <sup>3</sup> /g)	$d_{\text{ave}}$ (nm)	$W_0$ (cm <sup>3</sup> /g)	$w$ (nm)
CNT	213	0.94	17.59	0.076	1.76
CNTOX	230	1.48	25.69	0.083	1.71

\*  $S_{\text{BET}}$ : apparent surface area;  $V_{\text{tot}}$ : total pore volume;  $d_{\text{ave}}$  ( $=2V_{\text{tot}}/S_{\text{BET}}$ ): average pore width;  $W_0$ : micropore volume from DR;  $w=2kE_0^{-1}$  ( $k=13 \text{ kJ}\cdot\text{nm}\cdot\text{mol}^{-1}$ ): average micropore width from DR

The surface treatment enhanced the affinity of the surface towards water, as reflected in the water vapour adsorption isotherms (not shown here). The initial pH and the results of the Boehm titration are summarized in Table 2.

**Table 2. pH and results from the Boehm titration (µeqv/g)**

	pH	carboxyl	lactone	phenolic	Total acidic	Total basic
CNT	5.5	-	-	-	165.2	67.2
CNTOX	3.4	212.8	138.6	128.8	480.2	58.8

From the data in Table 2 it is clear that oxidation reduces the pH of the CNT through the development of the various acidic sites, among which carboxyl groups are in the highest concentration. It is worthwhile to note that the surface concentration of the total basic sites was not influenced by the surface treatment.

The experimental adsorption isotherms could be well fitted by the Langmuir model. Parameters calculated from the experimental data, i.e., the saturation adsorption capacities  $n_m$  as well as the interaction parameter  $K$  of the Langmuir fit, are listed in Table 3. The surface area occupied by phenol molecules  $S_{\text{phenol}}$  was also estimated. The surface coverage

was calculated as  $\frac{S_{\text{phenol}}}{S_{\text{BET}}} \cdot 100$ .

**Table 3. Parameters derived from the Langmuir adsorption isotherms**

		$n_m$ (mmol/g)	$K$ (l/mmol)	$S_{\text{phenol}}^{**}$ (m <sup>2</sup> /g)	surface coverage (%)
CNT	NB*	0.12	3.5	31.0	14.5
	pH 3	0.11	5.1	26.6	12.5
	pH 11	0.12	3.9	31.3	14.7
CNTOX	NB	0.087	5.8	21.9	9.5
	pH 3	0.081	3.9	20.4	8.9
	pH 11	0.11	2.5	28.0	12.2

\* NB: non-buffered; \*\*cross section area of phenol: 0.42 nm<sup>2</sup>/molecule [6].

The fitting parameters exhibit a limited dependence on the pH conditions for both CNTs. The sorption capacity and the surface coverage is always higher on the pristine CNT.

Introduction of oxygen functionalities increases the affinity towards water, which reduces the area available for the phenol molecules.

## Conclusions

The good agreement between SAXS and nitrogen adsorption surface areas confirms the openness of the porosity of the pristine CNT, i.e., the pores are available for adsorption. The surface treatment substantially increased the concentration of the acidic functional groups without significantly influencing the basicity. The oxygen functionalities increased the affinity towards water, which also reduced the adsorption of aromatic molecules. The adsorption of the aromatic weak acid, phenol, also shows a limited dependence on the pH of the adsorption medium.

**Acknowledgments.** This work was performed with the support of the FP7 Marie Curie IRSES program COMPOSITUM—Hybrid Nanocomposites PIRSES-GA-2008-230790). We express our gratitude to György Bosznai for his contribution to the adsorption measurements. The authors thank the European Synchrotron Radiation Facility for access to the French CRG beam line BM2.

## References

- [1] Murr LE, Soto KF, Esquivel EV, Bang JJ, Guerrero PA, Lopez DA, Ramirez DA., Carbon nanotubes and other fullerene-related nanocrystals in the environment: a TEM study. JOM 2004, 56, 28-31.
- [2] Koelmans AA, Jonker MTO, Cornelissen G, Bucheli TD, Van Noorte CM, Gustafsson O, Black carbon: The reverse of its dark side Chemosphere 2006, 63 (3), 365-377
- [3] Schierz A, Zaenker H: Aqueous suspensions of carbon nanotubes: surface oxidation, colloidal stability and uranium sorption, Environmental Pollution 2009, 157, 1088 - 1094
- [4] Christian NP, Von der Kammer F, Baalousha M, Hofmann Th, Nanoparticles: structure, properties, preparation and behaviour in environmental media, Ecotoxicology, 2008, 17, 326-343
- [5] Nowack B, Bucheli TD, Occurrence, behavior and effects of nanoparticles in the environment, Environmental Pollution, 2007, 150, 5-22
- [6] László K, Szűcs A, Surface characterization of polyethyleneterephthalate (PET) based activated carbon and the effect of pH on its adsorption capacity from aqueous phenol and 2,3,4-trichlorophenol solutions, Carbon, 2001,39 1945-1953