



The interactions of UV and/or H₂O₂ treated CNTOH and CNTCOOH with environmental fulvic acids



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ABSTRACT

The fate of carbon nanotubes (CNT) in the environment will be governed by the presence of natural dissolved organic matter (DOM). Many studies indicate that CNT create stabilized suspensions in the presence of DOM. Easier transport in the environment may indicate their greater hazard. However these studies describe the interactions of DOM with as produced CNT. In the present studies the interactions of UV and/or H₂O₂ treated wastewater containing CNTOH or CNTCOOH with the naturally occurred fulvic acids (FA) were presented. FA sorption, both kinetics and mechanism, were described using batch regime. The sorption of FA followed a pseudo-second order kinetics and was described with the highest accuracy by Langmuir or Dubinin-Radushkevich model for CNTOHs and Langmuir, Temkin or Dubinin-Radushkevich - for CNTCOOHs. The mechanism of FA sorption onto CNTOHs was ascribed to π - π , heterogeneous and electrostatic interactions. The π - π and electrostatic interactions can the mostly defined FA adsorption onto CNTCOOHs. The parameters affecting FA sorption were combination of porosity and dispersity.

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1. Introduction

The superior hydrophobicity, high specific surface area, and hollow and layered structure of carbon nanotubes (CNT) (Upadhyayula et al., 2009) confirm their growing application in sorption studies (Yu et al., 2014) or catalysis (Voitko et al., 2015). Increased CNT consumption will result in their enlarged disposal into the environment (Dale et al., 2015; Gottschalk et al., 2009; Yu et al., 2014). It was assumed (Gottschalk and Nowack, 2011; Keller and Lazareva, 2014) that one of CNT sources in the environment will be treated wastewater. CNT in the aquatic environment will interact with natural compounds (such as dissolved organic matter, DOM (Kennedy and Summers, 2015; Lerman et al., 2013; Safiur Rahman et al., 2013) or contaminants (Lerman et al., 2013; Oleszczuk et al., 2009) that will modify their stability, fate, bioavailability and toxicity (Dale et al., 2015; Loosli et al., 2014). Sorptive properties of CNT reduce also wastewater treatment efficiency (Qu et al., 2013).

The decomposition products of plants called as DOM are organic acids, carbohydrates, amino acids, amino sugars (hydrophilic) and lignin-derived, partly aromatic molecules: aromatic phenols, hydrocarbons, fats, and nucleic acids (hydrophobic (Gheraout, 2014; He et al., 2014; Zhu et al., 2013)). DOM in waters is easy adsorbed onto most particles and surfaces.

DOM sorption onto pristine CNT is widely examined (Jung

et al., 2015; Lin et al., 2009; Zhang et al., 2015). In many studies tannic acid (TA) or humic acids (HA) as DOM representatives are used (Jung et al., 2015; Lin et al., 2009; Lin and Xing, 2008). Fulvic acids (FA), however, are the largest fraction of DOM (45–65%) (Westhorpe et al., 2012), soluble in water under all pH. FA or fulvic acid-like materials adsorb and transport (by complexation) ions, heavy metals and radionuclides.

The studies of FA sorption onto CNT are scarce (Yang and Xing, 2009). FA, however, can be sorbed on CNT at the cylindrical external surface or in pores between the bundles. Most natural FA could not access to the micropores as their average size is 3.2 nm (Yang and Xing, 2009). The surface coating of CNT by DOM prevents the aggregation (an electrostatic repulsion due to the negative charge of the DOM coating) and increases the stability (due to steric stabilization (Sampaio et al., 2011)) of CNT. DOM, nevertheless, may also destabilize colloids (through bridging flocculation (Sousa and Teixeira, 2015)) or induce also the partial redispersion of already formed agglomerates (Loosli et al., 2015). Heterogeneous sorption occurred when the hydrophobic moieties of DOM adsorb to the hydrophobic surfaces of pristine CNT. Enhanced dispersability of CNT was observed as the result of hydrophilic moieties of DOM stretching towards the solution (Schwyzer et al., 2011). The increased CNT stability alters the environmental behavior and bioavailability of CNT (Zhang et al., 2015).

However, as-produced CNT, both pristine and functionalized for example with –OH –(CNTOHs) or –COOH (CNTCOOHs), are not

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observed finally in the environment. Our previous results indicate that UV and/or H₂O₂ treatment of wastewater containing CNT (both pristine (Czech et al., 2015b) and –OH or –COOH functionalized (Czech et al., 2015a)) affects also their physical properties: morphology (such as exfoliation of outer walls, shortening and opening up of their ends), chemical composition (the slight changes of *S*_{BET}, porosity, O% content, surface charge and mobility) but mostly increases the stability (Czech et al., 2015b). H₂O₂ plays a key role as a factor modifying CNTOHs surface, whereas the properties of CNTCOOHs are mostly affected by UV rays (Czech et al., 2015a). The results confirm that the extent of CNT aggregation is related with the number and type of surface functional groups, mainly oxygen ones, whereas the reactivity of various oxygen groups is not similar. It should, therefore, be expected that apolar compounds will be more easily adsorbed onto pristine nanotubes, and polar ones onto CNT after treatment with H₂O₂ and/or UV (Czech et al., 2015b). These observations imply that there is not possible to predict the environmental impact of CNT based only on previously published results. Similarly, both CNT fate and toxicity (Miao et al., 2015) will also be markedly different between pristine and altered materials (Al-Kattan et al., 2014).

To the best of my knowledge, no studies on the sorption of naturally occurred FA onto –OH and –COOH functionalized CNT released after wastewater treatment by H₂O₂ and/or UV have been done so far. As FA represents the largest fraction of DOM in the environment and DOM concentrations in natural waters are estimated for 0.5–30 mg L⁻¹ (Schwyzer et al., 2011), the concentration of 10 mg L⁻¹ FA was chosen for sorption studies. The aim of the presented studies was then the determination of the kinetics and mechanisms of FA sorption onto treated CNTOHs and CNTCOOHs. To simplify the interpretation, a single source of FA was applied. The obtained results will help to understand the interaction mechanism of present in wastewater altered CNT with the largest DOM fraction represented by FA. These interactions will affect the sorption of other contaminants or decide on the bioavailability of CNT.

2. Material and methods

2.1. Treatment of CNTOHs and CNTCOOHs

The detailed procedure of CNTOH and CNTCOOH (MWCNT, Timesnano, China) treatment by UV and/or H₂O₂ (5 h and/or 0.35 wt%, respectively) and their characteristics are presented in the previous paper (Czech et al., 2015b). Considering applied treatment procedure CNT treated by UV were labelled as CNTOH-UV or CNTCOOH-UV, by H₂O₂ – as CNTOH-H₂O₂ or CNTCOOH-H₂O₂, and by UV and H₂O₂ simultaneously – as CNTOH-UV+H₂O₂ or CNTCOOH-UV+H₂O₂. Pristine CNT were labelled as pCNTOH or pCNTCOOH.

2.2. Extraction of fulvic acids

For the extraction of fulvic acids the agricultural soil from Lublin (N 51°11'55, E 22°31'42, Poland) was applied. After mixing with 0.1 M NaOH (10:1 v:w) in 1 L bottle purged with N₂ and 24 h long shaking at room temperature the soil was centrifuged (3500 g for 30 min) and the supernatant was acidized to pH 1 by 1 M HCl. After centrifugation (3500 g for 30 min) the precipitated humic acids were removed and the extracts were treated by 0.5 M NaOH (for removal of Fe³⁺ and Al³⁺ salts) till pH increased to 6.00 ± 0.2. Filtered (0.45 μm) FA extracts were analyzed for Total Organic Carbon (TOC) in a Sievers InnovOx Laboratory Total Organic Carbon Analyzer (GE). Ionic strength of prepared solution was characterized by 0.2 mol L⁻¹ NaCl. For the prevention of

microorganism growth a biocide (0.2 mg L⁻¹ NaN₃ and 0.01 mol L⁻¹ CaCl₂ in deionized water) was used. Spectral characterization of FA was determined by UV-vis spectroscopy (Varian Cary 4000) measuring absorbance at 465 nm and 665 nm (E₄/E₆). For the determination of the presence of functional groups of FA, FT-IR spectroscopy was also applied (Nicolet 8700A, Thermo Scientific).

2.3. Sorption studies

Sorption kinetics (at 23 ± 1 °C) was tested using 10 mg L⁻¹ of FA in 40-mL Teflon centrifuge tubes filled with 2 mg of CNTOHs or CNTCOOHs (Czech et al., 2015a). Similarly, adsorption isotherms were determined using FA 1–200 ppm TOC. Detailed procedure of sorption process was described in SI. Each concentration point, including blanks (i.e., without CNT) was run in duplicate.

2.4. Data analysis

Sorption kinetics was tested applying Lagergren and Ho-McKay models (pseudo-first and pseudo-second order) (Supporting Information). In the literature for the description of DOM sorption onto pristine CNT Freundlich or Langmuir models are often used (Liu et al., 2015; Zhang et al., 2015). In this study for determination of the sorption mechanism four often used and notable adsorption isotherms: Freundlich, Langmuir, Temkin and Dubinin–Radushkevich were applied (Supporting Information).

3. Results and discussion

3.1. Physicochemical properties of FA

The extracted FA were characterized by simple aliphatic composition, low molecular weight, low degree of aromatization, polymerization and the increased amount of side aliphatic chains what was confirmed by the high E₄/E₆ ratio (13.44). E₄/E₆ ratio expressed the degree of aliphaticity or aromaticity of humic substances and indicated for higher bioactivity (Cai et al., 2015). Obtained E₄/E₆ ratio was higher than observed by (Yang and Xing, 2009) (3.5–7.5) but similar to (Schwyzer et al., 2011) (8–11.04).

The presence of O–H and N–H containing groups was evidenced by stretching vibrations noted at 3400–3300 cm⁻¹ in FT-IR spectra (Fig. S1). It confirmed the occurrence of –OH in alcohols, phenols and acids. Peak at 3380 cm⁻¹ indicated the presence of hydrogen bonded –OH. The aliphatic character of FA was confirmed by the peaks at 2985 cm⁻¹ (stretching vibrations of CH₃ and CH₂ groups), 2940–2900 cm⁻¹ (aliphatic C–H) and 1460 cm⁻¹ (aliphatic C–H, C–H₃). The stretching vibrations of C=O (peak at 1725–1720 cm⁻¹) indicated for the presence of –COOH groups and ketones or the presence of C=O in peptides (1660–1630 cm⁻¹), amides (1650–1620 cm⁻¹) or aromatics (1610 cm⁻¹). The vibrations of –COO⁻ and C–H in aliphatic chains were observed at 1380–1320 cm⁻¹. Peak at 1250 cm⁻¹ represented the stretching vibrations of C–O in phenols, carboxylic acids, esters or deformation of –OH in –COOH. Lignin derived –OCH₃ and –OH in alcohols were noted at 1160–1030 cm⁻¹ indicating the presence of polysaccharides (Tan, 2003).

3.2. Kinetics of FA sorption

The results of FA adsorption onto CNTOHs and CNTCOOHs were presented in Figs. 1–4 and Tables 1–4. The experimental data were fitted into different kinetic models to study the adsorption rate and model the process (physisorption or chemisorption mechanism) (Mobasherpour et al., 2012).

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