



Insight into the heterogeneous adsorption of humic acid fluorescent components on multi-walled carbon nanotubes by excitation-emission matrix and parallel factor analysis

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ABSTRACT

The heterogeneous adsorption behavior of commercial humic acid (HA) on pristine and functionalized multi-walled carbon nanotubes (MWCNTs) was investigated by fluorescence excitation-emission matrix and parallel factor (EEM- PARAFAC) analysis. The kinetics, isotherms, thermodynamics and mechanisms of adsorption of HA fluorescent components onto MWCNTs were the focus of the present study. Three humic-like fluorescent components were distinguished, including one carboxylic-like fluorophore C1 ($\lambda_{ex}/\lambda_{em} = (250, 310) \text{ nm}/428 \text{ nm}$), and two phenolic-like fluorophores, C2 ($\lambda_{ex}/\lambda_{em} = (300, 460) \text{ nm}/552 \text{ nm}$) and C3 ($\lambda_{ex}/\lambda_{em} = (270, 375) \text{ nm}/520 \text{ nm}$). The Lagergren pseudo-second-order model can be used to describe the adsorption kinetics of the HA fluorescent components. In addition, both the Freundlich and Langmuir models can be suitably employed to describe the adsorption of the HA fluorescent components onto MWCNTs with significantly high correlation coefficients ($R^2 > 0.94$, $P < 0.05$). The dissimilarity in the adsorption affinity (K_d) and nonlinear adsorption degree from the HA fluorescent components to MWCNTs was clearly observed. The adsorption mechanism suggested that the π - π electron donor – acceptor (EDA) interaction played an important role in the interaction between HA fluorescent components and the three MWCNTs. Furthermore, the values of the thermodynamic parameters, including the Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), showed that the adsorption of the HA fluorescent components on MWCNTs was spontaneous and exothermic.

1. Introduction

Carbon nanotubes (CNTs) have attracted great attention due to their unique and outstanding optical, electrical, and mechanical properties (Kymakis et al., 2002). Thus, CNTs have been investigated widely in terms of their potential applications in energy storage, microelectronics, biomedicine and environmental remediation (Colvin, 2003; Engel and Chefetz, 2015; Liang and Chen, 2010; Upadhyayula et al., 2009). More than 2500 metric tons of CNTs was estimated to have been synthesized in 2010, and production was expected to exceed 12,800 metric tons in 2016 (Hao et al., 2016). However, more and more evidence has indicated that CNTs are toxic to organisms and human beings (Ema et al., 2016; Liu et al., 2012). The mechanisms of CNT toxicity are manifested as pulmonary toxicity (Fujita et al., 2015), dermal toxicity

(Witzmann and Monteiro-Riviere, 2006), cardiovascular toxicity (Yan et al., 2015), neurotoxicity (Gao et al., 2015), and oxidative stress and inflammation (Dong and Ma, 2016; Johnston et al., 2010). Hence, CNTs have been the object of increasingly serious concerns over their transport and fate in water environments, and their environmental and health impacts have been evaluated (Zhou et al., 2012).

Dissolved organic matter (DOM) is a heterogeneous mixture of dissolved substances found ubiquitously in natural aquatic systems, which was divided into allochthonous and autochthonous DOM (McIntyre and Guéguen, 2013). Once CNTs are released into aquatic environments, they will inevitably come into contact with DOM (Hyung and Kim, 2008), which may further alter the environmental behaviors of both DOM and CNTs (Engel and Chefetz, 2015; Kim et al., 2009; Li et al., 2016). The interactions of DOM with CNTs not only are leading to

Abbreviations: HA, Humic acid; MWCNTs, Multi-walled carbon nanotubes; EEM, Excitation-emission matrix; PARAFAC, Parallel factor; EDA, Electron donor – acceptor; DOM, Dissolved organic matter

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enhanced suspension stability and environmental mobility of CNTs by inducing steric and electrostatic repulsion between CNT individuals but will also influence the environmental behavior and biotoxicity of toxic substances, such as heavy metals and organic pollutants (Glomstad et al., 2016; Wang et al., 2008; Zhang et al., 2010). For example, the potential eco-risks of heavy metals would be amplified with the concentration of DOM-associated CNTs due to the complexation or ion exchange between DOM functional groups and metal ions (Lin et al., 2012b; Sheng et al., 2010). Therefore, understanding the interactions between CNTs and DOM, especially the adsorption of DOM on CNTs, is vital for further insight into the environmental implications and bioavailability of CNTs (Engel and Chefetz, 2015, 2016; Lin et al., 2012a).

In addition, the adsorption behaviors and mechanisms of DOM with CNTs were more complicated due to the chemical and structural heterogeneity of DOM, possibly leading to different DOM components selectively adsorbing to CNTs (Engel and Chefetz, 2015; Zhang et al., 2015). For instance, Hyung and Kim (2008) observed that the higher-molecular-weight fractions of DOM were preferentially adsorbed to CNTs. Yang and Xing (2009) concluded that aromatic-rich polar fulvic acid fractions readily adsorbed onto CNTs. The heterogeneous adsorption of DOM onto CNTs was demonstrated by the studies mentioned above, but the binding characteristics between various fractions of DOM and CNTs were not described in detail in their research. To eliminate the DOM complexity, several studies have employed appropriate simple organic molecules with different characteristics (e.g., molecular weight, hydrophobicity and polarity) as DOM surrogates, which promoted the understanding of the interaction mechanisms between DOM and CNTs (Li et al., 2014; Liu et al., 2013, 2012). Nevertheless, a simple DOM surrogate proved difficult to accurately describe the interactions between naturally occurring DOM components and CNTs. Recently, Engel and Chefetz (2015) investigated the interaction of five structural fractions of DOM (hydrophobic acid, hydrophobic neutral, hydrophilic acid, hydrophilic base and hydrophilic neutral) from composted biosolids with CNTs; the results demonstrated that the adsorption of DOM to CNTs was primarily dominated by the hydrophobic acid fraction, resulting in the relative enhancement of the hydrophilic character of non-adsorbed DOM. However, the process of DOM separation might lead to a decrease in DOM mass through the XAD resin, resulting in certain important components of the DOM being lost. Thus, it is necessary to further investigate the binding characteristics and mechanisms of different fractions of DOM with CNTs, which might be beneficial to provide in-depth information about the environmental fate and ecological risk of CNTs.

Fluorescence spectroscopy is a popular analytical tool for tracking the changes in the structures and composition of DOM because of its rapid, sensitive, non-destructive and in situ measurement (Baldwin and Valo, 2015). In particular, fluorescence excitation-emission matrix (EEM) spectroscopy can be viewed as an overall “fingerprint” of DOM, which covers the major components including the protein-like and humic-like compounds (Lu et al., 2013). However, the EEM data of DOM were complicated, resulting in the interpretation of data becoming difficult. Thus, parallel factor (PARAFAC) analysis, as one of the most advanced chemometric algorithms, was introduced to analyze complex spectroscopic data for comprehensively acquiring more details on the dynamics of DOM in a range of cases (Ishii and Boyer, 2012; Yamashita et al., 2008). Our previous studies also showed that EEM-PARAFAC can be readily used to identify the major fluorescent components of DOM from algae (Yang et al., 2016, 2017). Recently, EEM-PARAFAC analysis has been effectively employed to investigate the interaction of DOM with CNTs, indicating that various fluorescent components of DOM exhibited significantly different adsorption characteristics (Peng et al., 2016). However, the heterogeneous adsorption mechanisms of DOM fluorescent components on CNTs are rarely discussed.

Humic acid (HA), one of the major ingredients of DOM, has been shown to facilitate the transport and bioavailability of CNTs in the

environment. Additionally, the composition of HA is also complex. Moreover, a previous study demonstrated that the functionalities (e.g., -OH, -COOH, -NH₂ and -Ni) of CNTs played an important part in the adsorption of HA (Wang et al., 2013). Another study showed the effect that temperature has on the interactions of different DOM analogues with CNTs (Liu et al., 2013). Therefore, the main objective of this work was to investigate the adsorption characteristics and mechanisms of various fluorescent components of HA on pristine multi-walled CNT (MWCNT), hydroxylated MWCNT (MWCNT-OH) and carboxylated MWCNT (MWCNT-COOH) by EEM-PARAFAC analysis. In addition, the adsorption thermodynamics of HA fluorescent components on MWCNTs were also explored. The results of the present study are expected to promote the understanding of the heterogeneous interaction between DOM and CNTs, which can further provide valuable information on estimating the environmental behavior of DOM and predicting the environmental impacts of CNTs.

2. Materials and methods

2.1. Materials and characterization

MWCNTs were obtained from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. The outer diameter of the MWCNTs was less than 8 nm, and they were labeled MWCNT8, MWCNT8-OH and MWCNT8-COOH. The three MWCNTs (purity > 98%) were directly used in the experiments without further purification. Surface area, mesopore, and micropore volumes of the three MWCNTs were measured from N₂ adsorption-desorption isotherms at 77 K with a TRISTAR II3020 analyzer (Micromeritics, USA) and calculated by the Brunauer-Emmett-Teller (BET) method (Liu et al., 2012). Other parameters (Table S1) and the MWCNT images of transmission electron microscopy (TEM)/scanning electron microscopy (SEM) (Fig. S1) were provided by the manufacturer. Despite the lengths and outer/inner diameters of the three MWCNTs being similar, the surface areas of MWCNT8-OH and MWCNT8-COOH are larger than that of the pristine MWCNT8, and the pore volumes of MWCNT8-OH and MWCNT8-COOH are less than that of the pristine MWCNT8. Aldrich HA, which has been frequently used as a representative HA for investigating the binding properties of CNTs, was purchased from the Aldrich Chemical Co., and used without further purification. Some of the physical and chemical properties of the HA are seen in Supplementary material. An aliquot of the HA was dissolved overnight in 40 mL of NaOH (0.5 mol/L) under N₂ conditions. Two liters of background solution (200 mg/L NaN₃, 0.1 mol/L NaCl and pH = 7.0) was mixed with dissolved HA. Then, the pH of the HA solution was adjusted to 7.0 using 0.5 mol/L HCl and 0.5 mol/L NaOH. Finally, the HA solution was filtered through 0.45 μm filter membranes, and the filtrate was used as an HA storing solution. The concentration of the HA storing solution was measured on a TOC analyzer (TOC-L CPH, Shimadzu, Japan) and expressed as organic carbon content (mgC/L). The HA storing solution (148 mgC/L) was placed at 4 °C in the dark and used within one month.

2.2. Adsorption kinetics experiments

The adsorption kinetics of HA by MWCNTs was conducted using batch experiments in 40 mL glass vials sealed with Teflon-lined screw caps at 25 °C. The initial concentration of HA was diluted to 20 mgC/L by the background solution, and the amount of each MWCNTs was 100 mg/L, the pH of adsorption system was adjusted to 7.0 ± 0.1 by 0.1 mol/L HCl and 0.1 mol/L NaOH. Then, the vials were shaken on a rotary shaker (150 rpm) in the dark. The samples were centrifuged (3000 rpm for 10 min) at each time interval, and the supernatants were further filtered through a 0.45 μm hydrophilic polyethersulfone membrane filter. Finally, the concentration and characteristics of the HA filtrate were measured by UV-visible absorption spectroscopy and fluorescence spectroscopy. To avoid changing the solid-liquid ratio of

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