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Environmental reduction of carbon nanomaterials affects their capabilities to accumulate aromatic compounds

Fanfan Wang [a,b], Lin Duan [a,b], Fang Wang [a,c], Wei Chen [a,b,*]

[a] College of Environmental Science and Engineering, Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin 300071, China
[b] Key Laboratory of Environmental Remediation and Pollution Control, Nankai University, Wei Jin Road 94, Tianjin 300071, China
[c] Tianjin Key Laboratory of Water Resources and Environment, Tianjin Normal University, Tianjin 300387, China

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ABSTRACT

Carbon nanomaterials (e.g., graphene oxides and carbon nanotubes) may undergo chemical transformation in the environment, resulting in significant changes in surface chemistry properties. This will affect their capabilities to accumulate toxic contaminants and therefore, may alter their risk. Herein, we demonstrate that ferrous iron (i.e., Fe(II), an environmentally abundant, mild reductant) can significantly affect the capabilities of four common carbon nanomaterials—including graphene oxide (GO), reduced graphene oxide (RGO), hydroxylated multi-walled carbon nanotubes (OH-MWCNT), and carboxylated multi-walled carbon nanotubes (COOH-MWCNT)—to accumulate two model organic contaminants, phenanthrene and 1-naphthol. Reduction of carbon nanomaterials enhances adsorption of phenanthrene consistently, by increasing the surface hydrophobicity of carbon nanomaterials and by increasing π–π interactions, through partial restoration of the carbon graphitic structures, even though the extent of adsorption enhancement varied among different carbon nanomaterials. Interestingly, reduction of nanomaterials can either enhance or weaken adsorption of 1-naphthol, depending on the type and distribution of surface O-functionalities of a given carbon nanomaterial. The net effects depend on the overall contribution of enhanced hydrophobic effect and π–π interactions, as well as enhanced or weakened polar interactions between 1-naphthol and surface O-functional groups (e.g., H-bonding and cation-bridging by Fe^{2+}/Fe^{3+}). The findings underline the reactive nature of carbon nanomaterials and may have important implications for their risk assessment.

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1. Introduction

Carbon nanomaterials—in particular, graphene-based nanomaterials and carbon nanotubes (CNTs)—have shown great potentials in many areas of applications due to their excellent electronic, mechanical, optical and catalytic properties (Geim and Novoselov, 2007; Liu et al., 2013). To date, these materials have been used in a number of commercial products (De Volder et al., 2013; Segal, 2009). It was estimated that the annual production of multi-walled carbon nanotubes (MWCNTs) reached 390 tons in 2008 and 3400 tons in 2010 (Dahm et al., 2012). Similarly, the annual production of graphene-based nanomaterials was projected to exceed 200 tons by 2010 (Segal, 2009). With the fast growing carbon nanomaterial industry, the environmental release of carbon nanomaterials seems to be inevitable (Zhao et al., 2014).

There is a significant concern over the potential health risks of carbon nanomaterials (Hu and Zhou, 2013; Lam et al., 2006). In aquatic environments carbon nanomaterials can accumulate toxic contaminants —

numerous studies have shown that carbon nanomaterials are superb adsorbents for both organic molecules and heavy metals (Shen and Chen, 2015; Shi et al., 2010; Yang and Xing, 2010), with adsorption coefficients orders of magnitude greater than those of environmental geosorbents (e.g., natural organic matter and clay minerals). The strong affinities of carbon nanomaterials for toxic contaminants can drastically increase the risks of carbon nanomaterials, and may alter contaminant bioavailability (De La Torre-Roche et al., 2013; Petersen et al., 2009; Qu et al., 2013a; Zhao et al., 2014).

When released into the environment, carbon nanomaterials may undergo a series of physical and chemical transformation processes, as affected by sunlight irradiation, oxidants, reductants, and dissolved organic matter, to mention a few (Lowry et al., 2012; Bitter et al., 2014; Feng et al., 2015; Hou et al., 2015; Qu et al., 2013b; Zhao and Jafvert, 2015). These transformation processes can result in significant alteration of the surface chemistry of carbon nanomaterials, and consequently, can change the capabilities of carbon nanomaterials to accumulate toxic contaminants. For example, Hüffer et al. (2013) reported that irradiation under UV light increased the amounts of O-functional groups on C_{60}, resulting in decreased adsorption affinities of C_{60} nanoparticles for polycyclic aromatic hydrocarbons. In our previous studies, we observed that graphene oxide (GO) can be reduced by low concentrations

* Corresponding author at: College of Environmental Science and Engineering, Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria, Tianjin, China.
E-mail address: chenwei@nankai.edu.cn (W. Chen).

of sulfide and ferrous iron, resulting in significantly enhanced adsorption of phenanthrene, 1-naphthol and bisphenol A (Wang et al., 2015a, 2015b).

Note that carbon nanomaterials are often surface modified or derivitized. For example, CNT has been functionalized to introduce an array of surface functionalities, such as hydroxyl, carboxyl, and amino groups (Karousis et al., 2010). Similarly, GO can be chemically reduced to obtain reduced graphene oxide (RGO), and depending on the specific reducing agents used, RGO may have different surface properties, in terms of type and abundance of surface O-functional groups (Pei and Cheng, 2012). To date, environmental transformation of these functionalized/modified carbon nanomaterials, as well as the associated effects on their capabilities to accumulate toxic contaminants, are not well understood.

The objective of this study was to further understand how environmental reduction of carbon nanomaterials may affect their adsorptive interactions with common organic contaminants. Four different commercial carbon nanomaterials—including a GO, an RGO, a hydroxylated MWCNT (OH-MWCNT), and a carboxylated MWCNT (COOH-MWCNT)—were selected to represent carbon nanomaterials with different physicochemical properties. Ferrous iron, i.e., Fe(II), was selected as the reducing agent, on the basis of its abundance in the environment (e.g., sediment and anaerobic groundwater (Pecher et al., 2002), with concentrations as high as several mM (Stumm and Morgan, 1996)). The changes of nanomaterial surface properties from Fe(II) reduction were characterized. The reduction-induced changes in adsorption affinities of the carbon nanomaterials for phenanthrene (a model nonionic, nonpolar, hydrophobic molecule) and 1-naphthol (a model polar aromatic molecule) were examined and the governing mechanisms were analyzed. The environmental implications are discussed.

2. Materials and methods

2.1. Materials

Graphene-based nanomaterials (GO and RGO, >99%) were purchased from Nano Materials Tech Co. (China). Based on the information provided by the supplier, GO was synthesized using a modified Hummers method, and RGO was obtained by reducing GO using hydrazine hydrate. Functionalized MWCNTs (OH-MWCNT and COOH-MWCNT) were purchased from Organic Chemicals Co. (China). Based on the information provided by the manufacturer, OH-MWCNT and COOH-MWCNT were obtained by oxidizing high-purity MWCNT with $KMnO_4$ in H_2SO_4 solutions, at different acid concentrations and temperatures, and the outer diameters of the MWCNTs ranged from 8 to 15 nm, and the average length was approximately 50 μm.

Glass optical fibers coated with polyacrylate (thickness 35 μm; volume 15.4 μL/m) were purchased from Polymicro Technologies (USA). The fibers were cut to the desired length (generally 3–5 cm, depending on the expected partition coefficient), cleaned three times by shaking in 50:50 methanol/water ($v{:}v$), then washed with deionized (DI) water to remove the solvent, and then stored in DI water for further use.

Phenanthrene (99%) and 1-naphthol (99%) were purchased from Sigma-Aldrich (China). Selected physicochemical properties of the two compounds are given in Supplementary information (SI) Table S1. Stock solutions of the compounds were prepared in methanol, and stored at −20 °C. The inorganic salts ($FeSO_4 \cdot 7H_2O$, $NaH_2PO_4 \cdot 2H_2O$, and $Na_2HPO_4 \cdot 12H_2O$) were obtained from VICTOR Co. (China).

2.2. Characterization of carbon nanomaterials

Surface elemental compositions of the as-received carbon nanomaterials and Fe(II)-reduced carbon nanomaterials were determined with X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe, Japan). Fourier transform infrared transmission (FTIR) spectra of the as-received and reduced nanomaterials were obtained using a 110

Bruker TENSOR 27 apparatus (Bruker Optics Inc., Germany), with a carbon nanomaterials-to-KBr ratio of 1 to 100. Raman spectra were recorded with a Renishew inVia Raman spectrometer (RM2000, UK). Relative hydrophobicity of the as-received and reduced carbon nanomaterials was assessed using the method of Walker et al. (2005). The detailed procedures are given in SI. The type and distribution of surface functional groups of the MWCNTs were determined using Boehm titration (1966). The reduced carbon nanomaterials were washed repeatedly and dried at 25 °C before the analysis. The ζ potential of the carbon nanomaterial suspension (in DI water) was obtained by measuring the electrophoretic mobility at 25 °C (Petersen and Henry, 2012), using a ZetaPALS (Zetasizer Nano ZS90, Malvern Instruments, UK).

2.3. Adsorption experiments

The adsorption experiments were conducted using a previously developed method (Wang et al., 2014; Wang et al., 2015a), and the experimental protocols are summarized in SI Table S2. Prior to initiating an adsorption experiment, an aqueous suspension of a carbon nanomaterial (in DI Water) was purged with N_2 for at least 30 min to remove dissolved oxygen (Fu and Zhu, 2013). Then, the suspension was spiked with phenanthrene or 1-naphthol (in methanol), as well as a Fe^{2+} stock solution (pre-purged with N_2), if applicable, to give a Fe^{2+} concentration of 0.5 or 1.0 mM per 10 mg/L of carbon nanomaterials. For all the experiments, pH of the suspension was adjusted to neutral (using a NaH_2PO_4/Na_2HPO_4 buffer) (Wang et al., 2014). The suspension of carbon nanomaterials, contaminant, and Fe^{2+} (if applicable) were equilibrated for 7 d by tumbling at 8 rpm in the dark (Wang et al., 2014). Then, for samples involving GO and RGO, the aqueous phase concentrations of phenanthrene or 1-naphthol were measured using a fiber-enabled negligible depletion-solid-phase microextraction approach (Wang et al., 2015a; see SI for detailed procedures). For samples involving OH-MWCNTs and COOH-MWCNTs, the vials were left undisturbed for 12 h to allow complete settlement of the MWCNT (Yang et al., 2006; Chen et al., 2007; the settlement was also checked by examining the UV–vis absorbance of the suspensions (SI Fig. S1)). Then, the supernatant was taken to analyze the aqueous phase concentration. The concentrations adsorbed to the carbon nanomaterials were calculated based on a mass balance approach. A separate set of experiments was run following the same experimental setups mentioned above, but without the contaminants. These samples were used to characterize the physicochemical properties of the Fe(II)-reduced carbon nanomaterials.

2.4. Analytical methods

The concentrations of phenanthrene and 1-naphthol were determined using a Waters high performance liquid chromatography system equipped with a symmetry reversed-phase C18 column (4.6×150 mm). Phenanthrene was detected with a Waters 2475 fluorescence detector at an excitation wavelength of 250 nm and an emission wavelength of 364 nm; the mobile phase was methyl cyanide–DI water (80:20, $v{:}v$; 1.0 mL/min). 1-Naphthol was detected with a Waters 2489 UV/visible detector at wavelengths of 328 nm; the mobile phase was methyl cyanide–DI water (50:50, $v{:}v$; 1.0 mL/min). No peaks were detected in the spectra for potential degraded/transformed products of the test compounds (SI Fig. S2).

2.5. Modeling of adsorption data

The adsorption isotherms were fitted with both Freundlich model and Polanyi-theory based Dubinin–Ashtakhov (DA) model; the latter has been used to fit the adsorption data of organic molecules to MWCNTs (Yang and Xing, 2010). The Freundlich adsorption model is expressed as: $q = K_F \cdot C_W^n$, where q (mmol/kg) and C_W (mmol/L) are the equilibrium concentrations of an adsorbate on carbon nanomaterials