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Adsorption of polar, nonpolar, and substituted aromatics to colloidal graphene oxide nanoparticles

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ABSTRACT

We conducted batch adsorption experiments to understand the adsorptive properties of colloidal graphene oxide nanoparticles (GONPs) for a range of environmentally relevant aromatics and substituted aromatics, including model nonpolar compounds (pyrene, phenanthrene, naphthalene, and 1,3-dichlorobenzene) and model polar compounds (1-naphthol, 1-naphthylamine, 2,4-dichlorophenol, and 2,4-dinitrotoluene). GONPs exhibited strong adsorption affinities for all the test compounds, with distribution coefficients on the order of 10^3–10^6 L/kg. Adsorption to GONPs is much more linear than to carbon nanotubes (CNTs) and C_{60}, likely because GO nanoflakes are essentially individually dispersed (rendering adsorption sites of similar adsorption energy) whereas CNT/C_{60} are prone to bundling/aggregation. For a given compound GONPs and CNTs often exhibit different adsorption affinities, which is attributable to the differences in both the morphology and surface chemistry between the two nanomaterials. Particularly, the high surface O-content of GONPs enables strong H-bonding and Lewis acid–base interactions with hydroxyl- and amino-substituted aromatics.

1. Introduction

Graphene oxide (GO) is a new class of carbonaceous nanomaterial that has shown great promises in a number of applications, such as energy-related materials, sensors, biomedicines, to mention a few (Chen et al., 2012). The rapidly increasing production and use of GO will eventually cause its release into the environment, with unknown implications. GO contains a range of surface O-functionalities such as carboxyl, carbonyl, hydroxyl, and phenol groups (Bai et al., 2011; Li et al., 2009; Lu et al., 2011). These functional groups markedly increase the hydrophilicity of GO, making it easily dispersible in aqueous solution and stable under common environmental conditions (Dikin et al., 2007; Kim et al., 2010; Li et al., 2008). Recently, it has been shown that colloidal GO nanoparticles (GONPs) can be quite mobile in porous media (Feriancikova and Xu, 2012; Lanphere et al., 2013). An important implication is that GONPs can become an effective contaminant carrier, resulting in the enhanced transport and enhanced bio-uptake of an array of environmental contaminants (ter Laak et al., 2009; Zhang et al., 2011).

The capabilities of GONPs to alter the transport and bio-uptake properties of organic contaminants depend largely on the adsorption affinities of GONPs for organic contaminants. Thus far, only a few studies have been conducted to understand the adsorptive interactions between environmentally relevant organic contaminants and GO, and only GO powder (rather than true colloidal GONPs) has been used as the adsorbent (Gao et al., 2012; Pavagadhi et al., 2013; Pei et al., 2013). Pei et al. (2013) found that GO exhibited relatively strong adsorption affinities for naphthalene, 1,2,4-trichlorobenzene, 2,4,6-trichlorophenol, and 2-naphthol, with distribution coefficients, K_d, on the order of 10^2–10^3. They proposed that the adsorption of naphthalene and 1,2,4-trichlorobenzene was driven mainly by π–π interaction, whereas the stronger adsorption of 2,4,6-trichlorophenol and 2-naphthol on GO was attributable to H-bonding between the hydroxyl groups of 2,4,6-trichlorophenol/2-naphthol and the O-functionalities of GO. Gao et al. (2012) proposed that tetracycline can strongly adsorb to GO via π–π interaction and cation–π bonding. Pavagadhi et al. (2013) found that GO had higher adsorption capacity for microcystin-LR and microcystin-RR than a commercial activated carbon.

It is important to note that compared with GO powder, colloidal GONPs can exhibit very different aggregation properties and even

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surface properties, and both can profoundly affect their adsorptive interactions with organic contaminants. Even though this has not been tested systematically (to the best of our knowledge, there are no published data on the adsorption of organic contaminants to colloidal GONPs), insights can be drawn from related work on C_{60} and carbon nanotubes (CNTs), in that colloidal aggregates can behave very differently from their non-colloidal counterparts in terms of adsorption properties (Cheng et al., 2004; Hou et al., 2013; Zhang et al., 2012). For example, it has been reported that when well-dispersed, the adsorption affinities of C_{60} or CNTs is significantly enhanced, because more adsorption sites become available (Cheng et al., 2004; Zhang et al., 2012). In our previous study it was found that for well-dispersed oxidized multi-walled carbon nanotubes (O-MWNT), the cross-linking between surface O-functionalities is weakened, which increases the surface hydrophilicity and weakens the adsorption of phenanthrene (Hou et al., 2013). Thus, it is evident that dispersion properties of carbon nanoparticles play an important role in adsorption. Nonetheless, dispersion properties likely can affect the specific adsorption mechanisms of different carbon nanoparticles in very different ways.

The objectives of this study were to systematically examine the adsorption affinities of true colloidal GONPs for a range of environmentally relevant aromatic contaminants, to understand the overarching mechanisms controlling GONPs–organic interactions, and to compare the adsorption properties of GONPs with other carbonaceous nanomaterials such as CNTs and C_{60}. Eight aromatics or substituted aromatics with different physicochemical properties (aromaticity, polarity, functional groups, etc.) were selected as the test adsorbates. The adsorption affinities of GONPs for the test adsorbates were examined over wide concentration ranges covering several orders of magnitude, to fully examine the effects of dispersion/aggregation properties and surface chemistry on adsorption. A negligible depletion-solid-phase microextraction (nd-SPME) method was used to measure contaminant concentrations in the aqueous phase, without having to separate the colloidal GONPs from aqueous solution (Heringa and Hermens, 2003; ter Laak et al., 2006). The adsorption data were modeled with Freundlich isotherm and the governing mechanisms are discussed. The adsorption data to GONPs were compared with those to CNTs and C_{60}, and the mechanisms controlling the carbon-nanomaterial-specific adsorption properties are discussed. The environmental implications of the findings are also discussed.

2. Materials and methods

2.1. Materials

Graphene oxide (>99%) was purchased from Plan Nano Materials Tech Co. (Tianjin, China). Based on the information provided by the supplier, the product was synthesized using a modified Hummers method (Tung et al., 2009). The surface elemental composition was determined with X-ray photoelectron spectroscopy (MultiLab 2000, Thermo Electron Corp., England). Fourier transform infrared (FTIR) transmission spectra were obtained on GO powder mixed with KBr at a ratio of 1–100 using a Bruker TENSOR 27 apparatus (Bruker Optics Inc., Germany). The Brunauer–Emmer–Teller (BET) surface area of freeze-dried GONPs was calculated using the multipoint adsorption and desorption data of N_2 at 77 K in the region of 10^{-7}–1 relative pressure.

Glass optical fibers coated with polyacrylate (thickness 35 μm; volume 15.4 μL/m) were purchased from Polymicro Technologies (Phoenix, AZ, USA). The fibers were cut to the desired length (generally 3–5 cm, depending on the expected partition coefficient), and cleaned three times with 50/50 methanol/water (*v*/*v*) by shaking, then washed with ultrapure water (Millipore, Amsterdam, the Netherlands) to remove all the solvent, and stored in water until further use.

Pyrene (99%), phenanthrene (98%), naphthalene (99%), 1,3-dichlorobenzene (99%), 2,4-dichlorophenol (99%), 2,4-dinitrotoluene (97%), 1-naphthol (99%), and 1-naphthylamine (99%) were purchased from Sigma–Aldrich (Zwijndrecht, the Netherlands). Selected properties of the compounds are listed in Table 1. The stock solutions of the compounds were prepared by dissolving the respective compound in methanol, and the stock solutions were stored at −20 °C. The inorganic salts (NaCl, NaH_2PO_4, $Na_2HPO_4\cdot 12H_2O$) were obtained from Merck (Darmstadt, Germany).

Table 1
Summary of adsorbate properties [water solubility (C_{sat}), *n*-octanol–water partition coefficient (K_{OW}), *n*-hexadecane–water partition coefficient (K_{HW}), acid dissociation constant (pK_a), and polarizability (α)].

Adsorbate	C_{sat} (mmol/L)	Log K_{OW}	Log K_{HW}	pK_a	α[h] (cm^3)
Pyrene	6.92E-04[a]	5.13[a]	5.18[c]	–	2.87E-23
Phenanthrene	6.31E-03[a]	4.57[a]	4.74[d]	–	2.45E-23
Naphthalene	2.51E-01[a]	3.33[a]	3.41[d]	–	1.75E-23
1,3-Dichlorobenzene	8.32E-01[a]	3.47[a]	3.69[d]	–	1.44E-23
1-Naphthol	3.04E+00[b]	2.85[b]	0.553[e]	9.34[b]	1.82E-23
1-Naphthylamine	1.20E+01[a]	2.25[a]	1.20[f]	3.92[a]	1.92E-23
2,4-Dichlorophenol	2.69E+01[a]	3.09[a]	1.48[d]	7.85[a]	1.50E-23
2,4-Dinitrotoluene	1.38E+00[a]	2.00[a]	1.41[g]	–	1.75E-23

[a] From Schwarzenbach et al. (2003).
[b] From Mackay et al. (2006).
[c] From Qu et al. (2008).
[d] From Zhu and Pignatello (2005a).
[e] Measured in this study; average of six replicates.
[f] From Chen et al. (2008).
[g] From Zhu and Pignatello (2005b).
[h] Predicted by ACD Lab prediction software and available in the Chemspider database (http://www.chemspider.com/).

2.2. Preparation and characterization of GONPs

A stock suspension of GONPs (300 mg/L) was made by sonicating 0.3 g of GO powder in 1000 ml of 0.5 mM NaCl for 4 h. The obtained stock suspension was stored in the dark at 4 °C. The ζ potential of GONPs was measured by electrophoretic mobility, using a ZetaPALS (Brookhaven Instruments, Holtsville, NY). Dispersion properties of GONPs were examined with atomic force microscopy (AFM) analysis, using a J scanner of a Veeco Multimode Nanoscope VIII (Santa Barbara, CA). The detailed sample preparation methods are given in the Supporting Information (SI).

2.3. Procedure of negligible depletion-solid-phase microextraction

To determine the sorption coefficients to the fiber, the sorption isotherms of the eight adsorbates to the fiber were obtained. To initiate a fiber sorption experiment, first 20 ml of electrolyte solution was transferred to a 20-ml glass scintillation vial. A solution of 10 mM phosphate buffer (NaH_2PO_4/Na_2HPO_4, pH 5.82) was used for 2,4-dichlorophenol, 1-naphthol, and 1-naphthylamine, and 0.5 mM NaCl was used for the other compounds. Next, a stock solution of an adsorbate (in methanol) was added to the vial, and the volume percentage of methanol was kept below 0.1% (*v*/*v*) to minimize cosolvent effects. Then, a piece of fiber was added to the vial. The vial was capped and stirred on a Stuart Roller Mixer SRT9 (Staffordshire, United Kingdom) at 40 rpm in a dark room until sorption equilibrium was reached. The time required to reach sorption equilibrium was predetermined (see SI for the procedures used to measure the sorption kinetics of the compounds to the fiber; the results are shown in SI Fig. S1). Finally, the fiber was taken out, wiped with a wet tissue, and extracted with cyclohexane (for 1,3-dichlorobenzene) or methanol (for all other compounds) to analyze the mass of the adsorbate on the fiber. The aqueous solution was also extracted with cyclohexane or diluted with methanol to analyze the concentration of the compound in the dissolved phase. All experiments were run in duplicate. The sorption data were fitted with the linear sorption isotherm: $C_{fiber} = K_{fiber}\cdot C_W$, where C_{fiber} (mg/L) and C_W (mg/L) are the equilibrium concentrations of an adsorbate on the fiber and in the solution, respectively; K_{fiber} (L/L) is the fiber–water distribution coefficient. The fiber sorption isotherms are shown in SI Fig. S2, and the fitted K_{fiber} values are summarized in SI Table S1.

2.4. Adsorption isotherms of organic contaminants to GONPs

Prior to initiating a GONPs adsorption experiment, a stock suspension of 300 mg/L GONPs was diluted to obtain a 50 mg/L suspension of GONPs in 0.5 mM NaCl or in 10 mM phosphate buffer (NaH_2PO_4/Na_2HPO_4, pH 5.82); the buffer was used in the adsorption experiments of the ionizable adsorbates, and a quality control experiment was conducted to verify that the buffer had negligible effects on the adsorption of the non-ionizable adsorbates (see SI Fig. S3). A volume of 20 ml of the 50 mg/L GONPs suspension was subsequently transferred to a 20-ml amber glass vial. Then, the suspension was spiked with a test adsorbate (in methanol) and equilibrated as stated above. All the adsorbates were equilibrated with GONPs for 7 d. Afterward, fibers were exposed in GONPs suspensions and were allowed to equilibrate for 28 d (for pyrene and phenanthrene), 14 d (for 1,3-dichlorobenzene, naphthalene, and 2,4-dichlorophenol), or 5 d (for 2,4-dinitrotoluene, 1-naphthol, and 1-naphthylamine), respectively. Finally, the fibers were treated as described above to analyze the concentrations of the adsorbates on the fibers. The concentrations of freely dissolved compounds were calculated based on the concentrations on the fibers and the fiber–water distribution coefficients. The concentrations of the compounds on GONPs were calculated based on a mass balance approach. All