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Adsorption of halogenated aliphatic contaminants by graphene nanomaterials

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ABSTRACT

In this study, adsorption of ten environmentally halogenated aliphatic synthetic organic compounds (SOCs) by a pristine graphene nanosheet (GNS) and a reduced graphene oxide (rGO) was examined, and their adsorption behaviors were compared with those of a single-walled carbon nanotube (SWCNT) and a granular activated carbon (GAC). In addition, the impacts of background water components (i.e., natural organic matter (NOM), ionic strength (IS) and pH) on the SOC adsorption behavior were investigated. The results indicated HD3000 and SWCNT with higher microporous volumes exhibited higher adsorption capacities for the selected aliphatic SOCs than graphenes, demonstrating microporosity of carbonaceous adsorbents played an important role in the adsorption. Analysis of adsorption isotherms demonstrated that hydrophobic interactions were the dominant contributor to the adsorption of aliphatic SOCs by graphenes. However, π-π electron donor-acceptor and van der Waals interactions are likely the additional mechanisms contributing to the adsorption of aliphatic SOCs on graphenes. Among the three background solution components examined, NOM showed the most influential effect on adsorption of the selected aliphatic SOCs, while pH and ionic strength had a negligible effects. The NOM competition on aliphatic adsorption was less pronounced on graphenes than SWCNT. Overall, in terms of adsorption capacities, graphenes tested in this study did not exhibit a major advantage over SWCNT and GAC for the adsorption of aliphatic SOCs.

1. Introduction

Graphenes are two-dimensional single layered, sp^2 hybridized carbon atoms densely packed as a hexagonal honeycomb lattice and they can be visualized as basic building blocks for fullerenes, carbon nanotubes (CNTs) and graphite (Novoselov et al., 2004). The unique structure endows graphenes with outstanding mechanical, optical and electronic properties (Geim, 2009; Lee et al., 2008; Novoselov et al., 2005), which make them ideal candidates for a wide range of commercial applications. Commercial production and industrial scale application of graphenes are expected to grow exponentially over the next decades (Geim and Novoselov, 2007; Li and Kaner, 2008). However, due to their mass production, the release of carbonaceous nanomaterials (such as graphenes) into environment possess various health and environmental risks for plants, animals and humans (Nowack et al., 2012; Upadhyayula et al., 2009; Yu et al., 2014; Zhang et al., 2010a,b,c; Zhao et al., 2014). Furthermore, some of the

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negative impacts might be increased as a result of adsorbing synthetic organic compounds (SOCs) by these nanomaterials, and the fate and transport of SOCs in the environment can be altered.”.

Graphenes are hydrophobic nanomaterials with large specific surface areas (SSA); and they have been evaluated as promising adsorbents to remove SOCs from water (Zhao et al., 2011a,b; Ramesha et al., 2011; Ji et al., 2013; Sharma and Das, 2013; Li et al., 2012, 2013; Gao et al., 2012; Apul et al., 2013; Wu et al., 2011). In our previous study (Apul et al., 2013), graphenes were shown to have higher or comparable adsorption capacities to selected carbon nanotubes and granular activated carbons. In addition, the impact of NOM competition on the adsorption capacity of graphenes was less severe. Therefore, from an engineering perspective, graphenes may serve as novel and alternative adsorbents in engineered treatment system in future (Yu et al., 2015). To date, the majority of the tested SOCs were aromatic compounds; and no study has examined the adsorption of aliphatics by graphenes. Several aliphatic SOCs are common organic pollutants that were either regulated by United States Environmental Protection Agency (US EPA) under Priority Pollutants List (e.g., trichloroethylene, tetrachloroethylene, 1,1-dichloroethylene) or listed under Candidate Contaminant List 3 (CCL3) (e.g., 1,1,1,2-tetrachloroethane, 1,1-dichloroethane). Given the paucity of data on this topic in literature, it is important to understand adsorption of aliphatic SOCs by graphenes to adequately assess the environmental impact and engineering applications of graphenes. Therefore, the main objectives of this study were to (i) investigate the factors controlling adsorption of halogenated aliphatic SOCs by graphenes in terms of adsorbent characteristics, adsorbate properties and background solution chemistry, and to (ii) evaluate the application potential of graphenes as alternative adsorbents in treatment systems by comparing their adsorption capacities with those of single-walled carbon nanotubes (SWCNT) and granular activated carbon (GAC).

2. Materials and methods

2.1. Adsorbents

Four carbonaceous adsorbents: pristine graphene nanosheets (GNS, Angstron Materials Inc.), reduced graphene oxide (rGO, Graphenea CO., Ltd.), SWCNT (Chengdu Organic Chemcials Co., Ltd.) and GAC (HD3000, Norit Inc.) were used. GNS, rGO, and SWCNT were used as received from the manufacturers, while HD3000 was ground to 200–325 μm mesh size prior to use. Selected physicochemical properties of the four carbonaceous adsorbents are summarized in Table 1.

2.2. Adsorbates

Ten aliphatic SOCs with different properties were purchased from Acros (PCE, >99%), Fluka (12DCP, >99%; 12DBE, >98%), Matrix Scientific (DBCP, > 98%), Alpha Easer (TCE, >99.5%), TCI (1112TeCA, >99%), Baker Analytical (111TCA, >96.7%) and Sigma Aldrich (112TCA, >96%; 11DCE, >99%; CCl_4, >99.9%). All of these aliphatic SOCs represented common organic pollutants that were either listed under Priority Pollutants List or CCL3, and they differ in molecular size, hydrophobicity, number of double bonds, and polarizability. Therefore, they were employed as probe molecules to cover some typical adsorbate–adsorbent interactions. Abbreviations, properties and molecular structures of the aliphatic SOCs are summarized in Table 2 and S1 in Supporting Information.

2.3. NOM solution

The natural organic matter (NOM) was isolated from the influent of Myrtle Beach drinking water treatment plant in South Carolina using a reverse osmosis and followed by resin fractionation, as described elsewhere (Song et al., 2009). $SUVA_{254}$, defined as the ratio of UV absorbance at 254 nm divided by the dissolved organic carbon (DOC) concentration, is a quantitative measurement of the aromatic content per unit concentration of organic carbon in water (Karanfil et al., 2003). Natural waters with high $SUVA_{254}$ values (e.g., more than 4.0 L/mg-m) have organic matter with relatively high contents of hydrophobic, aromatic, and high molecular weight components, whereas waters with low $SUVA_{254}$ values (e.g., less than 2.0 L/mg-m) contain mostly non-humic, hydrophilic and low molecular weight material. The $SUVA_{254}$ value of the NOM solution used was around 4.0 L/mg-m, indicating it was rich in aromatic components.

2.4. Characterization of adsorbents

Several techniques were used for the characterization of carbonaceous adsorbents. Nitrogen gas adsorption at 77 K was performed with a physisorption analyzer (Micromeritics ASAP

Table 1 – Physicochemical properties of adsorbents.

Adsorbent	SSA_{BET}[a] m^2/g	V_T[b] cm^3/g	DFT pore volume distribution[c]			Oxygen content %	pH_{pzc}
			V_{micro} (<2 nm) cm^3/g, (%)	V_{meso} (2–50 nm) cm^3/g, (%)	V_{macro} (>50 nm) cm^3/g, (%)		
GNS	666	3.138	0.065, (2.1)	1.196, (38.1)	1.877, (59.8)	0.8	9.8
rGO	497	0.530	0.081, (15.3)	0.377, (71.1)	0.072, (13.6)	17.5	4.1
SWCNT	537	1.240	0.117, (9.4)	0.581, (46.9)	0.542, (43.7)	0.9	7.5
HD3000	642	0.775	0.108, (13.9)	0.449, (57.9)	0.218, (28.1)	3.4	6.9

[a] Specific surface area calculated with the Brunauer-Emmett-Teller (BET) model.
[b] Total pore volume calculated from single point adsorption at $P/P_0 = 0.99$.
[c] Pore volume in each pore size range obtained from the density functional theory (DFT) analysis.