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## Adsorption of organic contaminants by graphene nanosheets, carbon nanotubes and granular activated carbons under natural organic matter preloading conditions

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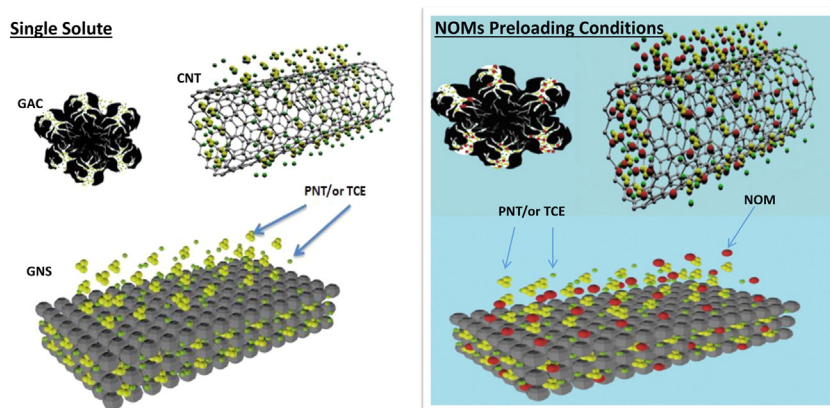
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### HIGHLIGHTS

- The impact of NOM preloading on OC adsorption by GNS, CNTs and GACs was examined.
- PNT uptake was higher than TCE by all adsorbents.
- The presence of NOM reduced the OC uptake of all adsorbents.
- NOM competition decreased with increasing equilibrium concentration of OCs.
- At similar DOC levels, NOM characteristics did not make a difference on OC adsorption.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The effect of NOM preloading on the adsorption of phenanthrene (PNT) and trichloroethylene (TCE) by pristine graphene nanosheets (GNS) and graphene oxide nanosheet (GO) was investigated and compared with those of a single-walled carbon nanotube (SWCNT), a multi-walled carbon nanotube (MWCNT), and two coal based granular activated carbons (GACs). PNT uptake was higher than TCE by all adsorbents on both mass and surface area bases. This was attributed to the hydrophobicity of PNT. The adsorption capacities of PNT and TCE depend on the accessibility of the organic molecules to the inner regions of the adsorbent which was influenced from the molecular size of OCs. The adsorption capacities of all adsorbents decreased as a result of NOM preloading due to site competition and/or pore/interstice blockage. However, among all adsorbents, GO was generally effected least from the NOM preloading for PNT, whereas there was not observed any trend of NOM competition with a specific adsorbent for TCE. In addition, SWCNT was generally affected most from the NOM preloading for TCE and there was not any trend for PNT. The overall results indicated that the fate and transport of organic contaminants by GNSs and CNTs type of nanoadsorbents and GACs in different natural systems will be affected by water quality parameters, characteristics of adsorbent, and properties of adsorbate.

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## 1. Introduction

Graphene nanosheets (GNSs) are two-dimensional sheet of sp<sup>2</sup>-hybridized carbon. Its extended honeycomb network is the basic building block of other important allotropes; it can be stacked to form 2-D graphite, rolled to form 1-D carbon nanotubes (CNTs), and wrapped to form 0-D fullerenes. Long-range  $\pi$ -conjugation in graphene yields extraordinary thermal, mechanical, and electrical properties, which have long been the interest of various researchers (Allen et al., 2010).

GNSs and CNTs are hydrophobic nanomaterials, and have also been considered as promising adsorbents due to their structure and high adsorption affinity towards different organic contaminants (OCs) in water (Stoller et al., 2008; Ramesha et al., 2011; Zhang et al., 2010, 2011; Zhao et al., 2011; Wu et al., 2011; Gao et al., 2012; Apul et al., 2013, 2015; Wang et al., 2014; Beless et al., 2014; Yu et al., 2015). CNTs and GNSs carry similar surface functional groups, however exhibit significant differences in pore structure and aggregation behavior, as compared to conventional granular activated carbons (GACs). Graphene oxide nanosheets (GO) are obtained by modification of GNS with covalently bonding oxygen containing functional groups. The oxygen containing functional groups decrease the surface hydrophobicity while increasing the dispersion of GO in water; both characteristics affecting its adsorption behavior as well (Apul et al., 2013).

Natural organic matter (NOM) is ubiquitous in natural waters, thus the interactions between NOM and carbon based nanomaterials are inevitable, and NOM may change their adsorption behavior of organic contaminants. Two opposing factors play roles in adsorption in the presence of NOM: accessible surface area of the carbon nanomaterials may increase due to their better dispersion, whereas the adsorption capacity may decrease because of competition by NOM with OCs through site competition and/or pore/interstice blockage (Hyung and Kim, 2008; Zhang et al., 2011; Apul et al., 2013). Previously, the effect of NOM on OCs adsorption by GACs and CNTs in aqueous solutions has been investigated, and it has been found to be a complex function of NOM types, NOM preloading conditions as well as charge, size and polarity of OCs, and the pore structure and surface chemistry of adsorbents (Carter et al., 1995; Karanfil et al., 2006; Pignatello et al., 2006a, 2006b; Lin and Xing, 2008a, 2008b; Wang et al., 2008, 2009; Zhang et al., 2010, 2011). However, only a limited number of studies has examined the effect of NOM on the adsorption of aromatic compounds (e.g., Chen et al., 2008; Apul et al., 2013; Zhu et al., 2015), and only one study on adsorption of aliphatic compounds (Zhou et al., 2015) by GNSs. Therefore, there is still a need for further understanding of the adsorption of OCs by GNSs to adequately assess the environmental impact and engineering applications of GNSs. The main objectives of this study were to (i) evaluate the adsorption of OCs by GNSs in distilled and deionized water (DDW) and under NOM preloading conditions, and (ii) compare side-by-side the adsorption behavior of GNS and GO with those of a single-walled carbon nanotube (SWCNT), a multi-walled carbon nanotube (MWCNT) and two GACs (F400 and HD3000).

## 2. Materials and methods

### 2.1. Materials

The adsorbents used in this study included one pristine GNS and GO (Graphene Laboratories Inc.), one SWCNT (Chengdu Organic Chemicals Co., Ltd.), one MWCNT (Nanostructured & Amorphous Materials Inc.) and two coal based GACs (HD3000, Norit Inc. and F400, Calgon Inc.). GNSs and CNTs were used as received from the manufacturers, while the GACs were ground to 250–325  $\mu$ m particle size prior to use.

Phenanthrene (PNT, 99.5%) and trichloroethylene (TCE, 99%) were selected as the target OCs and obtained from Fluka/Sigma-Aldrich Chemical Co. The selected properties of PNT and TCE are provided in Table S1 in Supporting information.

Four different NOM solutions were used in the experiments (Table 1). The first three were NOM isolates that were collected from the influent of drinking water treatment plants in South Carolina using reverse osmosis and followed by resin fractionation, as described elsewhere (Song et al., 2009). Use of NOM isolates allowed conducting the NOM preloading experiments at the same initial dissolved organic concentration. The last NOM solution was a water sample that was collected from a local reservoir (Bushy Park, SC). The SUVA<sub>254</sub> values of NOM isolates and local reservoir water were between 1.6 and 4.9 L/mg-m. Therefore, the four NOM solution used in this study had different degrees of aromaticity. All NOM solutions were added with phosphate buffer (adjusted to pH 7.0  $\pm$  0.3) and NaN<sub>3</sub> as biocide immediately after collection or preparation, and stored in dark at a refrigerator (~4 °C) until the experiments. According to our previous studies, pH exhibited negligible effects on the adsorption of non-ionic PNT and TCE by GNSs, CNTs and GACs in single solute (Zhang et al., 2010; Zhou et al., 2015). In this study, pH of all solutions was kept constant at pH 7. However, further research is needed to investigate the effect of pH on OCs adsorption by carbonaceous adsorbents in the presence of NOM.

### 2.2. Characterization of adsorbents

Various characterization methods were used to determine physical and chemical characteristics of adsorbents. The oxygen contents of adsorbents were analyzed by using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation). The value of pH of point of zero charge (pH<sub>PZC</sub>) of each adsorbent was determined. The BET surface areas, pore volumes and pore size distributions were measured from nitrogen physisorption data at 77 K obtained with ASAP 2020 analyzer (Micromeritics Instrument Corp. U.S.). The details for these characterization techniques have been provided in our previous publications (Dastgheib et al., 2004; Karanfil and Dastgheib, 2004).

### 2.3. Isotherm experiments

#### 2.3.1. Single-solute experiments

Constant dose batch adsorption isotherms for PNT and TCE were conducted by using amber bottles with Teflon lined screw caps at room temperature (20  $\pm$  2 °C). PNT and TCE stock solutions were prepared in methanol, where the methanol level was kept below 0.1% (v/v) to minimize the co-solvent effect. The background solution contained 1 mM phosphate buffer solution (adjusted to pH 7.0  $\pm$  0.3) in distilled and deionized water (DDW) and 200 mg/L NaN<sub>3</sub> as biocide. For the investigation of phosphate buffer and NaN<sub>3</sub> effects on the OCs adsorption, PNT experiments were presented with or without buffer and NaN<sub>3</sub> as an example in Fig. S1. The results showed that there is no significant difference with or without buffer and NaN<sub>3</sub>.

**2.3.1.1. PNT experiments.** 1 mg of GNSs, CNTs, and GACs were added in 255 mL bottles. The experiment bottles were first filled with background solution with no free headspace, and then spiked with predetermined (ranging from 0.03 to 1 mg/L) trace concentrations of PNT from the stock solution.

**Table 1**  
Selected characteristics of NOM solutions.

Code	NOM	pH	UV <sub>254</sub>	DOC	SUVA <sub>254</sub>	DON
CH	Isolated-TPH <sup>a</sup>	7.05	0.0510	3.2	1.6	0.226
CH	Isolated-HPO <sup>a</sup>	7.01	0.1258	3.0	4.3	0.086
MB	Isolated-HPO <sup>a</sup>	7.04	0.1580	3.2	4.9	0.124
BP	Reservoir water	7.03	0.1179	3.4	3.4	0.138

CH: Charleston, MB: Myrtle Beach and BP: Bushy Park; DOC: dissolved organic carbon (mg/L), SUVA<sub>254</sub>: specific UV absorption (UV<sub>254</sub>/DOC, L/mg-m), and DON: dissolved organic nitrogen(mg/L).

<sup>a</sup> As described elsewhere (Karanfil, et al., 2003 and Song et al., 2009).

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