1 **Adsorption of Organic Contaminants by Graphene Nanosheets, Carbon**
2 **Nanotubes and Granular Activated Carbons under Natural Organic Matter**
3 **Preloading Conditions**

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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.

Keywords: Adsorption, Graphene, Carbon Nanotubes, Granular Activated Carbon, Natural Organic Matter, Organic Contaminants

1. Introduction

Graphene nanosheets (GNSs) are two-dimensional sheet of sp^2 -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 π -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 (Zhang et al., 2011, 2012; Apul et al., 2013; Ji et al., 2013; Wang et al., 2014; Beless et al., 2014). 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 (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 and Kilduff, 1999; Karanfil et al., 2006; Lin and Xing, 2008; 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 (Zhao 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 μm 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 $SUVA_{254}$ values of NOM isolates and local reservoir water were between 1.6-4.9 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_3 as biocide immediately after collection or preparation, and stored in dark at a refrigerator ($\sim 4^\circ C$) 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 were 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_{PZC}) 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

(i) *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 ($20 \pm 2^{\circ}\text{C}$). 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 $\text{pH } 7.0 \pm 0.3$) in distilled and deionized water (DDW) and 200 mg/L NaN_3 as biocide. For the investigation of phosphate buffer and NaN_3 effects on the OCs adsorption, PNT experiments were presented with or without buffer and NaN_3 as an example in Figure S1. The results showed that there is no significant difference with or without buffer and NaN_3 .

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.

TCE experiments: 5 mg of GNSs, SWCNT and GACs were added in 125 mL bottles, and 25 mg of MWCNT was added in 65 bottles. The experiment bottles were filled with background

solution with no free headspace, and then spiked with predetermined (ranging from 0.03 to 3 mg/L) trace concentrations of TCE from the stock solutions.

The PNT and TCE isotherm bottles were then placed on a tumbler. The equilibrium time of PNT and TCE isotherm bottles was seven days for all adsorbents, which was proved to be sufficient to reach equilibrium by preliminary kinetic experiments (Zhang et al. 2009; Apul et al., 2013; Zhou et al., 2015).

(ii) *Preloading experiments:*

For preloading experiments, predetermined masses of adsorbent were transferred to isotherm bottles as described above for the single solute experiments and contacted for four days with NOM solution buffered with 1 mM phosphate buffer solution (adjusted to $\text{pH } 7.0 \pm 0.3$) and 200 mg/L NaN_3 as biocide. All preloading experiments were carried out with the same DOC level of NOM solution (~ 3 mg/L DOC). Thereafter, predetermined volumes of OCs stock solution were spiked into the bottles. The PNT and TCE isotherm bottles were then placed on a tumbler for seven days.

At the end of equilibrium period, 10 mL of samples were centrifuged to remove the adsorbents, and the supernatants in bottles were analyzed for PNT concentration using high performance liquid chromatography (HPLC) equipped with UV and fluorescence detector. For TCE detection, the upper aqueous phase was extracted with hexane and analyzed by gas chromatography (GC) coupled with micro electron-capture detection (μECD). Bottles without adsorbent were used as blanks to monitor the loss of adsorbates during the experiments, which were found to be negligible. Typically, PNT and TCE compounds are measured effectively to less than 0.03 ppb, when the blank samples were compared with their adsorption isotherms.

2.4. Isotherm modeling

In this study, four different nonlinear isotherm models, Freundlich (FM), Langmuir (LM), Langmuir-Freundlich (LFM) and Polanyi-Manes (PMM), were evaluated for data fitting (Table S3). Residual root-mean-square error (RMSE) and coefficient of determination (r^2) values for all models are provided in Table S3. Of the studied models, FM exhibited comparable goodness of fit to the experimental data which was in most cases better than LM, LFM and PMM. Therefore, FM parameter values were used in data analyses.

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

The selected physicochemical properties of all adsorbents were characterized and the results are presented in Table 2. The significant differences among their structure characteristics were indicated by their surface area and pore volume distributions. The BET surface areas of the adsorbents followed the order of: F400 > GNS ~ HD3000 > SWCNT > GO > MWCNT. The GNS had 2.5 times higher pore volume than SWCNT and 4.2 times higher pore volume than MWCNT, which may be attributed to their much less compact aggregate and bundle structures as compared to CNTs (Apul et al., 2013). The GNS, SWCNT and MWCNT had mainly consisted of meso- and macropores, while GO, HD3000 and F400 consisted of micro- and mesopores. While GOs had the highest oxygen content (11.1%), the lower oxygen content (0.5%) of MWCNTs was the lowest as compared to other adsorbents. The low pH_{PZC} values indicated that GO had acidic surface characteristics, while GNS, MWCNT, and F400 were basic carbons. The pH_{PZC} values of HD3000 and F400 was close to neutral pH.

3.2. Single-Solute Adsorption Isotherms

Adsorption isotherms of PNT and TCE by six adsorbents in DDW were presented in Figure 1, and the Freundlich isotherms parameters were listed on Table 3. The single point adsorption descriptors, K_d values (q_e/C_e) at three different equilibrium concentrations (i.e. at 10, 100 and 500 $\mu\text{g/L}$) were calculated and their actual values were presented on Table S4. There was a higher PNT uptake than TCE by all adsorbents on a mass and surface area basis, also as indicated by the Freundlich K_F parameter (Table 3). This was attributed to the difference in their molecular properties (Table S1). PNT is a hydrophobic OC with lower water solubility (1.1 mg/L) and higher log octanol-water partition coefficient (4.68) than TCE with water solubility of 1280 mg/L and a log octanol-water partition coefficient of 2.42.

The order of PNT and TCE single point adsorption coefficients represented by K_d at 500 $\mu\text{g/L}$ was $\text{GNS} > \text{HD3000} > \text{GO} > \text{SWNT} > \text{MWNT} > \text{F400}$, and $\text{HD3000} > \text{F400} > \text{SWNT} > \text{GNS} > \text{GO} > \text{MWCNT}$, respectively. At lower equilibrium concentrations (e.g., $K_{d,10}$) the order of PNT and TCE uptakes changed to $\text{GNS} > \text{HD3000} > \text{GO} > \text{SWCNT} \sim \text{MWCNT} > \text{F400}$, and $\text{HD3000} \sim \text{SWCNT} > \text{F400} > \text{GNS} > \text{GO} > \text{MWCNT}$, respectively (Table S4). In addition, K_d values at different equilibrium concentrations showed that PNT uptake was decreasing more than TCE uptake with increasing equilibrium concentrations for all carbons (Table S4), probably due to strong hydrophobic interactions and π - π bonding between PNT molecules and the open layer graphene surface.

GO exhibited lower OCs uptake than GNS, which was attributed to more polar surface of GO as suggested by its high oxygen content and low pH_{PZC} value. Polar regions on GO reduces adsorption of OCs due to water cluster formation around polar groups of GO. Water molecules can interact with polar surface functionalities of graphene surface via hydrogen bonding. Yang

et al., (2009) suggested that the removal of naphthalene, chlorophenol, and resorcinol can be suppressed by water cluster formation of oxidized CNTs surface. Since oxygen-containing groups on CNT surface are hydrophilic, they can form strong H-bonds with water molecules, which result in the reduction of especially hydrophobic organic compounds (Apul et al., 2013).

In order to examine the impact of surface area and molecular dimension of OCs on the adsorption, all isotherms were normalized by total surface area, and the surface areas in pores 5-8 Å and 5-13 Å (Figure 1). Total surface area normalization decreased the differences in adsorption capacities of PNT indicating that specific surface area (SSA) plays an important role on the adsorption of PNT (Figure 1b). On the other hand, similar normalization for TCE still resulted in notable differences among the isotherms. Different than PNT, three microporous adsorbents (SWCNT, F400 and HD3000) showed highest TCE uptake on both mass and surface area bases. This can be due to dominating pore-filling mechanism because there are plenty of high-energy sites in micropores. It has been reported that micropore-filling is a key mechanism affecting adsorption of small molecular weight organic compounds by porous adsorbents (e.g., Karanfil and Kilduff, 1999; Wang et al., 2007). In addition, isotherms were normalized with surface areas and pore volumes in different pore size regions. When the PNT isotherms were normalized with the surface area and pore volumes in pores 5-13 Å, all isotherms almost lined up much closer to each other except MWCNT which had a very small amount of micropores (Figure 1c and Figure S1-a). On the other hand, TCE adsorption isotherms lined up on a single trend line except micropores adsorbents when normalized with the surface area and pore volume in pores 5-8 Å (Figure 1d and Figure S2-b). Overall, the results showed that the adsorption capacity depended on the accessibility of the organic molecules to the inner regions of the adsorbent which was influenced from the molecular size of OCs.

3.3. Adsorption under Preloading Conditions by Different NOMs

Adsorption isotherms of PNT and TCE under NOM preloading by the six adsorbents are shown in Figure 2 and the corresponding Freundlich isotherm parameters are listed on Table 3. PNT and TCE adsorption isotherms of all preloaded adsorbents showed that the adsorptions of OCs were reduced as compared to their single-solute isotherms. The reductions of PNT and TCE adsorption capacity can be attributed to NOM competition with OCs by either site competition or pore/interstice blockage. The single point adsorption descriptors, K_d values at three different equilibrium concentrations for different NOMs are also provided in Table S4. In addition, the percent reductions of K_d values under different NOM preloading conditions (i.e., as compared to K_d in single solute) were calculated and provided in Table S5. The impact of NOM competition decreases with increasing equilibrium concentration of PNT and TCE (with a few exceptions, underline in Table S5. During preloading, NOM occupies high energy sorption sites. Adsorption of OCs is effected less from NOM preloading with increasing OCs concentration. This is attributed to OCs competition for limited sorption sites at elevated concentrations. Besides, no clear trends were observed on the PNT and TCE adsorption by GNSs, CNTs and GACs by changing background NOM types (i.e., hydrophobic, vs hydrophilic, isolated vs reservoir water and aromatic content). This may be due to the similar DOC concentration of NOM isolated solutions and reservoir water (3 ± 0.4 mg DOC/L).

Among all adsorbents, GO was generally effected least from the NOM preloading for PNT (see Figure 2 and Table S5). Apul et al., (2013) reported that the polarity of surface oxides results in better dispersion of GO in water reducing the influence of NOM on the OCs uptake, and/or the presence of oxygen functional group resulted in less NOM coating on the GO surface because of electrical repulsion between negatively charged NOM molecules and acidic GO

surfaces. For TCE, there was not an overall trend of NOM competition for a specific adsorbent. In addition, GO generally has lower PNT and TCE uptake than GNS which was attributed to more polar surface of GO. SWCNT was generally affected most from the NOM preloading for TCE and there was not a trend for PNT. The reduction in TCE uptake was lower than PNT for preloaded adsorbents. The presence of electron withdrawing groups (Cl⁻) on the TCE molecule would be expected to increase the interactions of the adsorbate with carbon surfaces having high electron density (Brooks et al., 2012).

The adsorption of PNT and TCE under NOM preloading conditions was showing differences on the same adsorbents. This was attributed to the stronger hydrophobic interactions and π - π bonding between the carbon nanomaterial surface and PNT molecules instead of NOM. Gotovac et al., (2007) reported that the adsorption behaviors of PNT and tetracene by using SWCNTs was remarkably different. Tetracene is a long four-ring molecule with a large π -electron system, which makes it more suitable for adsorption by π - π interactions along the nanotube axis than PNT. Hence, this difference may be associated with the molecular size and geometry difference between the molecules. The preloaded NOM molecules could have competed for sites with OCs on the SWCNT. And also, SWCNTs are extremely hydrophobic and prone to aggregation due to the strong van der Waals interactions along the length axis (Girifalco et al., 2000). Besides, PNT has more competition with NOM than TCE due to their molecular properties (e.g. molecular size and hydrophobicity). On the contrary, MWCNT was one of the least affected from the NOM preloading for PNT and TCE adsorption isotherms which had a very small amount of micropores (Table S5).

The adsorption of small molecules (TCE) by using GACs were less affected than large molecules (PNT) under different types of NOM solution (Figure 2). However, TCE molecules

have smaller molecular size than NOM, and TCE molecules are able to penetrate into pore throats in carbonaceous adsorbents, whereas most of the NOM molecules are too large to diffuse deeply into the pores of adsorbents. As the micropores increase in size, there is a continuous transition towards a surface (or multi-layer) adsorption mechanism (Pelekani and Snoeyink, 2000; Menendez-Diaz and Martin-Gullon, 2006). Karanfil et al. (2006) emphasized that if the pore size region less than 10 Å its critical for adsorption of small molecule OCs (e.g., TCE), the microporous adsorbents are expected to act as a molecular sieve and may minimize competition from the NOM, as long as NOM molecules do not completely block the adsorbent pores and/or the OC is able to diffuse by the adsorbed NOM at the pore entrances. As seen in Figure 2, HD3000 and F400 act as a molecular sieve and PNT adsorption decreased notable. Therefore, the impact of different types of NOM preloading on the adsorption of PNT was smaller on GNS and CNTs than GACs. This was attributed to microporous structure of GACs.

In literature, several studies have investigated the effect of NOM on the adsorption of different OCs by GNSs, CNTs and/or GACs (i.e., Carter and Weber, 1994; Wang et al., 2008; Zhang et al., 2010, 2011; Apul et al., 2013; Zhou et al., 2015 etc.). The Freundlich isotherm parameters of OCs reported in literature were summarized in Table S6. These results showed that the presence of NOM in the background reduces the OC uptake by all adsorbents. The adsorption behavior of all OCs by GNSs, CNTs and/or GACs under NOM preloading conditions was also remarkably different due to either their molecular structure (planarity, flexibility, hydrophobicity etc.) and/or adsorbent type (specific surface area, pore volume, pore size distribution and functional groups etc.). The adsorption of biphenyl (non-planar and flexible structure) was less affected by NOM preloading as compared to PNT molecules (planar and rigid) (Apul et al., 2013). Besides, NOM competition was more severe on the 2-phenylphenol (nonplanar and

hydrophilic) than PNT (planar and hydrophobic) (Zhang et al., 2010; 2011). Furthermore, the impact of NOM on the adsorption of OCs was smaller on GNSs than CNTs and GAC, which was attributed to less hindrance of OC molecules to adsorption sites on sheet-like GNSs. This difference was attributed to the total pore volumes and surface structure of GNS. Overall, the results suggested that the competitive mechanisms between NOM and OCs were controlled by not only NOM, but also the molecular properties of OCs and characteristics of adsorbent.

The Freundlich nonlinear index n value indicates the heterogeneity of the surface and a higher n value is indicative of a homogeneous surface with narrow adsorption site distributions (Carter et al., 1995). The change in the Freundlich n values of six adsorbents as a result of NOM preloading for PNT and TCE are shown on Table 3. After NOM preloading, the Freundlich n values of all adsorbents (except F400) increased for PNT and TCE adsorption, suggesting that NOM molecules were expected to compete and/or occupy the high-energy sites, leading to a reduction of surface heterogeneity (Yang et al., 2010; Zhang et al., 2011). The Freundlich n values of all OCs adsorption were increased for GNSs, CNTs and GACs in the presence of NOM. The increases in the n values of all adsorbents suggest the NOM coating significantly change the surface heterogeneity of GNSs, CNTs and GACs.

Overall, the impact of different NOM types on the PNT and TCE adsorption isotherms of all preloaded adsorbents were not likely depend on the select NOM's characteristics (i.e., hydrophobic, vs hydrophilic, isolated vs reservoir water and aromatic content). The difference in the NOM aromaticity as indicated with the difference in $SUVA_{254}$ values was not a predominant factor on the PNT and TCE adsorption process. This may be due to similar DOC concentration of NOM solutions (3 ± 0.4 mg/L DOC). Besides, the experiments performed with NOM preloading conditions suggested that adsorption behavior depended on the surface area, pore size

distribution, and oxygen content of adsorbents as well as hydrophobicity and molecular structure of adsorbates.

Conclusions

In this study, the impact of NOM preloading on the PNT and TCE adsorption by GNSs, CNTs and GACs was investigated and compared side-by-side by their adsorption behaviors under single solute and preloading conditions by different NOMs. The results shown that:

- PNT uptake was much higher than TCE by all adsorbents on a mass and surface area basis according to adsorption capacity. This was attributed to their molecular properties.
- The adsorption capacity depended 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 capacity of PNT and TCE on all preloaded adsorbents were decreased in the presence of NOM molecules because of competition by NOM with OCs either site competition or pore/interstice blockage.
- No clear trends were observed on the PNT and TCE adsorption by GNSs, CNTs and GACs by changing background NOM types (i.e., hydrophobic, vs hydrophilic, isolated vs reservoir water and aromatic content).
- PNT uptake was decreasing more than TCE uptake with increasing equilibrium concentrations for all carbons, due likely to strong hydrophobic interactions and π - π bonding between PNT molecules and the carbon surface.

- Overall, the adsorption capacity of OCs on CNTs, GNSs and GACs depend more on the physicochemical properties and molecular structures of OCs and characteristics of carbon nanomaterials than the type of NOM.

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Table 1. Selected Characteristics of NOM Solutions

Code	NOM	pH	UV₂₅₄	DOC	SUVA₂₅₄	DON
CH	Isolated-TPH*	7.05	0.0510	3.2	1.6	0.226
CH	Isolated-HPO*	7.01	0.1258	3.0	4.3	0.086
MB	Isolated-HPO*	7.04	0.1580	3.2	4.9	0.124
BP	Reservoir water	7.03	0.1179	3.4	3.4	0.138

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(*: as described elsewhere Karanfil, et al., 2003 and Song, et al., 2009; **CH** : Charleston, **MB**: Myrtle Beach and **BP**: Bushy Park; DOC: Dissolved organic carbon (mg/L), SUVA₂₅₄: Specific UV absorption (UV₂₅₄/DOC, L/mg-m), DON: Dissolved organic nitrogen(mg/L).

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Table 2. Selected Properties of Adsorbents

Carbon	SA _{BET} ^a (m ² /g)	V _T ^b (cm ³ /g)	V _T ^c			Oxygen content %	pH _{pzc}
			V _{micro} <2 nm	V _{meso} 2-50 nm	V _{macro} 50 nm >		
GNS	666	3.138	0.065	1.196	1.331	0.8	9.8
GO	497	0.530	0.081	0.377	0.008	11.1	3.9
SWCNT	537	1.240	0.117	0.581	0.570	0.9	7.5
MWCNT	179	0.752	0.011	0.246	0.265	0.5	8.5
F400	849	0.505	0.312	0.071	0.046	3.7	9.2
HD3000	642	0.775	0.108	0.449	0.100	6.2	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/P₀ = 0.99, ^c The pore volume fraction in each pore size range obtained from the density functional theory (DFT) analysis.

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Table 3. Freundlich isotherm parameters of PNT and TCE adsorption under single solute and NOM preloading conditions

Adsorbent	Background Solution	$K_F[(\text{mg/g})/\text{Ce}^\eta]^a$		n (-)		r ² (-)	
		PNT	TCE	PNT	TCE	PNT	TCE
GNS	Single Solute	24.98 (28.40-21.98)	0.20 (0.04-0.01)	0.28 (0.31-0.25)	0.96 (1.09-0.84)	0.979	0.968
	Charleston HPO	12.14 (13.75-10.71)	0.03 (0.12-0.01)	0.40 (0.43-0.37)	0.86 (1.14-0.58)	0.989	0.843
	Charleston TPH	10.11 (11.28-9.05)	0.01 (0.018-0.005)	0.45 (0.48-0.42)	1.06 (1.18-0.94)	0.991	0.975
	Myrtle Beach HPO	8.43 (9.67-7.35)	0.01 (0.013-0.002)	0.44 (0.47-0.41)	1.10 (1.27-0.93)	0.989	0.955
	Bushy Park treated	6.03 (8.36-4.35)	0.006(0.016-0.002)	0.42 (0.49-0.35)	1.12 (1.32-0.93)	0.936	0.952
GO	Single Solute	16.36 (20.27-13.21)	0.02 (0.03-0.01)	0.33 (0.38-0.28)	1.07 (1.21-0.93)	0.954	0.971
	Charleston HPO	11.32 (12.11-10.59)	0.02 (0.03-0.01)	0.35 (0.36-0.33)	0.92 (1.03-0.80)	0.995	0.97
	Charleston TPH	11.24 (12.55-10.08)	0.02 (0.03-0.01)	0.34 (0.37-0.32)	0.99 (1.12-0.85)	0.987	0.965
	Myrtle Beach HPO	10.14 (11.94-8.61)	0.02 (0.03-0.01)	0.36 (0.40-0.32)	0.88 (0.95-0.80)	0.975	0.985
	Bushy Park treated	6.44 (7.13-5.82)	0.01 (0.02-0.01)	0.38 (0.40-0.36)	1.02 (1.11-0.93)	0.992	0.987
SWCNT	Single Solute	12.71 (15.10-10.70)	1.44 (1.81-1.15)	0.49 (0.54-0.44)	0.49 (0.56-0.42)	0.977	0.964
	Charleston HPO	5.65 (6.25-5.10)	0.29 (0.35-0.24)	0.56 (0.59-0.54)	0.63 (0.67-0.59)	0.995	0.991
	Charleston TPH	7.54 (9.17-6.19)	0.30 (0.42-0.21)	0.52 (0.57-0.47)	0.58 (0.65-0.51)	0.98	0.972
	Myrtle Beach HPO	6.07 (7.58-4.86)	0.76 (0.84-0.69)	0.54 (0.59-0.49)	0.36 (0.38-0.33)	0.977	0.993
	Bushy Park treated	5.42 (6.75-4.35)	0.57 (0.64-0.50)	0.58 (0.63-0.53)	0.43 (0.45-0.41)	0.98	0.993
MWCNT	Single Solute	7.23 (8.37-6.24)	0.003 (0.0043-0.0016)	0.30 (0.33-0.27)	0.80 (0.88-0.71)	0.978	0.981
	Charleston HPO	3.02 (3.50-2.60)	0.005 (0.02-0.002)	0.40 (0.43-0.37)	0.67 (0.86-0.49)	0.988	0.882
	Charleston TPH	4.02 (5.09-3.18)	0.0014 (0.0178-0.0001)	0.32 (0.36-0.27)	0.86 (1.26-0.47)	0.952	0.765
	Myrtle Beach HPO	1.78 (1.97-1.62)	0.001 (0.0026-0.0003)	0.49 (0.51-0.47)	0.88 (1.06-0.71)	0.996	0.956
	Bushy Park treated	1.84 (2.39-1.41)	0.0025 (0.0115-0.0006)	0.48 (0.54-0.43)	0.75 (0.99-0.52)	0.974	0.879
HD3000	Single Solute	26.37 (42.87-16.21)	1.61 (2.02-1.29)	0.40 (0.54-0.26)	0.49 (0.56-0.42)	0.846	0.966
	Charleston HPO	8.29 (11.63-5.91)	0.68 (0.85-0.55)	0.56 (0.65-0.47)	0.63 (0.68-0.57)	0.94	0.981
	Charleston TPH	16.62 (25.88-10.68)	0.70 (0.83-0.58)	0.44 (0.57-0.32)	0.63 (0.68-0.59)	0.862	0.99
	Myrtle Beach HPO	7.84 (13.41-4.58)	0.78 (0.97-0.62)	0.59 (0.74-0.44)	0.66 (0.72-0.59)	0.863	0.979
	Bushy Park treated	10.87 (17.05-6.94)	0.98 (1.17-0.82)	0.49 (0.61-0.36)	0.61 (0.66-0.55)	0.869	0.982
F400	Single Solute	3.80 (7.11-2.04)	1.24 (1.36-1.13)	1.45 (1.78-1.11)	0.60 (0.63-0.57)	0.912	0.996
	Charleston HPO	7.32 (9.30-5.76)	1.54 (2.15-1.10)	0.84 (0.93-0.76)	0.48 (0.56-0.39)	0.975	0.958
	Charleston TPH	6.93 (11.34-4.23)	0.47 (0.59-0.38)	0.96 (1.16-0.76)	0.73 (0.78-0.67)	0.909	0.985
	Myrtle Beach HPO	1.46 (2.00-1.06)	0.61 (0.70-0.54)	1.20 (1.31-1.10)	0.63 (0.66-0.59)	0.984	0.993
	Bushy Park treated	0.91 (2.15-0.38)	0.63 (0.74-0.53)	1.25 (1.50-1.00)	0.64 (0.69-0.59)	0.91	0.988

^a Concentration of adsorbate expressed in (mg/L) units. The numbers in parentheses are 95% confidence intervals.

Figure 1. PNT and TCE adsorption isotherms of GNS, GO, SWCNT, MWCNT, F400 and HD3000 in DDW on a mass basis (a), a surface area normalized basis (b), PNT adsorption isotherms on a surface area in pores 5-13 Å normalized (c), TCE adsorption isotherms on a surface area in pores 5-8 Å normalized (d)

Figure 2. PNT and TCE adsorption isotherms under different types of NOMs preloading conditions.

Single Solute

NOMs Preloading Conditions