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2 **Adsorption of Halogenated Aliphatic Contaminants by Graphene**

3 **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 SOC 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 SOC by graphenes. However, π - π electron donor-acceptor and van der Waals interactions are likely the additional mechanisms contributing to the adsorption of aliphatic SOC on graphenes. Among the three background solution components examined, NOM showed the most influential effect on adsorption of the selected aliphatic SOC, 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 SOC.

Keywords: Adsorption, Aliphatic Synthetic Organic Compounds, Graphenes, Carbon Nanotubes, Activated Carbons, Natural Organic Matter

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 Kraner, 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., 2010; Zhao et al., 2014]. Furthermore, some of the 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 et al., 2011; Ramesha et al., 2011; Ji et al., 2013; Sharma and Das, 2013; Zhao et al., 2011; Li et al., 2012; Gao et al., 2012; Li et al., 2013; 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 SOC_s 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 SOC_s 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 SOC_s 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, Angstrom Materials Inc.), reduced graphene oxide (rGO, Graphenea CO., Ltd.), SWCNT (Chengdu Organic Chemicals 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 SOC_s 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%; CCl₄, > 99.9%). Both of these aliphatic SOC_s 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 SOC_s are summarized in Tables 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]. SUVA₂₅₄, 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 SUVA₂₅₄ 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 SUVA₂₅₄ values (e.g., less than 2.0 L/mg-m) contain mostly non-humic, hydrophilic and low molecular weight material. The

SUVA₂₅₄ 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 2010) to determine the SSA, total pore volumes (PV) and pore size distributions (PSD) of the four adsorbents. The Brunauer-Emmett-Teller (BET) equation was used to calculate SSA. The total PV were obtained from the adsorbed volume of nitrogen near the saturation point ($P/P_0 = 0.99$). PSD of adsorbents were determined from the nitrogen isotherms using the Density Functional Theory (DFT) model. Oxygen contents of the carbonaceous adsorbents were measured using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation). In addition, pH of the point of zero charge (pH_{PZC}) of adsorbents was determined using pH equilibration technique. The details about these characterization methods have been provided elsewhere [Dastgheib et al., 2004].

2.5. Adsorption experiments

Constant carbon dose aqueous phase isotherm experiments were conducted using completely mixed batch reactors (125 mL glass bottles with Teflon-lined screw caps). Two types of isotherms were conducted at room temperature (20 ± 3 °C):

(1) Distilled and deionized water (DDW) experiments: Concentrated stock solution of each aliphatic SOC was prepared in methanol. Bottles containing about 5 mg of adsorbents were

first filled with DDW and no headspace, and spiked with predetermined volumes of aliphatic SOC_s from their methanol stock solutions. For the graphene experiments, the bottles with adsorbents were initially half filled with DDW, sonicated for 20 min, and completely filled with DDW prior to spiking aliphatic SOC_s. The volume percentage of the methanol spiked solution per bottle was kept below 0.4% (v/v) to minimize the co-solvent effect. Preliminary kinetic experiments were performed for TCE adsorption onto four carbonaceous adsorbents; and the results showed that a time period of seven days was sufficient to reach equilibrium (Figure S1). Thus, the bottles with no headspace were placed into a rotary tumbler for one week. The solution pH remained around 6.5 during the experiments. To investigate the effect of pH on adsorption, additional adsorption isotherm experiments were conducted at pH 3 and 11, where the solution pH was adjusted by 0.1 mol/L HCl and NaOH. For ionic strength (IS) effect experiments, the same experimental procedure was used, except the ionic strength was adjusted with NaCl to three levels (IS=0.001, 0.01, 0.1 M). The ranges for pH and ionic strength were kept wider than those typically used in water and wastewater treatment or found in natural water systems to examine their impact in a wider parametric range.

(2) Preloading experiments: The NOM effect on adsorption of aliphatic SOC_s by different carbonaceous adsorbents was examined under preloading condition, giving an advantage to NOM adsorption prior to that of the SOC_s, which represents the most severe NOM competition condition. For the preloading experiments, bottles containing about 5 mg adsorbents were first filled fully with 3 mg DOC/L NOM solution buffered with 1mM NaH₂PO₄·H₂O/Na₂HPO₄·7H₂O and adjusted to pH 7.0, then the bottles with zero headspace were placed into a rotary tumbler. After four days, predetermined volumes of aliphatic SOC stock solutions were directly spiked into the bottles, and then the headspace-free bottles were tumbled

again for an additional week. In NOM preloading experiments, 200 mg/L NaN₃ was added to NOM solution to minimize any biological activity.

After the equilibrium period of isotherm experiments, bottles were placed on a bench overnight to allow settling of the adsorbents, and supernatants of samples in the bottles were transferred to 10 mL centrifuge tube for centrifugation to remove the remaining adsorbents. The supernatants were extracted with hexane by liquid: liquid extraction and analyzed using a gas chromatograph with a micro-electron capture detector (GC-μECD) equipped with a Rxi-624Sil MS Column (Restek, USA). Bottles without any adsorbents served as blanks to monitor the loss of adsorbates during the experiments, which were found to be negligible.

2.6. Isotherm modeling

Four common isotherm models, Freundlich (FM), Langmuir (LM), Langmuir-Freundlich (LFM) and Polanyi-Manes models (PMM), were employed to fit the experimental data. The modeling results showed that FM model resulted in good fits with meaningful parameter values for every case (Tables S2 to S5). Therefore, the FM model was selected to fit the adsorption data in this study:

$$q_e = K_F C_e^n \quad (1)$$

where q_e and C_e represent the solid-phase equilibrium concentration (mg/g) and the liquid-phase equilibrium concentration (μg/L or mg/L), respectively, K_F is the unit-capacity parameter ((mg/g)/C_eⁿ), equal to the amount adsorbed at a value of C_e equal to unity, and n is a dimensionless parameter related to the surface heterogeneity. Two K_F parameters ($K_{F\mu}$ and K_{Fm})

were examined for SOC's adsorption capacities at equilibrium concentrations of 1 µg/L and 1 mg/L, respectively.

3. Result and discussion

3.1. Adsorbent characterization

The results of SSA, total PV, PSD, oxygen content and pH_{PZC} of the four carbonaceous adsorbents are summarized in Table 1. The SSA of GNS and rGO were 666 and 497 m²/g, respectively; and they were considerably smaller than the theoretically calculated SSA of single-layered graphene nanomaterials (2630 m²/g) [Stoller et al., 2008]. The much lower SSA indicated that graphenes were not present as exposed single-sheets, instead they formed bundles decreasing the SSA. Very high total PV (> 3 cm³/g) of GNS indicated aggregation may be confining large amounts of space within its 'house-of-cards' like bundle structure. GNS had six times higher total PV than rGO, indicating the oxygen content of rGO may be inhibiting the formation of bulky pores (especially macropores) within its bundle structure. The lacking macropores may also be attributed to tighter aggregation of rGO due to hydrogen bonding between the oxygen containing functional groups within the graphene bundle. When comparing the graphenes with SWCNT and HD3000, no major difference was observed in SSA, total PV and PSD besides the notably large macropore volume of GNS. In addition, rGO had higher oxygen content (17.5%) than other adsorbents as expected, which suggested that the surface of rGO is more hydrophilic. The low pH_{PZC} value of rGO indicated a net negative charge under neutral conditions due to the presence of oxygen-containing functional groups.

3.2. The effect of adsorbent properties on adsorption of aliphatics

Adsorption isotherms of PCE, TCE and 1,1-DCE by the four carbonaceous adsorbents in DDW are presented in Figure 1 and the Freundlich isotherm parameters were summarized in Table S6. Some major observations from the isotherms and isotherm parameters are as follow: HD3000 and SWCNT exhibited higher adsorption capacities than graphenes for all aliphatic SOC_s tested. The adsorption isotherms were normalized according to the SSA and micropore volumes of adsorbents. However, after normalization, the adsorbed amount of aliphatic SOC_s by HD3000 and SWCNT were still higher than those of GNS and rGO (Figures 1-D, E, F, G, H, I). Adsorbents with higher micropore volumes (HD3000 and SWCNT) showed higher adsorption capacities; however, SSA or micropore volume difference did not completely explain the adsorption capacity difference. Because, SSA, total PV and PSD parameters were obtained in the bulk phase of adsorbents via N₂ adsorption, the aggregation of CNTs and graphenes in aqueous phase may change the availability of sorption sites for aliphatic SOC_s unlike rigid activated carbon pore structure.

Pristine GNS exhibited higher uptake for the aliphatic SOC_s than rGO even after surface area normalization, which was attributed to its low surface polarity. Oxygen-containing functional groups on carbonaceous adsorbents can decrease the accessibility of adsorbents for aliphatic SOC_s either through (i) a decrease due to increasing hydrophilicity (i.e. polarity) of the surface, or (ii) a decrease in the number of available adsorption sites due to water cluster formation around the oxygen-containing functional groups. Similar effect of oxygen content of graphenes was also observed on the adsorption of aromatic organic contaminants [Apul et al., 2013].

3.3. The effect of aliphatic SOC properties on adsorption

To investigate the effect of aliphatic SOC properties, adsorption isotherms of the aliphatic SOC on GNS and rGO are compared in Figures 2-A, B. Hydrophobic interactions are important driving forces for adsorption of SOC from aqueous solutions. To investigate the contribution of hydrophobicity of the aliphatic SOC on adsorption, the adsorption isotherms were normalized according to their solubilities (Figures 2-C, D). After the solubility normalization, the separation in the adsorption isotherms on both GNS and rGO were greatly reduced but isotherms did not converge on a single line. This indicates that hydrophobicity of the aliphatic SOC was an important driving force for adsorption, and there were other factors contributing to adsorption.

To further investigate the effect of the other SOC properties on adsorption, the PCE, TCE and 11DCE isotherms were compared. These compounds have similar molecular structures and configurations but different number of chlorine atoms. As shown in Figures 3-A, B, adsorption affinities of the three aliphatic SOC by GNS and rGO followed the same order: PCE > TCE > 11DCE. Solubility normalization greatly reduced the differences in the adsorption isotherms, although isotherms did not converge on a single line (Figures 3-C, D), and still followed the same order with smaller differences. The difference in the strengths of π - π electron donor-acceptor (EDA) interactions of these three aliphatics with the graphenes might influence their adsorption. The highly polarizable graphene sheet can play an amphoteric role attracting both π electron-acceptors and π electron-donors to the surface; and chlorine atoms on carbon double bonds of the three SOC can serve as π electron acceptors, which can involve in adsorption interactions between the SOC and graphenes through π - π EDA complex formation. Therefore, adsorption affinities of the three aliphatic SOC by graphenes increase with increasing number of

chlorine atoms. Another possibility influencing adsorption of these three compounds is the nonspecific interactions generally referred to as van der Waals forces. These interactions can exist between molecules regardless of their chemical structures; and they are proportional to the product of polarizability or dipole moment of adsorbates and adsorbents. Thus, stronger van der Waals interactions between PCE and graphenes might occur due to its higher polarizability. The separation in solubility-normalized isotherms of the three aliphatic SOC_s on both GNS and rGO were further reduced after polarizability normalization (Figures 3-E, F). This additional reduction suggested that increasing polarizability of aliphatic SOC_s may also have positive effects in their adsorption. To further examine the effect of polarizability, two isomer aliphatic SOC_s (111TCA and 112TCA) with different polarizability were selected. Figure 4 compares their adsorption isotherms on GNS and rGO after solubility normalization to eliminate the difference in the hydrophobicity of these two compounds. The results showed both GNS and rGO showed higher adsorption capacities for 112TCA than 111TCA. As seen in Table 2, 112TCA has higher polarizability than 111TCA (0.68 vs. 0.41); thus stronger van der Waals interactions between 112TCA and graphenes may be expected.

Presence of π -electrons in the structure of aliphatic SOC_s may be another factor affecting their adsorption on graphenes. Aromatic SOC_s have strong π - π bonding interactions with graphene surface due to presence of resonating π -electrons in their benzene rings [Apul et al., 2013]. To investigate whether the π -electrons of aliphatic SOC_s exert the effect on their adsorption, solubility-normalized adsorption isotherms of PCE vs. 1112TeCA and TCE vs. 112TCA were compared (Figure 5) because they have similar molecular structures but different carbon bonds. After the solubility normalization, the separation between their adsorption isotherms was reduced greatly; and the isotherms almost converged on a single line, which

indicated the π -electrons of aliphatic SOC_s might have positive effect on their adsorption by graphenes. Both 1112TeCA and 112TCA were expected to have stronger van der Waals interactions with graphenes than PCE and TCE, respectively due to their higher polarizabilities, which would enhance their adsorption on graphenes. However, after solubility normalization, 1112TeCA and 112TCA did not show higher adsorption affinities to graphenes as compared to PCE and TCE, which therefore indicated that the π -electrons of PCE and TCE possibly contributed to their adsorption on graphenes through π - π EDA complex to counterbalance the contribution of van der Waals interactions to 1112TeCA and 112TCA adsorption. In addition, their solubility-normalized adsorption isotherms once again demonstrated hydrophobic interactions were dominant contributor for the adsorption of aliphatic SOC_s on graphenes.

3.4. The effect of background water components on adsorption of aliphatics

3.4.1. The effect of NOM

To investigate the effect of NOM on adsorption of aliphatic SOC_s by graphenes and compare NOM effects on adsorption capacities of GNS, rGO and SWCNT, adsorption of six SOC_s (PCE, TCE, 11DCE, 112TCA, 1112TeCA, and DBCP) with different properties by GNS, rGO and SWCNT were tested in NOM solution. Their adsorption isotherms in DDW and NOM solutions are presented in Figure 6. Freundlich isotherm parameters in DDW and NOM solution are provided in Table S6 and S7 in Supporting Information, respectively. Two parameters, R_{μ} and R_m , as the ratios of $K_{F\mu}$ and K_{Fm} in NOM preloading conditions to those in DDW, respectively, were calculated to quantify the effect of NOM on the adsorption of the six aliphatic

SOCs by different adsorbents. The lower R_{μ} and R_m values indicate a greater reduction of adsorption capacity due to NOM preloading.

For GNS and rGO, the NOM effect on adsorption capacity of GNS were stronger than rGO, as indicated by lower R_m values of GNS; and rGO exhibited comparable adsorption capacity in the presence of NOM and in DDW as reflected by R_m values of rGO for the six SOC's ranging from 0.72 to 0.91, which can be attributed to electrostatic repulsion of negatively charged NOM molecules and rGO surface. Because the low pH_{PZC} value of rGO (Table 1), it had a net negative charge under neutral pH conditions; and NOM molecules generally carry a net negative charge at the same pH, which would result in less NOM coating on the rGO surface. Furthermore, adsorption of six SOC's by GNS and rGO under NOM preloading conditions was compared to SWCNT adsorption. As shown in Table S7, R_m values of SWCNT for all six SOC's were smaller than those of rGO and GNS, indicating that preloaded NOM exhibited stronger suppression on the adsorption of the aliphatic SOC's by SWCNT. This was attributed to more hindrance of the aliphatic SOC access to the adsorption sites on SWCNT due to the microporous structure of SWCNT bundles in water, in contrast to the flat sheet structure of GNS and rGO. These findings were similar to those of aromatic organic contaminant adsorption, where preloaded NOM exhibited much smaller impact on adsorption capacity of rGO than that of SWCNT [Apul et al., 2013]. However, although preloaded NOM exerted smaller effects on the adsorption capacities of GNS and rGO as compared to SWCNT, graphenes did not exhibit a major advantage, in terms of adsorption capacities, over SWCNT for the adsorption of aliphatic SOC's in the NOM solution (Figure S2).

The uptakes of all six SOC's decreased under NOM preloading conditions as reflected by R_m values. However, there were no clear trends observed in R_m values for each SOC; and the R_m

values did not correlate with the SOC's properties such as solubility, molecular size or polarizability. In fact, preloaded NOM did not exert significantly different effects on the six SOC's adsorption in terms of the R_m values. Therefore, for the six aliphatic SOC's, their different physicochemical properties did not cause large differences in NOM effects on their adsorption.

3.4.2. The effect of pH and ionic strength

Three aliphatic SOC's (CCl_4 , TCE, and DBCP) with different molecular structure, molecular size and chain lengths were employed as probe molecules to explore the effect of solution pH on adsorption of aliphatic SOC's by graphenes. The adsorption isotherms of CCl_4 , TCE and DBCP on GNS and rGO under different pH conditions are presented in Figure S3 in the Supporting Information. The change in pH did not influence the adsorption of these three aliphatic SOC's on GNS and rGO (except for DBCP under pH 11 conditions). Since the tested compounds are non-ionic, their adsorption was independent from solution pH. However, as pH increased, the dissociation of oxygen-containing functional groups on graphene surfaces (especially rGO) also did not show any influence indicating that adsorption of these three aliphatic SOC's occurred on the hydrophobic sites of graphene surface where there were no oxygen-containing functional groups. For DBCP at pH 11, we observed a higher adsorption by graphenes, but actually this does not reflect its real adsorption affinity. Because degradation and transformation of DBCP at high pH might occur during the adsorption experiments indicated by the very low ratio (0.10-0.15) between measured blank concentrations and calculated ones.

To investigate the effect of ionic strength, the same aliphatic SOC's selected for pH experiments were used in the adsorption experiments. Two potential impacts can be observed: (1) increasing ionic strength enhances the activity coefficient of hydrophobic organic

compounds, leading to a decrease in their solubility (i.e. salting out effect), which is favorable for SOC's adsorption [Zhang et al., 2010]; and (2) the ions may penetrate into the diffuse double layer surrounding the graphene surfaces and eliminate the repulsive energy between the adsorbents, facilitating the formation of a more compact aggregation structure (i.e. squeezing-out), which is unfavorable for SOC's adsorption [Zhang et al., 2010]. Increasing ionic strength had negligible effect on adsorption of the aliphatic SOC's by both GNS and rGO (Figure S3). Therefore, the results indicated that either the contribution of salting-out effect to the adsorption of these aliphatic SOC's was equivalent to that of the squeezing-out effect or both the salting-out effect and squeezing-out effect were too weak to influence the adsorption of the SOC's on graphenes.

4. Conclusions

Graphene nanomaterials adsorbed halogenated aliphatic SOC's, however the overall adsorption capacities of graphene nanomaterials were smaller than those of carbon nanotubes and activated carbon in the presence of NOM. Hydrophobicity was the dominant contributor for the adsorption of aliphatic SOC's on graphenes, but it was not the only mechanism controlling the adsorption, π - π EDA interaction and van der Waals interaction appear to be the additional mechanisms contributing to the adsorption of aliphatic SOC's on graphenes. It should be noted that these adsorption interactions were observed for the selected halogenated aliphatic contaminants with comparable molecular configuration and sizes in this study. Further research is warranted to confirm and extend the findings to larger and more complex aliphatic molecules or different classes of contaminants. Among the three background water characteristics examined, NOM showed the most important effect on adsorption, whereas the changes in pH and ionic strength had a negligible effect on the

adsorption of selected halogenated aliphatic SOC_s. NOM preloading exerted minimal effect on adsorption capacities of rGO for aliphatic SOC_s, which was attributed to low degree of NOM coating on rGO surface due to electrostatic repulsion between negatively charged NOM molecules and rGO. NOM exhibited severe suppression on adsorption capacities of SWCNT than those of graphenes. This was attributed to microporous structure of SWCNT aggregates as compared with flat sheet structure of graphenes. In terms of adsorption capacities, graphenes did not exhibit a major advantage over SWCNT and HD3000 for the adsorption of aliphatic SOC_s. Future studies also need to examine adsorption kinetics to assess whether graphenes exhibit advantages over other carbonaceous adsorbents for halogenated aliphatic SOC_s.

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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} (2-50nm) cm ³ /g, (%)	V _{macro} (> 50nm) 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

520 ^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 Pore
 521 volume in each pore size range obtained from the density functional theory (DFT) analysis.

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Table 2. Selected properties of aliphatic SOC_s

SOC	Abbreviation	MW ^a	Density	MV ^b	C _s ^c	LogK _{ow} ^d	Polarizability ^e
		g/mol	g/cm ³	cm ³ /mol	mg/L		
trichloroethylene	TCE	131	1.46	89.7	1183	2.42	0.37
tetrachloroethylene	PCE	166	1.62	102.5	224	3.40	0.44
1,1,1-trichloroethane	111TCA	133	1.32	100.8	1358	2.49	0.41
1,1,2-trichloroethane	112TCA	133	1.44	92.4	4483	1.89	0.68
carbon tetrachloride	CCl ₄	154	1.59	96.9	790	2.83	0.38
1,1-dichloroethylene	11DCE	97	1.21	80.2	2375	1.32	0.34
1,2-dichloropropane	12DCP	113	1.16	97.4	2819	2.28	0.68
1,2-dibromoethane	12DBE	188	2.17	86.6	4177	1.96	0.76
1,1,1,2-tetrachloroethane	1112TeCA	168	1.55	108.3	1103	2.93	0.63
1,2-dibromo-3-chloropropane	DBCP	236	2.08	113.5	985	2.43	0.78

523 ^a molecular weight; ^b molar volume; ^c water solubility at 25 °C obtained from the Material Safety Data Sheet of each compound; ^d octanol-water partitioning coefficient
524 simulated with ACDLABS11.0 (ChemSketch and ACD/3D Viewer); ^e polarizability obtained from ACD/ADME Suite 5.0.

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Figure 1. Adsorption isotherms in DDW (A) PCE mass basis, (B) TCE mass basis, (C) 11DCE mass basis, (D) PCE surface area normalized, (E) TCE surface area normalized, (F) 11DCE surface area normalized, (G) PCE micropore volume normalized, (H) TCE micropore volume normalized, and (I) 11DCE micropore volume normalized.

Figure 2. Adsorption isotherms of ten aliphatic SOC by GNS and rGO in DDW (A) GNS mass basis, (B) rGO mass basis, (C) GNS solubility normalized, (D) rGO solubility normalized .

Figure 3. Adsorption isotherms of PCE, TCE and 11DCE in DDW (A) GNS mass basis, (B) rGO mass basis, (C) GNS solubility normalized, (D) rGO solubility normalized, (E) GNS polarizability normalized, and (F) rGO polarizability normalized.

Figure 4. Comparison of 111TCA and 112TCA solubility-normalized adsorption isotherms on GNS and rGO in DDW.

Figure 5. Comparison of PCE vs. 1112TeCA and TCE vs. 112TCA solubility normalized adsorption isotherms on GNS and rGO in DDW (A) PCE vs. 1112TeCA-GNS, (B) PCE vs. 1112TeCA-rGO, (C) TCE vs. 112TCA-GNS, and (D) TCE vs. 112TCA- rGO.

Figure 6. Adsorption isotherms in DDW and under NOM preloading conditions (A) PCE, (B) TCE, (C) 11DCE, (D) DBCP, (E) 112TCA, and (F) 1112TeCA.

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