NOVEL GRAPHENE BASED MATERIALS FOR SORPTION PROCESSES IN WATER TREATMENT AND PURIFICATION APPLICATIONS

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ABSTRACT

Graphene materials are increasingly being incorporated into water treatment technologies due to their rapid and non-selective sorption abilities to small molecular weight organic contaminants. This study first examines some of the mechanistic interactions between commercial graphene oxides and endocrine disrupting compounds, pharmaceuticals, and natural organic matter in order to determine which physicochemical properties should be considered when choosing a graphene material. In addition, two more graphene based nano composites including ethylenediamine functionalized graphene (ED-G) and black carbon magnetite (BC-Mag) was synthesized in the lab and tested for their sorption performance on targeted contaminants. Graphene oxides of varied particle sizes, specific surface areas, and surface chemistries were evaluated within batch reactors. Specific surface area (SSA), surface charge, and phenolic content of graphene oxides was determined to have the greatest control on sorption extent of carbamazepine, an anticonvulsant used as a probe compound. Only graphene with SSA much larger than 100 m²g⁻¹ could out-compete granular activated carbon or multi-walled carbon nanotubes, other carbonaceous sorbents currently used in water technologies. Pi-pi dispersion interactions appear to govern sorption of neutral compounds, and electrostatic interactions also strongly influenced cationic and anionic compounds, increasing or decreasing sorption two-fold, respectively, as graphene surface charge becomes more negative at higher pH. Sorption extents for various humic acids, fulvic acids, and organic matter by graphene showed good correlation with aromatic content,
indicating a preference for the more hydrophobic fraction in organic matters. A concomitant decrease in specific UV absorbance was also observed. Size exclusion chromatography revealed a preference for sorption of the larger molecular weight fraction of organic matters. Enhanced or diminished sorption of organic compounds in the presence of organic matter depended on compound charge. ED-G with positive surface charge was observed to have preferable sorption of negative charged ibuprofen over neutral and positive charged compounds carbamazepine and atenolol, which suggested ED-G as a strong addition to widely present negative charged graphitic materials. BC-Mag has the fastest sorption kinetic among all of tested sorption materials, and its retrieval, regeneration and reuse could be easily achieved by a strong magnet and washing with alcohol.
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# TABLE OF CONTENTS

ABSTRACT

LIST OF TABLES

LIST OF FIGURES

Chapter 1  **Introduction**

1.1 Hypotheses

1.2 Overview of the research

Chapter 2  **Sorption of Carbamazepine by Commercial Graphene Oxides: A Comparative Study with Granular Activated Carbon and Multiwalled Carbon Nanotubes**

2.1 Abstract

2.2 Introduction

2.3 Materials and Methods

2.3.1 Materials

2.3.2 Sorption Experiments

2.3.3 Desorption Experiments

2.3.4 Quantification of EDCs

2.4 Results and Discussion

2.4.1 Graphene characterization

2.4.2 Carbamazepine Sorption Kinetics


2.4.3 Carbamazepine Sorption Isotherms .......................................................... 21
2.4.4 Carbamazepine Desorption and Mechanism Observations .................. 24
2.4.5 Factors affecting sorption extent using probe sorbates ....................... 27
2.5 Conclusions ................................................................................................. 32

Chapter 3 Factors influencing natural organic matter sorption onto commercial graphene oxides ................................................................. 43
3.1 Abstract ....................................................................................................... 43
3.2 Introduction .................................................................................................. 45
3.3 Materials and Methods ................................................................................ 49
  3.3.1 Materials .................................................................................................. 49
  3.3.2 Sorption experiments ............................................................................. 51
3.4 Results and Discussion ................................................................................ 53
  3.4.1 NOM sorption kinetics .......................................................................... 53
  3.4.2 SRNOM sorption isotherms .................................................................. 55
  3.4.3 Evidence for π–π interactions. .............................................................. 58
  3.4.4 Aromatic fractionation ........................................................................... 62
  3.4.5 Size fractionation .................................................................................... 63
  3.4.6 Evidence for electrostatic interactions .................................................. 65
3.5 Conclusions .................................................................................................. 71

Chapter 4 Ethylenediamine Functionalized Graphene: Synthesis and Application in Charged Contaminants Removal ........................................................................ 87
4.1 Abstract ....................................................................................................... 87
4.2 Introduction .................................................................................................. 88
Chapter 4

4.3 Experimental Method .............................................................................................................. 92
  4.3.1 Material Synthesis ............................................................................................................ 92
  4.3.2 Sorption Experiments ...................................................................................................... 93

4.4 Results and Discussion ........................................................................................................... 94
  4.4.1 Material TEM and XPS Analysis ......................................................................................... 94
  4.4.2 Effect of pH ...................................................................................................................... 96
  4.4.3 Sorption Capacity ............................................................................................................. 98
  4.4.4 Competitive Sorption ...................................................................................................... 100

4.5 Conclusions .......................................................................................................................... 102

Chapter 5

Facile Synthesis and Reuse of Magnetic Black Carbon Magnetite (BC-Mag) for Fast Carbamazepine Removal ................................................................. 110

5.1 Abstract ............................................................................................................................... 110

5.2 Introduction .......................................................................................................................... 111

5.3 Methods ............................................................................................................................... 113
  5.3.1 Material synthesis and characterization ........................................................................... 113
  5.3.2 Sorption experiments ..................................................................................................... 114
  5.3.3 Desorption and regeneration .......................................................................................... 115
  5.3.4 Quantification of carbamazepine .................................................................................. 116

5.4 Results and Discussion ........................................................................................................ 116
  5.4.1 Characterization of Black Carbon Magnetite .............................................................. 116
  5.4.2 Sorption rates and capacity ........................................................................................... 117
  5.4.3 Effect of solution pH ...................................................................................................... 119
  5.4.4 Recovery of carbamazepine and regeneration of BC-Mag ........................................... 119
5.5 Conclusions .................................................................................................................. 120

Chapter 6  Conclusions ........................................................................................................ 127

6.1 Conclusions .................................................................................................................. 127

6.2 Recommendations for further work .............................................................................. 130

REFERENCES .................................................................................................................. 131

Chapter 1 ......................................................................................................................... 131

Chapter 2 ......................................................................................................................... 137

Chapter 3 ......................................................................................................................... 143

Chapter 4 ......................................................................................................................... 148

Chapter 5 ......................................................................................................................... 152

APPENDIX ....................................................................................................................... 154

APPENDIX A: SUPPLEMENTARY DATA OF CHAPTER 2 .............................................. 154

APPENDIX B: SUPPLEMENTARY DATA OF CHAPTER 3 .............................................. 167
LIST OF TABLES

Table 2.1 Specific surface area, particle sizes (as reported from manufacturers) and elemental composition from XPS spectra of graphene oxide powders. ............................... 36

Table 2.2 Values of fitted parameters for the pseudo-second-order kinetic model (equation 1) of carbamazepine sorption on graphene oxides (C, M, and A), carboxyl-functionalized multilwalled carbone nanotubes, and granular activated carbon (90 mg l-1 initial carbamazepine concentration, 20 mM NaCl, 1 mM NaHCO₃, pH 7.2). R² > 0.99 for all model simulations. ........................................................................................................... 37

Table 2.3 Freundlich model parameters for carbamazepine sorption on graphene oxides (C, M, and A), carboxyl-functionalized multilwalled carbone nanotubes, and granular activated carbon at pH 7.2. ........................................................................................................................................ 38

Table 2.4 Selected physical and chemical properties of endocrine disrupting compounds in this study. ........................................................................................................................................... 39

Table 3.1 Values of fitted parameters for the pseudo-second-order kinetic model of SRNOM sorption on graphene oxides (C, M, and A-heated), and granular activated carbon (20 mM NaCl, 1 mM NaHCO₃, pH 7.2). R² > 0.99 for all model simulations.... 73

Table 3.2 Freundlich model parameters for SRNOM sorption on graphene oxides (C, C500, C300, M, and A-heated), pristine multilwalled carbon nanotubes, and granular activated carbon at pH 7.2. ........................................................................................................................................... 74

Table 3.3 Freundlich model parameters for sorption of various NOM types with graphene C at pH 7.2. ........................................................................................................................................... 75
Table 3.4 Values of solution E4/E6 recorded before and after sorption of SRNOM to graphenes C, M, and A-heated at pH 5.1 and 7.1. ................................................................. 76

Table 4.1 X-ray photoelectron spectroscopy fitted model parameters for ethylenediamine-functionalized graphene oxide. ................................................................. 104

Table 5.1 Pseudo-second-order kinetic model parameters of carbamazepine sorption on BC-Mag. $R^2 > 0.99$ for all model simulations. ................................................................. 122

Table 5.2 Isotherm parameters for fitted Freundlich and Langmuir isotherm models of carbamazepine sorption on BC-Mag. ................................................................. 122
LIST OF FIGURES

Figure 2.1 Time profile of carbamazepine sorption on different graphitic sorbents (C 0.5 g l\(^{-1}\), red open diamonds; M 0.5 g l\(^{-1}\), green open circles and 2 g l\(^{-1}\), green filled circles; A 0.5 g l\(^{-1}\), blue open triangles and 2 g l\(^{-1}\), blue filled triangles), MWCNT-COOH (0.5 g l\(^{-1}\), pink open inverted triangles), and GAC (0.5 g l\(^{-1}\), black open squares) and. The solid lines are pseudo-second order kinetic model simulation, described in equations 1 and 2. Experimental conditions: pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\). ................................................................. 40

Figure 2.2 Sorption isotherms of carbamazepine on graphene C (red diamonds), M (green circles), A (blue triangles), MWCNT-COOH (pink inverted triangles), and GAC (black squares). Solid lines are Freundlich model simulations. Experimental conditions: 1.0 g l\(^{-1}\) sorbent, pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\). ................................................................. 40

Figure 2.3 Desorption of carbamazepine (CBZ) from graphene C. Red open squares: [CBZ] 80 mg l\(^{-1}\), graphene C 0.2 g l\(^{-1}\), desorbed with pH 7.2 buffer solution. Red filled squares: [CBZ] 40 mg l\(^{-1}\), graphene C 0.2 g l\(^{-1}\), desorbed with pH 7.2 buffer solution. Red open diamonds: [CBZ] 80 mg l\(^{-1}\), graphene C 0.5 g l\(^{-1}\), desorbed with pH 7.2 buffer solution. Blue open diamonds: [CBZ] 80 mg l\(^{-1}\), graphene C 0.5 g l\(^{-1}\), desorbed with pH 9.2 buffer solution. Red open triangles: [CBZ] 80 mg l\(^{-1}\), graphene C 0.5 g l\(^{-1}\), desorbed with ethanol. ................................................................................................................................. 41

Figure 2.4 Partition coefficient (\(K_d\)) of the EDCs arranged according to \(log\ D\) values. Experimental conditions: 0.1 g l\(^{-1}\) graphene C, initial EDCs concentration 30 mg l\(^{-1}\), pH
7.2, 20 mM NaCl, 1 mM NaHCO₃, contact time 4 h. CBZ = carbamazepine, E3 = estriol, AT = atenolol, SMZ = sulfamethoxazole, CAF = caffeine, APAP = acetaminophen, IBU = ibuprofen, GEM = gemfibrozil, ATZ = atrazine, BPA = bisphenol A.

**Figure 2.5** Effect of pH on EDC sorption onto graphene C. (a) Surface charge of graphene C. (b) Effect of pH on the positive charged sorbate atenolol (AT), the negative charged sorbate ibuprofen (IBU), and the neutral sorbate carbamazepine (CBZ).

Experimental conditions for both a and b: 0.5 g l⁻¹ graphene C and initial EDCs concentration of 80 mg l⁻¹ in buffer solution 1 mM NaHCO₃ and 20 mM NaCl.

**Figure 3.1** Kinetic profile of SRNOM sorption on different graphene sorbents (C 0.25 g l⁻¹, red open diamonds; M 0.25 g l⁻¹, green open circles; A-heated 0.25 g l⁻¹, blue filled triangles), MWCNTs (0.25 g l⁻¹, pink open triangles), and GAC (0.25 g l⁻¹, black open squares). The solid lines are pseudo-second-order kinetic model simulations.

Experimental conditions: initial SRNOM UV absorbance 0.2, TOC concentration range 6.2 to 13.3 mg l⁻¹, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours.

**Figure 3.2** (a) Sorption isotherms of SRNOM on graphene C (red open diamonds), C500 (red dotted circles), C300 (red open triangles), M (green open circles), A-heated (blue filled triangles), pristine MWCNT (pink inverted open triangles), and GAC (black open squares). Solid lines are Freundlich model simulation. (b) Normalize sorption data on various sorbents to SSA. Experimental conditions: 0.05 to 1.1 g l⁻¹ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours.

**Figure 3.3** Sorption isotherms of graphene C with varied sorbates including, from left to right, LeoHA (green dotted circles), ESHA (red open triangles), SRNOM (red open diamonds), PPHA (black filled circles), SRHA (blue open circles), NordFA (black open
squares), SRFA (green dotted squares), and NordNOM (blue dotted diamonds). Solid lines are Freundlich model simulation. Experimental conditions: 0.05 to 1.1 g l⁻¹ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours.

**Figure 3.4** (a) Linear relationship between Freundlich constant $K_F$ with percent aromatic content of various NOM types. (b) Linear relationship between Freundlich constant $K_F$ related to sorption capacity with initial SUVA₂₅₄ of various NOM types. (c) Linear relationship between SSA-normalized $K_F$ and Csp² percentage for various graphene materials except for graphene C. (d) Linear relationship between SSA-normalized $K_F$ and O percentage for various graphene materials except from graphene C. Data for graphene C was not included in (c) and (d) due to its great difference from the trend.

**Figure 3.5** SUVA₂₅₄ values for sorption of varied natural organic matter types onto graphene C from the isotherm experiments in Fig. 3. Experimental conditions: 0.05 to 1.1 g l⁻¹ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours. NOM in legend are listed in order of highest to lowest initial SUVA₂₅₄ values.

**Figure 3.6** (a) HPSEC chromatogram for SRNOM, SRHA, SRFA before and after 24 hours sorption with graphene C before and after reaction. Experimental conditions: graphene C mass 8 mg, volume 11 ml, initial SUVA₂₅₄ 0.78, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours. (b) HPSEC chromatogram for SRNOM before and after 24 hours with various sorbents. Experimental conditions: sorbent mass 8 mg, volume 11 ml, initial SUVA₂₅₄ 0.78, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours.

**Figure 3.7** (a) Zeta potential of graphene C (red diamonds), A-heated (blue triangles), and M (green circles). Experimental conditions for a: 0.1 g l⁻¹ graphene in 5 mM NaCl.
(b) Effect of pH on SRNOM sorption by graphene C (red diamonds), A-heated (blue triangles) and M (green circles). (c) SUVA at 254 nm for sorption of SRNOM with graphene C (red diamonds), A-heated (blue triangles), and M (green circles) at pH range of 2 to 12. Experimental conditions for b and c: 0.25 g l\(^{-1}\) graphene and initial SRNOM concentration of 5.6 to 6.5 mg l\(^{-1}\) TOC, initial UV absorbance 0.2, in buffer solution 1 mM NaHCO\(_3\) and 20 mM NaCl, reaction time 24 hours.

**Figure 3.8** (a) Kinetics of dissolved TOC concentrations for SRNOM exposed to 0.25 g l\(^{-1}\) graphene C at pH 7.2 in 20 mM NaCl and 1 mM NaHCO\(_3\). (b) Bulk SUVA\(_{254}\) values of dissolved SRNOM in samples in part (a). (c) UV absorbance values (measured as difference between peak value and baseline value) for the three UV-absorbing peaks (at elution times 7.2, 8.8, and 10.7 min) in HPSEC-UV chromatograms in part (d). (d) HPSEC-UV chromatograms obtained for selected time points in part (a).

**Figure 4.1** TEM images of ethylenediamine-functionalized graphene oxide after exfoliation by sonication followed by drying.

**Figure 4.2** XPS spectra of ethylenediamine-functionalized graphene oxides. Fitted model parameters appear in Table 4.1.

**Figure 4.3** (a) Zeta potential of amine graphene. Experimental conditions for a: 0.1 g l\(^{-1}\) graphene in 5 mM NaCl. (b) Effect of pH on the positive charged sorbate atenolol (AT, pK\(_a\) 9.4), the negative charged sorbate ibuprofen (IBU, pK\(_a\) 4.9), and the neutral sorbate carbamazepine (CBZ). Experimental conditions: 0.5 g l\(^{-1}\) amine graphene and initial sorbate concentrations of 80-90 mg l\(^{-1}\) in a buffer solution of 1 mM NaHCO\(_3\) and 20 mM NaCl. (c) Speciation diagram of IBU and AT. Positive species (red line), netual species
(blue line) and negative species (green line) coexist in the solution with varied percentages for pH from 2 to 12.  

**Figure 4.4** Sorption isotherms of amine graphene with varied sorbates including carbamazepine (red open diamonds), ibuprofen (blue filled triangles), and atenolol (green open circles). Solid lines are Freundlich model simulations. Experimental conditions: 1 g l\(^{-1}\) graphene, initial concentration of CBZ and AT 5 ~ 200 mg l\(^{-1}\), initial concentration of IBU 5 ~ 100 mg l\(^{-1}\), pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\), reaction time 20 min. 

**Figure 4.5** Competitive sorption of ibuprofen (blue filled triangles) and atenolol (green open circles) at equal initial molar concentrations in dual sorbate reactors with amine graphene. Dotted lines are Freundlich models of single solute sorption of ibuprofen (blue) and atenolol (green) from Figure 3. Experimental conditions: 1 g l\(^{-1}\) graphene, initial concentration of ibuprofen and atenolol ~20-480 µmol/L, pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\), reaction time 20 min. 

**Figure 4.6** Competitive sorption of ibuprofen onto amine graphene in dual sorbate systems with other selected negatively charged compounds including sodium acetate (black open square), NOM (pink dotted circle), acetaminophen (red open diamond), and salicylate (green open circle), compared to ibuprofen alone (blue filled triangles). Experimental conditions: 0.5 g l\(^{-1}\) graphene, initial concentration of ibuprofen ~10-60 mg l\(^{-1}\), initial concentration of NOM 22 mg l\(^{-1}\) TOC, initial concentration of salicylate, sodium acetate, and acetaminophen 50 mg l\(^{-1}\), pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\), reaction time 20 min. 

**Figure 5.1** TEM image of BC-Mag particles synthesized at 1000 °C. Electron-dense regions are iron minerals, and lighter particles are black carbon. Scale bar is 100 nm.
Figure 5.2 XRD pattern of BC-Mag particles synthesized at 1000 °C. M = magnetite, H = hematite, Fe(0) = iron metal (alpha form), Gr = graphite.......................... 123

Figure 5.3 Time profile of carbamazepine sorption on black carbon magnetitie 0.5 g l⁻¹, solid lines are pseudo-sceond order kinetic model simulation............................ 124

Figure 5.4 Sorption isotherms of carbamazepine on black carbon magnetite. Red solid line is Freundlich model simulation, and black dotted line is Langmuir model simulation. Experimental conditions: 1.0 g l⁻¹ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃... 124

Figure 5.5 Zeta potential of black carbon magnetitie compared to graphene C (Cai 2015 CEJ). Experimental conditions for a: 0.1 g l⁻¹ graphene in 5 mM NaCl....................... 125

Figure 5.6 Effect of pH on the neutral sorbate carbamazepine. Experimental conditions: 0.5 g l⁻¹ black carbon magnetite and initial sorbate concentrations of 70-80 mg l⁻¹ in a buffer solution of 1 mM NaHCO₃ and 20 mM NaCl......................................................... 125

Figure 5.7 Six repeated steps of BC-Mag reuse by ethanol washing (bar graph) and the recovery of carbamazepine by ethanol as desorbent from every step (dots and line). Experimental conditions: carbamazepine initial concentration 10 mg l⁻¹, mass of BC-Mag 10 mg, solution volume 10 ml, buffer solution of 1 mM NaHCO₃ and 20 mM NaCl..... 126
Chapter 1  **Introduction**

Graphene is a two-dimensional single sheet of pure carbon with 6-member ring in hybrid sp$^2$ electronic configuration. Graphene possesses remarkable structural, electrical, thermal and mechanical properties [1] for broad applications in material sciences as semiconductors [2], supercapacitors [3], catalyst support [4], sensors [5] and solar cells [6]. Graphene also has exceptional high surface area, and while thickness can be as low as 1 nm, sheet dimensions can stretch from nanosized to several microns, often folding upon itself, and possibly containing oxygen and hydrogen impurities. These properties allow for its extensive and varied interactions with organic contaminants in water. In fact, carbon nanotubes (CNT, visualized as rolled graphene) are now fairly well known for their sorptive and electronic capabilities in relation to organic contaminants in water. However, graphene sheets, as individuals and small stacks, have only recently been investigated for water treatment applications, and several concerns warrant future study including reaction mechanisms, dispersive ability, ease of manufacture, any required surface modifications, particle recovery, and overall performance in natural waters. The central motivation of this work is to expand our fundamental understanding of graphene and graphene-like surface coatings (herein collectively referred to as ‘graphitic’) with respect to sorption processes with organic pollutants at the same time addressing practical considerations of their use in water treatment and purification application. Graphene’s higher specific surface area (theoretical 2630 m$^2$g$^{-1}$, modified up to 3100 m$^2$g$^{-1}$, but in practice often <1000 m$^2$g$^{-1}$) and possible lower toxicity compared to CNT may promote
graphene-based materials as a preferred carbonaceous sorbent for organic contaminants removal, especially for some new emerging contaminants in water systems.

A broad class of endocrine disrupting compounds (pharmaceuticals, personal care products, hormones, pesticides, and others, hereafter collectively referred to as EDCs) have been detected in wastewater effluents, surface waters and even finished drinking water throughout the U.S. and Europe [7-10]. Found as a result of municipal discharge and diverse industrial and agriculture activities near water resources, EDCs have received considerable public attention regarding their occurrence, fate and toxicity because they can lead to adverse effects on the reproductive, neurological, and immune systems of aquatic organisms and humans [11-14]. Natural organic matter (NOM) is also commonly present in source water. It can react with chlorine and bromine, drinking water disinfectants, to form disinfection byproducts, such as the trihalomethanes (THMs) and the haloacetic acids (HAAs), which pose a threat to human health. Moreover, NOM is considered as the main reason for membrane fouling, a major constraint on the application of membrane processes for drinking water treatment [15]. NOM can also compete with targeting synthetic organics for sorption sites on activated carbon in drinking water treatment.

Since NOM and EDCs likely coexist in water systems, the reaction mechanism and removal processes should be addressed simultaneously. Complete removal of EDCs and NOM is desired prior to wastewater discharge or drinking water distribution, but conventional treatment operations may not produce suitable removal efficiencies [16-19]. Therefore, new treatment technologies are being examined for polishing EDC-containing waters [20], with a focus on sorption processes due to EDCs’ hydrophobic nature and low
solubility, or advanced oxidation processes due to reactivity of some structural moieties. Conventional activated carbon is a commonly used sorbent of organic molecules because of its high capacity, low cost, and ease of use, although sorption kinetics are highly variable and regeneration can be difficult. In contrast to activated carbon, carbon-based nanosorbents such as CNT or graphene may offer a more physically homogeneous surface with high surface area without pore diffusion restrictions, all of which could lead to more rapid or higher extent of sorption for small organic compounds.

Graphene-based materials are now being investigated for water treatment applications as an alternative to conventional carbonaceous materials. Graphene particles in lab studies are typically exfoliated from graphite by using modified Hummers method [21] and can be used as graphene oxide [22], reduced graphene oxide [23,24] or as a composite with mineral sorbents such as magnetite or ferric hydroxide [25-28,29] or mineral catalysts such as TiO2 and ZnO [30-34]. Graphene-based materials have demonstrated excellent sorption ability for the removal of dyes (methyl blue, natural red, rhodamine B, and methyl orange) [22,23,25,28,35,36], heavy metals (Pb, Cd, Cr and Hg) [37-39], aromatic compounds (tetracycline and naphthalene) [40], pesticides [41], algal toxins [42] and arsenic [27,29,43]. Comparing to traditionally used activated carbon, graphene can offer higher capacities and faster equilibration over a wide pH range, due to more homogeneous sites, less pore diffusion, and rapid π-π electron doner-acceptor (EDA) kinetics [44]. Although π-π EDA are often invoked as an important mechanism of sorbate-sorbent interactions for graphene and CNT alike, other mechanisms may be happening concurrently including hydrophobic interactions, electrostatic interactions, and hydrogen bonding with oxygen-bearing impurities (e.g. hydroxyl, carboxyl groups). The
relative abundances of surface functional groups and the relative occurrences of these mechanisms are closely linked to the overall sorption performances [45]. If surface functional groups on graphene behaves similarly to those on CNT, the presence of them can change the wettability of material surfaces, improve colloidal stability, provide H bond sites, and, in the case of hydroxyl groups, improve π-π electron donating character of C [46,47,14] even though in the case of CNT, they may hinder sorption by decreasing available Csp² area for nonpolar organics [48,49]. Therefore, an optimal arrangement of graphene surface properties should exist for any target organic sorbate and be achievable through fine-tuning graphitic surface chemistries.

Now that graphene particles are available commercially in high volume with a wide range of sizes and specific surface areas and represent a probable source for engineering applications, investigations are needed to address how these products are best suited for water treatment applications. Moreover, surface chemistries (functional groups, surface charges) of graphene particles can be technically adjusted or modified to achieve better sorption performance for targeted organic compounds. A second form of graphitic structure with growing interest for water treatment is graphitic carbon-coated magnetic iron oxides. These oxides, often magnetite, are coated with a high surface area, mildly hydrophilic carbon surface with graphitic structure suitable for sorption of targeted organics and followed by magnetic retrieval. The magnetic core may offer convenient separation of sorbent from the water prior to further treatment, and the resilient graphitic structure may allow product recovery through facilitated desorption, sorbent regenerability, and aggregation prevention.
The recent attention on graphene in water treatment has not included EDCs and NOM sorption, how sorption mechanisms change with surface chemistry, and natural water applications. The detailed mechanistic evaluation of CNT is now necessitated for graphene. This work will determine the efficacy and mechanisms of sorption and desorption of EDCs and NOM onto commercial graphene powders, study whether antagonistic or synergistic effect is dominating while EDCs and NOM adsorb onto graphene simultaneously, explore ways of modifying the surface charges of graphene with respect to surface functional groups in order to improve its sorption performance, and develop a way to synthesize magnetically-retrievable graphene.

1.1 Hypotheses

The overall objective of this work is to investigate and characterize removal of EDCs and NOM by commercial and laboratory-synthesized graphene particles under conditions relevant to drinking water treatment practice. To address this objective, the flow of work is divided into four main hypotheses which will be covered in four separate dissertation chapters. The four hypotheses and their respective expected results and contributions are listed below.

**Hypothesis 1**: Commercial graphene powders can be used as sorbents for rapid and high-capacity sorption of low molecular weight EDCs, and the rate and extent of EDCs sorption strongly depends on graphene specific surface area and surface chemistries.

**Hypothesis 2**: Commercial graphene powders can be used for rapid sorption of natural organic matter (NOM), and, similar to hypothesis 1, the rate and extent of NOM sorption strongly depends on graphene specific surface area and NOM aromatic character.
**Hypothesis 3:** Lab synthesized graphene modified to have positive surface charges, created by adding amine-functional groups, can enhance the sorption of negative EDCs compared to previously studied graphene with negative surface charges.

**Hypothesis 4:** Black carbon magnetite powders can be synthesized to possess fine-tuned surface chemistry, to be dispersible in aqueous solution, and to be retrievable with powerful magnet. Black carbon magnetite can be used as suitable sorbents for rapid and high-capacity sorption of EDCs.

### 1.2 Overview of the research

The dissertation has four main topics of studies: (1) Sorption of carbamazepine by commercial graphene oxides: a comparative study with granular activated carbon and multiwalled carbon nanotubes (Chapter 2). (2) Factors influencing natural organic matter sorption onto commercial graphene oxides (Chapter 3). (3) Ethylenediamine functionalized graphene: synthesis and application in charged contaminants removal (Chapter 4). (4) Facile synthesis and reuse of black carbon magnetite for fast carbamazepine removal (Chapter 5).

In Chapter 2, sorption rates and capacity of carbamazepine and other EDCs by various commercial graphene with different surface area and surface chemistries are investigated and compared to conventional sorbents activated carbon and carbon nanotubes. Physicochemical factors involved in π-π interactions, hydrophobic interaction and electrostatic interaction governing sorption of EDCs on commercial graphene are evaluated, and the results are expected to help identify which sources of graphene and which properties are most suitable for water treatment applications.
In Chapter 3, sorption kinetics and extents of NOM by commercial graphene are studied and compared to traditional sorbents. The study evaluates important removal mechanisms including \( \pi-\pi \) interactions and electrostatic interactions in the sorption of NOM by commercial graphene, and governing factors of sorption extent including available specific surface area of graphene, aromatic character of different types of NOM, NOM molecule charge and weight, and graphene surface charge.

In Chapter 4, a novel amine-functionalized graphene with positive charge on the surface was synthesized in laboratory through amidation processes using enthylenediamine. Sorption capacity of charged and neutral contaminants including ibuprofen, carbamazepine and atenolol by positive ethylenediamine functionalized graphene is evaluated under different water chemical conditions. Competitive sorption of negative ibuprofen with positive atenolol and other negative inorganic and organic compounds is also studied in this part of work.

In Chapter 5, a facile and easy synthesis of black carbon magnetite has been achieved and this graphitic magnetic powder can sorb carbamazepine with very fast rate and great extent. The magnetic black carbon magnetite can also be retrieved by magnet and regenerated using ethanol to prolong product life as sorbent for EDCs removal in water treatment applications. Sorption mechanism including \( \pi-\pi \) interaction, hydrogen bonding and electrostatic interaction is discussed and expected to govern the sorption performance.

Chapter 6 summarizes the conclusions, lists engineering significances and gives recommendations for future studies.
Chapter 2  
**Sorption of Carbamazepine by Commercial Graphene Oxides: A Comparative Study with Granular Activated Carbon and Multiwalled Carbon Nanotubes**

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2.1 Abstract

*Hypothesis*

Graphene nanosheet materials represent a potentially new high surface area sorbent for the treatment of endocrine disrupting compounds (EDCs) in water. However, sorption behavior has been reported only for laboratory graphene prepared by a laborious and hazardous graphite exfoliation process. A careful examination of commercially available, clean, high-volume produced graphene materials should reveal whether they are appropriate for sorbent technologies and which physicochemical properties most influence sorption performance.

*Experiments*

In this study, three commercially available graphene oxide powders of various particle sizes, specific surface areas, and surface chemistries were evaluated for their sorption performance using carbamazepine and nine other EDCs and were compared to that of conventional granular activated carbon (GAC) and multi-walled carbon nanotubes (MWCNTs).

*Findings*
Sorption kinetics of carbamazepine on graphene oxide powders were rapid and reversible with alcohol washing, consistent with π–π interactions. The various sorption extents as described by Freundlich isotherms were best explained by available surface area, and only the highest surface area graphene oxide (771 m²/g) out-performed GAC and MWCNTs. Increasing pH caused more negative surface charge, a two-fold decrease in sorption of anionic ibuprofen, a one-fold increase in sorption of cationic atenolol, and no change for neutral carbamazepine, highlighting the role of electrostatic interactions.

**Keywords:** Graphene; Carbamazepine; Endocrine Disrupting Compounds; Sorption Processes; Freundlich Isotherm; Water Treatment.

2.2 Introduction

A broad class of endocrine disrupting compounds (pharmaceuticals, personal care products, hormones, pesticides, and others, hereafter collectively referred to as EDCs) have been detected in water resources servicing drinking water facilities throughout the U.S. and Europe [1-3]. Found as a result of municipal, agricultural, and industrial waste activities, EDCs have received considerable public attention regarding their occurrence, fate, and biological activity because their observed amounts (often 1-1000 ng l\(^{-1}\)) can lead to adverse effects on the reproductive, neurological, and immune systems of aquatic organisms and humans [4-7]. Complete removal of EDCs is desired prior to wastewater discharge or drinking water distribution, but conventional treatment operations may not produce suitable removal efficiencies [8-11]. Therefore, new treatment technologies are being examined for polishing EDC-containing waters [12], with a focus on sorption processes due to EDCs’ mild to strong hydrophobic nature and wide range of solubilities, or on advanced oxidation processes due to susceptibility of some structural moieties to oxidative transformation.

Conventional activated carbon is a commonly used sorbent of organic molecules in practice because of its high capacity, low cost, and ease of use, although sorption kinetics are highly variable due to pore size irregularity, and performance problems can arise from biofilm growth or pore clogging. In contrast to activated carbon, carbon-based nano-sized sorbents such as carbon nanotubes (CNT) or graphene may offer a more physically homogeneous surface with high surface area without pore diffusion restrictions, all of which could lead to more rapid or greater extent of sorption for small organic compounds [13]. Ideal graphene is a two-dimensional single sheet of pure carbon
with 6-member ring in hybrid sp$^2$ electronic configuration with remarkable structural and electrical properties suitable for a variety of applications [14]. While thickness can be as low as one nanometer, planar dimensions can stretch from nanometer-sized to several microns, often folding upon itself due to self-adhesion. Individual graphene particles used within laboratory studies are typically exfoliated from parent graphite via a modified Hummers method [15] that includes chemical oxidation and expansion under acid, ultrasonicated exfoliation, and separation to form a final aqueous particle suspension. This process usually result in abundant oxygen and hydrogen impurities, leading to a graphene oxide material [16], which could be further chemically purified to reduced graphene oxide [17, 18]. The range of planar and edge surface sites, chemistries, and charges caused by graphene production may allow for various interactions with organic contaminants in water.

Graphene-based materials have recently been investigated for water treatment applications as an alternative to conventional carbonaceous materials. Graphene oxide and reduced graphene oxide have demonstrated excellent sorption ability for the removal of dyes [16, 17, 19-21], tetracycline compounds [22], aromatic compounds [23], pesticides [24], and algal toxins [25]. Among these studies, $\pi-\pi$ interactions (or $\pi-\pi$ stacking) are commonly invoked to explain sorption rate and extent for many organic compounds due to the wide availability of delocalized $\pi$ electrons at the graphene surface which can noncovalently overlap in a stacking arrangement with $\pi$ electrons within benzene rings of organic sorbates. Hydrophobic interactions, electrostatic interactions, other diverse $\pi$ interactions and dispersion interactions (van der Waals), and hydrogen bonding with oxygen-bearing impurities (e.g. carboxyl functional groups) may
also be important sorption mechanisms depending on sorbate and sorbent properties. Charged surface functional groups may improve the wettability of material surfaces, improve colloid stability, promote electrostatic attraction or repulsion for charged sorbates, and alter \( \pi \) electron donating character of Csp\(^2\) [26-28]. The relative abundances of surface functional groups and the relative occurrences of these mechanisms are closely linked to the overall sorption performances for CNTs [29] and may influence sorption on graphene materials similarly.

Now that graphene materials are available commercially in high production volume with a wide range of sizes and specific surface areas, investigations are needed to address how these products are best suited for water treatment applications. Laboratory-prepared exfoliated graphene oxide suspensions can effectively remove other EDCs rapidly [22], but a broader investigation is needed into the physicochemical factors affecting sorption for pre-made graphene materials that may be more likely utilized in large-scale applications in order to avoid the laborious procedures of Hummers method. The graphene materials studied here differ from the previously studied laboratory-synthesized graphene oxide suspensions in that they were pre-made by industrial processes, some of which may be circumventing the Hummers method and utilizing either thermal shock treatment or direct, one-step ultrasonication for exfoliation and a final drying step to a powder. These procedures are assumed to influence the surface properties and specific surface areas of the final powders which in turn likely influence the relative importance of the different sorbate-sorbent interactions. These materials are representative of those currently tested in water treatment technologies [30], and
comparative studies among available commercial graphene materials could identify the most desirable surface property, manufacturer, or product for targeted applications.

This work describes sorption kinetics, isotherms, and mechanisms of three types of commercially available graphene oxide powders for the removal of carbamazepine using wet chemical techniques. Carbamazepine, an anticonvulsant widely used for the treatment of epilepsy, was chosen as the primary target sorbate (in addition to nine other EDCs) because it is one of the 11 most frequently detected EDCs in water systems [1] and has a moderate solubility (~200 mg l\(^{-1}\)) which allows studying a range of concentrations. As a reference to other conventional and new carbonaceous sorbents, the sorption rates and extents on commercial graphene oxide powders are compared to granular activated carbon (GAC), carboxyl-functionalized hollow multi-walled CNTs (MWCNT-COOH), and similar carbonaceous sorbents reported in the literature [31-33]. Compared to conventional activated carbon, graphene may offer higher sorption capacities and faster equilibration over a wide pH range, due to more homogeneous sites, less pore diffusion, and rapid \(\pi-\pi\) interaction kinetics. Graphene’s higher specific surface area (theoretical 2630 m\(^2\)g\(^{-1}\) [34], but in practice often <1000 m\(^2\)g\(^{-1}\)) compared to CNT may promote graphene-based materials as a preferred carbonaceous sorbent for interfacial organic contaminant reactions.

### 2.3 Materials and Methods

#### 2.3.1 Materials
Three commercial graphene materials were purchased as powders and denoted as “C” (xGnp-C-750, XG Sciences, Inc), “M” (xGnp-M-25, XG Sciences, Inc), and “A” (N006-010-P, Angstron Materials, Inc.). MWCNTs were chosen in the carboxyl-functionalized form and denoted as “MWCNT-COOH” (PD15L1-5-COOH, Nanolab, up to 7% functionalized) instead of the pure form in order to more closely resemble the graphene oxide surface chemistry, surface charge, and dispersability in water. Granular activated carbon (GAC, Ducher) was briefly washed with deionized water to remove soluble matter and dried at 100°C.

Specific surface area (SSA) was measured by 5-point Brunauer-Emmett-Teller (BET) analysis following degassing at 80°C using a Quantachrome Nova 2200e instrument. The carbon structure and carbon-oxygen surface functional groups of the graphene oxides were identified by X-ray photoelectron spectroscopy (XPS) using a Surface Science Instrument SSX-100 (Cornell Center for Materials Research Facilities). Samples were mounted on double-sided carbon tape. Spectra were characterized using CasaXPS software. Transmission electron microscopy was performed with a Jeol JEM-1010 instrument. Samples were prepared by dispersing graphene oxides in water by sonication and applying droplets to holey carbon grids followed by drying. Surface charge as a function of solution pH was estimated by titration of 200 mg of graphene oxide in 100 ml of deoxygenated, deionized water within an anoxic chamber (98% N₂, 2% H₂). Solution pH measurements were taken after incremental additions of 0.1 M HCl or 0.1 M NaOH solutions and waiting for pH stabilization, and net surface charge was calculated by difference between the sum of known solute charges and electroneutrality.
2.3.2 Sorption Experiments

All sorption experiments for organic compounds and graphene oxides were conducted in batch reactors containing buffer solution of 20 mM NaCl and 1 mM NaHCO₃ in deionized water (>18 MΩ-cm) with small additions of 0.1 M HCl or 0.1 M NaOH to set solution pH. This NaCl concentration was chosen to poise ionic strength for a wide range of sorbate and sorbent concentrations, after verifying NaCl concentrations up to 40 mM have no influence on carbamazepine sorption extent on graphene C (Figure S2.1 in the Supplementary Materials). EDC stock solutions (4000 mg l⁻¹) were prepared in methanol, and spike volumes were kept below 0.1% of reactor volumes to minimize cosolvent effects. For all experiment types, EDCs were first spiked to buffer solution, and initial samples were taken by syringe and filtered through 0.2 µm PTFE filters. Reaction was initiated by addition of sorbents and immediately agitated. Aqueous samples were taken at predetermined time points by filtering through 0.2 micron PTFE syringe-tip filters. Samples containing MWCNT-COOH were also filtered via centrifugation ultrafiltration at 7,500 g using Amicon® Ultra-4 filters (3,000 MW cutoff) due to incomplete filtration with syringe-tip filters. The amount of EDCs sorbed was determined by difference between initial and final concentrations and normalized to mass of sorbent added.

Kinetic experiments with carbamazepine at an initial concentration of 90 mg l⁻¹ and either graphene oxide, MWCNT-COOH, or GAC at an initial concentration of 0.5 or 2.0 g l⁻¹ were performed at pH 7.2 in 100-ml glass bottles under magnetic stirring at room temperature for up to 24 hours. Isotherm experiments with carbamazepine at initial concentrations of 5-220 mg l⁻¹ and 1.0 g l⁻¹ of either graphene oxide, MWCNT-COOH, or
GAC were carried out at pH 7.2 within 30-ml glass vials with PTFE lined septa rotated end-over-end at room temperature with a contact time of 20 min. The solution pH remained at 7.2 ± 0.2 after completion of experiment. pH edges of neutral (carbamazepine) and ionizable organic compounds (ibuprofen, atenolol) were generated in a pH range of 3.0 – 11.0 with an initial concentrations of 80 mg l⁻¹ and 0.5 g l⁻¹ graphene C for 20 minutes. Single-point distribution coefficient experiments with other individual EDCs (atenolol, caffeine, sulfamethoxazole, acetaminophen, ibuprofen, atrazine, estriol, carbamazepine, bisphenol A, and gemfibrozil ) were performed in 30-ml glass vials, 0.1 g l⁻¹ graphene C, and initial EDCs concentration of 30 mg l⁻¹ in 20 ml buffer solution over 4 hours. Molecular structures (Table S2.1) and speciation diagrams over the pH range of 2 to 12 (Figure S2.2) for each EDC are presented in the Appendix.

### 2.3.3 Desorption Experiments

Carbamazepine at an initial concentration of 80 or 40 mg l⁻¹ was first exposed to graphene C at a concentration of 0.2 or 0.5 g l⁻¹ in 10 ml of buffer solution (20 mM NaCl, 1 mM NaHCO₃ at pH 7.2 or 9.2) within 20-ml glass vials for 20 minutes. Solids were then centrifuged at 5000 rpm for 5 minutes, and 8 ml of supernatant was carefully removed and replaced with either fresh buffer solution or ethanol to promote desorption. The suspension was immediately sonicated for 5 minutes to better disperse graphene oxide particles and then agitated by rotating end-over-end for 20 minutes. A total of eight desorption steps were carried out. Desorbed carbamazepine mass was determined by calculating the change in concentrations before and after each step, and cumulative percent desorption was calculated by summing mass desorbed at each step and normalizing to mass of initially sorbed carbamazepine.
2.3.4 Quantification of EDCs

Concentrations of EDCs and pharmaceuticals were analyzed by high performance liquid chromatography (HPLC) (Agilent 1260 Infinity Quaternary LC) with a UV detector using a 4.6 x 50 mm ODS Hypersil C18 column (Thermo Scientific) with injection volume of 10 µL and flow rate of 1 ml min^{-1}. HPLC eluent conditions and wavelengths of UV absorbance for each investigated compound are listed in Table S2.2 in the Supplementary Materials. Sample concentrations were determined by calibration to standard solutions of known concentration (0.5-150 mg l^{-1}).

2.4 Results and Discussion

2.4.1 Graphene characterization

Graphene oxides were characterized to describe surface features and chemistry prior to sorption experiments. The physical characteristics measured here and as reported by manufacturers are listed in Table 2.1. Graphene C possesses the smallest particle size and largest specific surface area (771 m² g⁻¹) among the purchased materials. Measured BET surface areas closely resemble reported values for C and M but were much smaller for A, possibly due to dry powder aggregation which could not be broken up by any means, such as by sieving, thereby minimizing N₂ gas adsorption. The particles were irregular in shape and planar with intermittent folds, as revealed by TEM for graphene A (Figure S2.3).

XPS survey spectra indicated the elemental composition to include significant amounts of carbon and trace amounts of sodium, sulfur, aluminum, or silicon resulting from the manufacturing process (Table 2.1). Higher resolution scans of the C1s and O1s
peaks provided insight to likely surface functional groups (Figure S2.4). Carbon sp² was most abundant as expected for graphene with a conjugated π system, although C sp³ was also prevalent likely due to C-C bonds within incomplete benzene structures. Oxygen bearing groups identified included hydroxyl (C-OH), ether (C-O-C), carbonyl (C=O), and carboxyl (O=C-OH). Complete model fitting values can be found in the Supplementary Materials (Table S2.3). Acid-base chemistry of the carboxyl groups (pKₐ values typically 4-5) and hydroxyl groups (pKₐ values typically 9-11) likely provide some negative surface charge and particle stability over a wide range of pH (discussed below).

2.4.2 Carbamazepine Sorption Kinetics

Fast sorption kinetics of carbamazepine was observed within suspensions of graphene oxides C, M, and A and on MWCNT-COOH (Figure 2.1). The kinetic profiles all show an initial rapid uptake step (<5 min) followed by a slower, incremental uptake step with equilibrium reached within less than one hour and a nearly constant sorbed concentration observed over 24 hours. This rapid approach to equilibrium with graphene oxide and MWCNT-COOH is in contrast to the slower kinetics observed for carbamazepine sorption on more pure MWCNTs with only 1-2 % oxygen impurities (2-15 hours until 80% sorption [33]). Enhanced particle stability caused by abundant deprotonated and therefore negatively charged carboxylic groups with our sorbents may be promoting particle dispersion, more reactive surface area, and faster sorption kinetics; in fact, agitated suspensions were not observed to settle quickly. Rapid sorption of charged organic compounds (within seconds) has been observed on charged MWCNT filters [35]. Uptake of carbamazepine on GAC was far slower and reached equilibrium after about 5 hours, most likely due to slow diffusion into pores. Readily available
surface area and electrostatic interactions between sorbate and sorbent, therefore, are likely two important factors governing sorption rate.

To further characterize the role of surface area and to better describe the sorption mechanism, the kinetic profiles were evaluated with the pseudo-first order, pseudo-second order, and intraparticle diffusion reaction models which are frequently applied to sorbate uptake but based on different physical-chemical assumptions. Of the three possible models, the pseudo-second order rate law best described the kinetics of carbamazepine sorption onto graphene oxides C, M, A and MWCNT-COOH with excellent model fits ($R^2 > 0.99$) (Figure 2.1). The equation of the rate law is:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$

where $q_t$ (mg g$^{-1}$) is the amount of sorbed carbamazepine on graphene at time $t$ (h), $q_e$ is the equilibrium sorbed concentration, and $k_2$ (g mg$^{-1}$ h$^{-1}$) is the pseudo-second order rate constant. This model assumes that sorption is controlled by the availability of sorbent surface sites rather than by aqueous sorbate concentration (sorbate concentration is assumed controlling in the pseudo-first order model), and that chemisorption or physisorption is the rate-limiting step rather than mass transfer (mass transfer is assumed rate-limiting in the intraparticle diffusion model) [36, 37]. The applicability of pseudo-second order models reflect the physical nature of sites on graphene oxide, most of which are exposed on planar surfaces for rapid sorption instead of hidden in pores of GAC or within bundles of aggregated CNTs. The pseudo-second-order model describing carbamazepine sorption on graphene is consistent with all other reports of organic
molecules sorption on graphene, graphene oxide, or modified graphene composites including methylene blue [19], methyl orange [20], bisphenol A [38], and tetrabromobisphenol A [39]. Carbamazepine sorption on MWCNT [33], a magnetic molecularly imprinted polymer [40], and Amberlite™ XAD-7 resin [41] also follows pseudo-second-order, but a pore diffusion model best described carbamazepine sorption on GAC [32]. Here, the intraparticle diffusion model did fit the data well for the first 20 minutes with GAC, and the pseudo-first order model poorly described sorption on all sorbents (Figure S2.5).

The integrated rate equation for \( q_t \) and relaxation time \( t_r \) are:

\[
q_t = q_e \frac{t}{(t + t_r)} \quad \text{(equation 2)}
\]

\[
t_r = \frac{1}{(k_2 q_e)} \quad \text{(equation 3)}
\]

Table 2.2 summarizes the kinetic model parameters of carbamazepine sorption. The rapid initial sorption step on all graphene oxides and MWCNT-COOH is reflected in the high values of \( k_2 \) and low values of \( t_r \) (1.4 s to 2.5 min), which represents the time required for sorbent sites to reach half-saturation. Carbamazepine sorption on GAC, however, showed a much slower \( t_r \) value of 36 min likely due to a slow mass transfer, although sorption extent after 24 hours was greater due to higher surface area. The \( k_2 \) values here are two to three orders of magnitude higher than those for carbamazepine on pure MWCNT [33] or tetrabromobisphenol A on graphene oxide [39] but similar for methylene blue on graphene-magnetite composite [19]. Consequently, the time to equilibrium sorption for graphene materials could take minutes instead of hours for GAC, a time scale more adaptable to full-scale treatment operations. Practically, considering twenty minutes as a commonly used empty-bed contact time (EBCT) in drinking water
treatment plant practice [42, 43], graphene oxide with sorption properties similar to C (95% carbamazepine removal) could out-perform GAC (only 25% removal).

Equilibrium sorption extent $q_e$ at a graphene oxides concentration of 0.5 g l$^{-1}$ increased in the order of A < M < C (Table 2.2), which is the same order of BET specific surface area (Table 2.1). Therefore, the higher sorption extent on graphene oxide C is likely due to a greater availability of surface sorption sites. In fact, normalizing sorption extent to surface area concentration results in similar $q_e$ values within a factor of two for all graphenes (except A at 0.5 g l$^{-1}$), which indicates specific surface area is a primary control on equilibrium sorption extent regardless of structural differences for carbonaceous sorbents. Increasing the concentration of graphene M and A from 0.5 g l$^{-1}$ to 2.0 g l$^{-1}$ also increased the equilibrium mass of carbamazepine sorbed, although less sorbed carbamazepine per unit mass graphene was observed. The small variations in sorption extent among all conditions could be caused by other factors such as surface chemistry, which can modulate types of sites, and particle aggregation or dispersion, which can influence availability of sites.

### 2.4.3 Carbamazepine Sorption Isotherms

A more complete description of the relationship between solid and solution phase carbamazepine partitioning was obtained in isotherm experiments at circumneutral pH and room temperature after twenty minutes. Sorption extent increased as each graphene was exposed to increasing concentrations of dissolved carbamazepine (Figure 2.2). Under all conditions tested, sorption extent was greater for graphene with the greater specific surface area according to the order C > M > A. GAC has comparable sorption extent as graphene oxide M, and MWCNT-COOH has higher sorption extent than
graphene M and A, but still much lower than the sorption extent of graphene oxide C (Table 2.3).

To better quantify sorption capacity among the three graphitic sorbents, GAC and MWCNT-COOH, the Freundlich, Langmuir, and Polanyi-Mane isotherm models were evaluated for best fit of experimental data. These models have been applied to describe carbamazepine sorption on activated carbon [31], CNT/Al₂O₃ composites [44], and MWCNTs [33], respectively. The Freundlich model matched the observations with excellent fits (0.95< $R^2$ <0.99) (Figure 2.2) with the equation:

$$q = K_F C_w^n$$

(4)

where $q$ (mg g⁻¹) and $C_w$ (mg L⁻¹) are solid-phase and aqueous-phase concentrations of carbamazepine respectively, $K_F$ (mg⁻¹Lⁿ/g) is the empirical constant related to sorption capacity, and $n$ (unitless) is the Freundlich linearity index. The applicability of the Freundlich model indicates graphene oxide possesses a distribution of surface sites of varying type, strength, or abundance, which is plausible for graphene here that contains oxygen-bearing functional groups, both planar surface and edge sites, and possible regions of different polarizability [45]. The Langmuir model, which assumes one type of surface site and monolayer coverage only, did not fit the data sets consistently well (0.42< $R^2$ <0.98, Figure S2.6) and therefore is considered an unreasonable descriptor. The Polanyi-Manes model, which is used to describe sorbent pore-filling by the sorbate, did fit the data sets almost as well as the Freundlich model (0.94< $R^2$ <0.97, Figure S2.6), which is reasonable considering its applicability to both porous and flat surfaces [46].

Further analysis of sorbent isotherms involves the fitted Freundlich model parameters for easier comparison to literature reports (Table 2.3). Values of $n$<1 show
incremental sorption becomes less at higher carbamazepine concentrations, a nonlinear behavior likely due to filling of preferred surface sites at lower concentrations. For the same mass concentrations of the three graphenes, $K_F$ values vary almost two orders of magnitude and increase with greater SSA and therefore greater availability of surface sites. In fact, a comparison of $K_F$ values for graphene sorbents with several different organic compound sorbates reported in the literature (Table 2.3) reveals a wide range of sorption capacities over two orders of magnitude, with our purchased M and A powders having the smallest and C among the highest. Normalizing the $K_F$ values to surface area results in similar values that vary less than four-fold, and a close range in values again suggests that available surface area is a primary factor to explain sorption extent for different graphene oxides. $K_F$/SSA values were identical for graphene oxide C and MWCNT-COOH, which shows remarkably similar sorption behavior for the two well-dispersed graphene-based nano-sized sorbents. Moreover, graphene oxide C exhibited the highest sorptive capacity with $K_F$ 94.1 mg$^{1-n}$L$^n$g$^{-1}$ for carbamazepine among any sorbent reported in the literature and described with the Freundlich model, including (i) a pristine 10 nm inner diameter MWCNT with $K_F \sim$20 mg$^{1-n}$L$^n$g$^{-1}$ (estimated from their Figure S2.3) [33]; (ii) a molecularly imprinted polymer with $K_F$ 28.7 mg$^{1-n}$L$^n$g$^{-1}$ [47]; and (iii) two GACs with higher specific surface area (1030 and 1156 m$^2$g$^{-1}$ GAC with $K_F$ 73.79 and 57.56 (ng/mg)(L/ng)$^{1/n}$ respectively [31]) compared to graphene C with a converted $K_F$ of 3881 (ng/mg)(L/ng)$^{1/n}$. Dispersions of high surface area graphene particles, therefore, may provide faster sorption kinetics and greater sorption capacity than any other carbonaceous sorbents, but care must be taken to select or synthesize highest possible surface area materials in order to promote greatest sorption extent.
The isotherm patterns begin to level off, or have already leveled off, as sorbed concentrations approach the expected coverage for one monolayer of carbamezepine for all graphene oxides and MWCNT-COOH. Monolayer coverage is expected to be between 4-25, 19-30, 28-101, and 181-195 mg g\(^{-1}\) for A, M, MWCNT-COOH, and C, respectively, depending on whether measured or reported SSA is used and assuming planar carbazepine orientation (calculations appear in Table S2.4). For A and M, these coverages bracket observe maximum sorption (16 and 24 mg g\(^{-1}\), respectively). MWCNT-COOH and graphene oxide C, with a maximum sorption of 110 and 215 mg g\(^{-1}\), respectively, may be hosting slightly greater (10%) than one monolayer coverage, consistent with reported pristine MWCNT [33]. These differences may reflect a small amount of sorbed carbamazepine in non-planar orientation or additional surface area not indicated by measured or reported SSA. The coincidence of monolayer coverage and maximum sorption with monolayer coverage indicates that the preferred sorption sites all exist on bare surfaces and that sorbate-sorbate stacking is not a significant sorption mechanism here.

2.4.4 Carbamazepine Desorption and Mechanism Observations

Incremental desorption of carbamazepine from graphene oxide C was observed during repeated washings and mostly ceased within eight desorption cycles for different aqueous conditions (Figure 2.3). Only partial sorbate removal occurred (26% or less), leaving a significant fraction of carbamazepine firmly sorbed that may be resistant to desorption caused by changing water conditions in treatment applications. Less percent desorption occurred when the initial concentration of carbamazepine was lowered or when the mass of graphene oxide was raised, and these observations suggest that lower
sorbate:sorbent ratios provide a greater relative amount of preferred, strongly-bound sites resistant to desorption. Similar sorption and desorption hysteresis has been widely observed for the sorption of organic compounds on CNTs including atrazine [48], 17R-ethinyl estradiol (EE2) [49], bisphenol A (BPA) [49], carbamazepine [33], oxytetracycline (OTC) [33], and cationic dyes [50].

Different types of surface sites and sorbate-sorbent interactions have been invoked to explain desorption hysteresis for organic compounds with graphitic surfaces. Strong and weak surface sites have been hypothesized to exist on MWCNT based on kinetic modeling, which could allow different degrees of desorption [33]. For more porous sorbents, capillary condensation in mesopores [51], irreversible pore deformation [51], and penetration and entrapment of sorbate into closed interstitial spaces, like bundles between CNTs [33, 48, 49], have been proposed. However, these mechanisms are less likely to explain desorption hysteresis on graphene oxide due to its planar surfaces with far fewer pore spaces. Formation of covalent bonds such as those observed between the functional groups on organic chemicals and CNTs [46, 52, 53] could be possible between the amide group of carbamazepine and surface functional groups on graphene oxide. To test the possibility of chemisorption versus physisorption, desorption with ethanol was performed, which should easily remove physisorbed carbamazepine due to preferred hydrophobic interactions and higher solubility (20.8 g l⁻¹). A recovery of 93% was achieved when desorbing with ethanol, revealing that carbamazepine molecules were not chemically transformed and likely only bound through physisorption. This observation also shows that regeneration of graphene oxides could be realized with
alcohol or other organic solvents, which could be an important cost-saving measure for the practical employment of graphene in the treatment applications.

The mechanism of $\pi-\pi$ stacking can best explain carbamazepine physisorption with surfaces. Like many organic sorbates with one or more benzene rings [17, 22, 38], carbamazepine has planar conjugated $\pi$-electron systems that can overlap with surface $\pi$-orbitals of graphene oxide in a favorably attractive geometric configuration. $\pi-\pi$ interactions can be influenced by surface functionalization [54], and we find evidence of supporting this interaction considering the SSA-normalized Freundlich affinity coefficients and the surface chemistry characterization for the different graphene oxides. Electron-activating groups can increase $\pi$-electron density and result in increased or stronger sorption when $\pi-\pi$ interactions are important. Our XPS results for all graphenes revealed the presence of phenol and ether groups which are strongly and moderately electron-activating, respectively. The phenolic/ether percentages of C1s spectra (Table S2.3) rank in the same order as the $K_f$/SSA values (A < M < C), indicating that enhanced $\pi$-electron density could explain the subtle improvement of SSA-normalized affinities.

Furthermore, the aromatic-aromatic interactions could be facilitated by the formation of a $\pi-\pi$ electron donor-acceptor (EDA) complex. Carbamazepine’s benzene ring structures are expected to act as a $\pi$-electron acceptor due to the electron withdrawing capability of the amide group, whose N atom, along with the heterocyclic ring N, are in sp$^2$ configurations with their lone pairs of electrons delocalized in bonds with the electron-withdrawing carbonyl group [55, 56]. $\pi$-electron donor groups on graphene include the aromatic benzene rings and electron-rich carbonyl groups. In fact,
the greatest $K_{p}/SSA$ value of graphene C could also be explained by having the highest percentage of carbonyl groups. $\pi-\pi$ EDA interactions have been hypothesized between carbamazepine and CNTs [33, 44], activated carbon [56], soil [57], and smectite with associated phenyl groups [58]. The strong $\pi-\pi$ coupling of benzene-ring-containing compounds with CNT surfaces was purposed as a mechanism for hysteresis [59] and should apply to graphene oxide materials as well. Hydrophobic interactions with ethanol, then, likely overcomes the $\pi-\pi$ EDA interactions and results in near complete desorption. Finally, because $\pi-\pi$ EDA interactions may be sensitive to pH [23], desorption was performed with higher pH solution (pH 9.2) and lead to more carbamazepine release (Figure 2.3), perhaps by a weakening of sorbate-sorbent interactions as graphene oxide surface functional groups deprotonate.

2.4.5 Factors affecting sorption extent using probe sorbates

In addition to $\pi-\pi$ stacking by aromatic compounds, the potential roles of other sorption mechanisms including hydrophobic interactions, $\pi-\pi$ EDA interactions, electrostatic interactions, and H-bonding were first investigated for several EDCs using values of the single-point distribution coefficient $K_d$:

$$K_d = \frac{q_e}{C_e}$$  \hspace{1cm} (equation 5)

where $q_e$ and $C_e$ are solid-phase and aqueous-phase concentration of EDCs at equilibrium. Based on the kinetics of carbamazepine sorption onto graphene C, a time of four hours was chosen to establish sorption equilibrium for all EDCs with graphene C.

In order to evaluate whether hydrophobic interactions dominate among sorption mechanisms, ten EDCs were chosen with fairly similar structures (low molecular weights with about one or two aromatic rings containing various moieties) but widely varying
tendencies to partition to organic phases. If hydrophobic interactions are the primary responsible sorption mechanism, the extent of sorption (here, $K_d$ value at pH 7.2 with 30 mg l$^{-1}$ initial sorbate concentration) should well correlate with a molecular descriptor for organic phase partitioning such as octanol-water partitioning coefficient ($K_{ow}$). Here, hydrophobicity is indicated by log $D$, which is equivalent to log $K_{ow}$ (octanol-water distribution coefficient) for neutral compounds, and corrected log $K_{ow}$ for anionic and cationic compounds (Table 2.4). No correlation between Log $K_d$ and log $D$ is apparent for this broad class of compounds examined with graphene C (Figure 2.4). No other correlations were observed considering molecular surface area or polarizability. Lack of any meaningful correlation is also reported across several classes of organic sorbates with CNTs [29, 60], indicating partitioning is a combination of several structural and electronic factors.

If hydrophobic effects, in the form of Log $D$ values, alone cannot explain sorption extent among these EDCs, the electrostatic, steric, or aromatic properties of individual molecules might be considered to gain some insights to what molecular factors influence sorption. If $\pi-\pi$ interactions between sorbate molecules and graphene surfaces are important, the molecules with greater aromatic character and planar arrangement may prove greater sorption extent due to greater availability of sorbate $\pi$ electrons to orient favorably with the graphene surface. If electrostatic interactions are important, sorbate molecules with charged moieties may enhance or inhibit sorption extent through attractive or repulsive interactions, respectively, with the partially negative graphene surface at pH 7.2. Eight of the ten compounds have $K_d$ values within a narrow range of about 10-19 L g$^{-1}$ (Table 2.4). Among these, the lowest $K_d$ value belongs to
sulfamethoxazole that has, in addition to possessing a low \( \log D \) value, two non-planar ring structures that are bent by the sulfonamide group, which may be unconducive to \( \pi-\pi \) stacking on surfaces, and a negative charge at pH 7.2, which may cause some repulsion from the partially negative graphene surface. Caffeine has the next lowest \( K_d \) value which could be explained by its two heterocyclic rings structures possessing lower aromatic character. Atenolol, gemfibrozil, acetaminophen, and ibuprofen all possess one aromatic ring and exhibit nearly identical \( K_d \) values (12.6-14.9 L/g) despite over four orders of magnitude difference in hydrophobicity. Next greatest in \( K_d \) value are Bisphenol A, which possesses two aromatic rings but in non-planar orientation, and atrazine, which has the substitutes \(-\text{NHC}_2\text{H}_5\) and \(-\text{NHCH(CH}_3)_2\) that may enhance \( \pi-\pi \) interactions by pushing electron density toward s-triazine ring [61]. Estriol and carbamazepine are most extensively sorbed likely due to both their multiple ring structures and fairly planar orientations.

\( \pi-\pi \) EDA interactions are regularly invoked as among the important binding mechanisms for organic sorbates containing benzene rings on carbon nanotubes [60, 62] and graphite [45, 63]. The graphene structure is thought to contain both \( \pi \)-electron donor regions, such as near edge defects containing oxygen functional groups acting as \( \pi \)-donors, and \( \pi \)-electron acceptor regions, such as among planar surfaces in between defects sites [45]. This property explains why several classes of aromatic compounds, whether possessing strongly \( \pi \) electron-donating groups such as \( \text{OH} \) in phenols [64, 65] or strongly \( \pi \) electron-accepting groups such as \( \text{NO}_2 \) in nitrobenzene [60, 64], readily bind to graphene surfaces, whether as individual sheets or rolled CNTs. Most of EDCs studied here possess either entirely electron donating groups (e.g. \( \text{OH} \) groups in BPA) or
a combination of both types (e.g. electron donating NH$_2$ and electron withdrawing sulfonamide in sulfamethoxazole). There is no trend among these EDCs in sorption extent and the amounts or types of electron donating or withdrawing groups, which underscores the notion that sorption extent is the product of several simultaneous mechanisms [29]. Moreover, the polarizability of the graphene surface suggests that the preferred sorption sites should vary for different molecules depending on their role as a $\pi$ electron donor or acceptor and that the strengths of the $\pi$$-$$\pi$ EDA may vary as well.

Overall, our results show that high surface area graphene oxide may sorb moderate concentrations of EDCs to similar extents and may not be selective to sorbate structural properties due a wide range of surface electronic properties.

To further probe electrostatic interactions for carbamazepine and charged compounds, sorption extent was quantified over pH 3-11, which covers a range of acid group deprotonation and therefore charge for both molecules and graphene surfaces. As solution pH increases, the hydroxyl and carboxyl surface functional groups deprotonate and produce a net negative surface charge on graphene C (Figure 2.5a). The increasingly negative surface charge has no effect on sorption extent for carbamezepine (Figure 2.5b). As a neutral molecule over this pH range, carbamazepine is not expected to have any electrostatic interactions caused by attractive or repulsive forces between charged functional groups of molecules and surfaces. Moreover, the lack of diminished sorption extent at higher pH indicates that hydrogen bonding between lone pairs of electrons on the carbonyl group do not interact significantly with protonated surface functional groups that lessen in abundance at higher pH. After eliminating electrostatic interactions and hydrogen bonding as possible mechanisms, $\pi$$-$$\pi$ interactions (and to some extent
hydrophobic interactions) are therefore expected to be the primary mechanisms of sorption for carbamazepine on graphene.

The increasingly negative surface charge at basic pH, though, significantly affects sorption extent of charged molecules, and the solution pH dependence of EDC sorption can be explained considering the pKₐ value of the sorbate. Ibuprofen and atenolol were selected for pH-edges because their respective carboxyl and amino groups deprotonate and change molecular charge from 0 to -1 and +1 to 0, respectively, over this pH range, allowing observations of sorption extent under different sorbate-sorbent charge relationships. Ibuprofen sorption is greatest when the molecule is neutral (pH < 4), and sorption extent decreases as pH is raised beyond its pKₐ of 4.91, when both ibuprofen and graphene acquire negative charge. Electrostatic repulsion is most likely responsible for the nearly two-fold drop in sorption, similar to anionic dye behavior with exfoliated graphene oxide [21]. Atenolol, whose cationic form predominates at pH below pKₐ of 9.43, steadily increases in sorption extent as the graphene surface becomes more negatively charged, and levels off once atenolol molecules are neutral. The sorbate-sorbent electrostatic attraction can best explain the pH-dependent trend, as observed for cationic dyes with graphene oxide [16, 21]. An additional atenolol reaction mechanism consistent with the observed trend is cation-π binding, an interaction between the positive secondary amine and the π-electron system of graphene, which has been suggested for tetracycline [22]. Because of the interest in graphene-based materials for treating dye-containing wastewaters [16, 19-21], commercial graphene oxide here was also examined for dye sorption ability with respect to molecule charge. The cationic dye crystal violet and anionic dye mordant blue 3 showed similar sorption trends across the same range of
solution pH (Figure S2.7), further confirming the role of electrostatic interactions to strongly influence sorption extent. The relationship between organic molecule charge and graphene oxide surface functional group charge should cause solution pH to be a critical factor for optimizing compound removal.

Overall, the primary mechanisms of EDC sorption to commercial graphene oxides studied here are likely π–π stacking interactions with strong influences of electrostatic forces if sorbate molecules possess charge. More subtle interactions in H-bonding and π–π interactions could be explored by examining classes of sorbate compounds with slightly varied moieties and creating structure-activity relationships or even observing shifts in bond vibrations using Fourier transform infrared spectroscopy [38]. The π-donating character of graphene oxide could be further characterized in such a way with compounds with known significant π-accepting ability, similar to observations with CNTs [29, 64]. Determining their relative contributions of several sorption mechanisms, though, would benefit from additional computational modeling to determine likely conformations of sorbed molecules and additional spectroscopic observations to probe functional groups involved in sorbate-sorbent interactions.

2.5 Conclusions

Our results and prior literature reports show that graphene materials, either purchased commercially or prepared in the laboratory, can possess a wide range of physicochemical properties and sorption behavior for dissolved organic compounds [16, 17, 21]. All graphene materials studied to date exhibit very fast sorption rates when used as aqueous dispersions and most effectively described using the pseudo-second order rate
model, reflective of their nature in aqueous dispersions as high surface area particles with well-exposed surface sites and little mass transfer limitations. Sorbed carbamazepine is held fairly strongly when washed with water, and near complete recovery is possible with alcohol washing.

This work provides insights to some practical considerations for incorporating graphene materials in water treatment technologies. For one, isotherm results suggest that specific surface area is a significant factor governing sorption extent, and selected graphene materials should be of the highest specific surface area, likely possessed by the smallest available particle size. Graphene oxide C (xGnp-C-750, XG Sciences, Inc, with 771 m² g⁻¹ SSA) showed one of the greatest sorption capacities for small organic molecules for carbonaceous sorbents. Graphene powders may be preferred over GAC and CNTs if graphene specific surface area is sufficiently high, in this case greater than 100 m² g⁻¹. While purchasing commercial graphene materials may be a practical alternative to preparing exfoliated graphene particles on-site, not all commercial graphene powders, though, may possess sorption capacities superior to other carbonaceous sorbents, as demonstrated with low-surface area products M and A here. This work also compares sorption extent among other studies with graphene sorbents made from graphite chemical exfoliation, and we found a wide variation in Freundlich sorption affinity values, further suggesting that any graphene material should first be tested for their sorption behavior (and SSA value) for the removal of targeted organics for specific water conditions.

Water chemistry may significantly affect sorption extent by altering the charges of graphene surfaces or organic molecules and therefore modifying electrostatic
interactions. An approximately two-fold increase (for cationic molecules) or decrease (for anionic molecules) in sorption extent could be possible for negatively-charged graphene oxide within the typical pH limits (about 6-10) of natural and treated water. The oxygen impurity contents (responsible for surface functional group acidity) among graphene powders should therefore be considered along with the charges of the organic compounds targeted for removal. We hypothesize that graphene surface charge could be modified through doping of element impurities or charged functional groups in order to manipulate sorption extent for particular compounds. Promotion of phenolic content may be helpful as well.

Graphene powder removed several different EDCs to fairly similar extents, and together with the removal of different dyes reported in the literature, graphene can be counted among carbonaceous sorbents universally applicable among many classes of organic compounds. We expect graphene powders, like GAC and CNTs, to also readily sorb other dissolved solutes including natural organic matter, and a broader investigation of sorption ability with respect to water chemistry is needed. The fundamental descriptions of sorption behavior here may support the incorporation of graphene materials in water treatment applications, such as their use in batch reactors or coatings or filtration membranes [30].

Acknowledgements

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**Appendix A: Supplementary Materials**

Supplementary data in the form of figures and tables associated with this article can be found in the end of the dissertation.
Table 2.1 Specific surface area, particle sizes (as reported from manufacturers) and elemental composition from XPS spectra of graphene oxide powders.

<table>
<thead>
<tr>
<th>Name</th>
<th>SSA (reported) (m²/g)</th>
<th>SSA (BET) (m²/g)</th>
<th>Particle size (reported)</th>
<th>XPS Percent relative area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cls</td>
</tr>
<tr>
<td>C</td>
<td>720</td>
<td>771</td>
<td>X-Y Dimension 2 micron, thickness 2 nm</td>
<td>79.5</td>
</tr>
<tr>
<td>M</td>
<td>120</td>
<td>74</td>
<td>X-Y Dimension 25 micron, thickness 6 nm</td>
<td>88.0</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>15</td>
<td>X-Y Dimension 14 micron, thickness 10 nm</td>
<td>85.2</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>200-400</td>
<td>112</td>
<td>Length 1-5 microns, outer diameter 15 nm</td>
<td>--</td>
</tr>
</tbody>
</table>
Table 2.2 Values of fitted parameters for the pseudo-second-order kinetic model (equation 1) of carbamazepine sorption on graphene oxides (C, M, and A), carboxyl-functionalized multiwalled carbone nanotubes, and granular activated carbon (90 mg L-1 initial carbamazepine concentration, 20 mM NaCl, 1 mM NaHCO₃, pH 7.2). R² > 0.99 for all model simulations.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbent Concentration g L⁻¹</th>
<th>tᵣ h</th>
<th>k₂ g mg⁻¹ h⁻¹</th>
<th>qₑ mg g⁻¹</th>
<th>qₑ mg m⁻²</th>
<th>Mass CBZ sorbed mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.5</td>
<td>0.007</td>
<td>0.8</td>
<td>169</td>
<td>0.22</td>
<td>4.21</td>
</tr>
<tr>
<td>M</td>
<td>0.5</td>
<td>0.019</td>
<td>1.6</td>
<td>32.5</td>
<td>0.44</td>
<td>0.99</td>
</tr>
<tr>
<td>M</td>
<td>2</td>
<td>0.041</td>
<td>1.0</td>
<td>24.4</td>
<td>0.33</td>
<td>2.83</td>
</tr>
<tr>
<td>A</td>
<td>0.5</td>
<td>4.0 × 10⁻⁴</td>
<td>157</td>
<td>16.2</td>
<td>1.09</td>
<td>0.39</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>7.0 × 10⁻⁴</td>
<td>200</td>
<td>7.2</td>
<td>0.48</td>
<td>0.76</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>0.5</td>
<td>1.0 × 10⁻⁴</td>
<td>93</td>
<td>108</td>
<td>0.96</td>
<td>2.52</td>
</tr>
<tr>
<td>GAC</td>
<td>0.5</td>
<td>0.606</td>
<td>0.01</td>
<td>200</td>
<td>0.17</td>
<td>4.46</td>
</tr>
</tbody>
</table>
Table 2.3 Freundlich model parameters for carbamazepine sorption on graphene oxides (C, M, and A), carboxyl-functionalized multiwalled carbon nanotubes, and granular activated carbon at pH 7.2.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>$R^2$</th>
<th>$n$</th>
<th>$K_F$ †</th>
<th>$K_F$ / SSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.97</td>
<td>0.24</td>
<td>94.1</td>
<td>0.12</td>
</tr>
<tr>
<td>M</td>
<td>0.95</td>
<td>0.30</td>
<td>5.61</td>
<td>0.08</td>
</tr>
<tr>
<td>A</td>
<td>0.99</td>
<td>0.53</td>
<td>1.17</td>
<td>0.07</td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>0.98</td>
<td>0.48</td>
<td>13.9</td>
<td>0.12</td>
</tr>
<tr>
<td>GAC</td>
<td>0.97</td>
<td>0.57</td>
<td>2.98</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*Literature reports for Freundlich models with graphene or graphene oxide tetrabromobisphenol A [39] 123.9  --
  bisphenol A [38] 54.7  0.16
  oxytetracycline, doxycycline, tetracycline [22] 41.6-  46.5  --
  methylene blue [19], 16.6  --
  methylene blue, rhodamine b [66], 11.2-  16.6  0.04-0.06
  methylene blue, methyl violet, rhodamine b, orange G [21] 0.5-9.4  --

†All Freundlich modeling was performed on data with units of dissolved sorbate concentration in mg l$^-1$ and sorbed sorbate concentration of mg g$^-1$. 
Table 2.4 Selected physical and chemical properties of endocrine disrupting compounds in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type(^a)</th>
<th>MW (g mol(^{-1}))</th>
<th>(pK_a)</th>
<th>Charg e, pH(^{7.2})</th>
<th>(S_w) (mg l(^{-1}))</th>
<th>Log (K_{ow})</th>
<th>Log (D)^(b)</th>
<th>(K_d)^(c) (L g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estriol</td>
<td>Steroid</td>
<td>288.4</td>
<td>10.4</td>
<td>0</td>
<td>441</td>
<td>2.45</td>
<td>2.45</td>
<td>39.7</td>
</tr>
<tr>
<td>Caffeine</td>
<td>PCP</td>
<td>194.1</td>
<td>0.6, 14</td>
<td>0</td>
<td>2.16×10(^4)</td>
<td>-0.07</td>
<td>-0.07</td>
<td>11.6</td>
</tr>
<tr>
<td>BPA</td>
<td>Plasticizer</td>
<td>228.3</td>
<td>10.3</td>
<td>0</td>
<td>120</td>
<td>3.32</td>
<td>3.32</td>
<td>17.0</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>Pharm.</td>
<td>206.3</td>
<td>4.9, 1</td>
<td>-1</td>
<td>21</td>
<td>3.97</td>
<td>1.60</td>
<td>14.8</td>
</tr>
<tr>
<td>Carbamazepin</td>
<td>Pharm.</td>
<td>236.3</td>
<td>2.3, 13</td>
<td>0</td>
<td>170</td>
<td>2.45</td>
<td>2.45</td>
<td>44.0</td>
</tr>
<tr>
<td>Atenolol</td>
<td>Pharm.</td>
<td>266.3</td>
<td>9.4, 8</td>
<td>+1</td>
<td>1.35×10(^4)</td>
<td>0.16</td>
<td>-2.02</td>
<td>12.6</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>Pharm.</td>
<td>151.2</td>
<td>9.3, 1</td>
<td>0</td>
<td>1.4×10(^4)</td>
<td>0.46</td>
<td>0.46</td>
<td>14.4</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Antimicr.</td>
<td>253.3</td>
<td>1.4, 5.8</td>
<td>-1</td>
<td>610</td>
<td>0.89</td>
<td>-0.58</td>
<td>9.8</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Pesticide</td>
<td>215.7</td>
<td>1.7, 2</td>
<td>0</td>
<td>35</td>
<td>2.61</td>
<td>2.61</td>
<td>19.1</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>Pharm.</td>
<td>250.3</td>
<td>4.4, 2</td>
<td>-1</td>
<td>19</td>
<td>4.77</td>
<td>1.94</td>
<td>13.1</td>
</tr>
</tbody>
</table>

\(^a\) PCP = personal care product, Pharm.= pharmaceutical. Antimicr. = antimicrobial compound.

\(^b\) Corrected values of log \(K_{ow}\) are, anionic: log \(D\) = log \(K_{ow}\) – log \((1 + 10^{(pH-pK_a)})\)
cationic: log \(D\) = log \(K_{ow}\) – log \((1 + 10^{(pK_a-pH)})\).

\(^b\) Measured single-point distribution coefficient at pH 7.2, 30 mg l\(^{-1}\) EDC, 0.1 g l\(^{-1}\) graphene C.
LIST OF FIGURES

Figure 2.1 Time profile of carbamazepine sorption on different graphitic sorbents (C 0.5 g l\(^{-1}\), red open diamonds; M 0.5 g l\(^{-1}\), green open circles and 2 g l\(^{-1}\), green filled circles; A 0.5 g l\(^{-1}\), blue open triangles and 2 g l\(^{-1}\), blue filled triangles), MWCNT-COOH (0.5 g l\(^{-1}\), pink open inverted triangles), and GAC (0.5 g l\(^{-1}\), black open squares) and. The solid lines are pseudo-second order kinetic model simulation, described in equations 1 and 2. Experimental conditions: pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\).

Figure 2.2 Sorption isotherms of carbamazepine on graphene C (red diamonds), M (green circles), A (blue triangles), MWCNT-COOH (pink inverted triangles), and GAC (black squares). Solid lines are Freundlich model simulations. Experimental conditions: 1.0 g l\(^{-1}\) sorbent, pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\).
Figure 2.3 Desorption of carbamazepine (CBZ) from graphene C. Red open squares: [CBZ] 80 mg l⁻¹, graphene C 0.2 g l⁻¹, desorbed with pH 7.2 buffer solution. Red filled squares: [CBZ] 40 mg l⁻¹, graphene C 0.2 g l⁻¹, desorbed with pH 7.2 buffer solution. Red open diamonds: [CBZ] 80 mg l⁻¹, graphene C 0.5 g l⁻¹, desorbed with pH 7.2 buffer solution. Blue open diamonds: [CBZ] 80 mg l⁻¹, graphene C 0.5 g l⁻¹, desorbed with pH 9.2 buffer solution. Red open triangles: [CBZ] 80 mg l⁻¹, graphene C 0.5 g l⁻¹, desorbed with ethanol.

Figure 2.4 Partition coefficient ($K_d$) of the EDCs arranged according to $log D$ values. Experimental conditions: 0.1 g l⁻¹ graphene C, initial EDCs concentration 30 mg l⁻¹, pH 7.2, 20 mM NaCl, 1 mM NaHCO₃, contact time 4 h. CBZ = carbamazepine, E3 = estriol, AT = atenolol, SMZ = sulfamethoxazole, CAF = caffeine, APAP = acetaminophen, IBU = ibuprofen, GEM = gemfibrozil, ATZ = atrazine, BPA = bisphenol A.
Figure 2.5 Effect of pH on EDC sorption onto graphene C. (a) Surface charge of graphene C. (b) Effect of pH on the positive charged sorbate atenolol (AT), the negative charged sorbate ibuprofen (IBU), and the neutral sorbate carbamazepine (CBZ). Experimental conditions for both a and b: 0.5 g l\(^{-1}\) graphene C and initial EDCs concentration of 80 mg l\(^{-1}\) in buffer solution 1 mM NaHCO\(_3\) and 20 mM NaCl.
Chapter 3  **Factors influencing natural organic matter sorption onto commercial graphene oxides**

*This paper was published in Chemical Engineering Journal in 2015*

### 3.1 Abstract

Nanosized graphene materials are being considered as a class of new, high surface area sorbents suitable for water treatment applications. This study explored commercially available graphene powders of differing sizes, surface areas, and surface compositions for their ability to sorb dissolved natural organic matter (NOM) from water under varying solution conditions within batch reactors. The sorption kinetics of NOM on graphene powders were rapid and reached equilibrium within hours. Sorption isotherms for all graphenes and all NOM types were all best described with the Freundlich model. Sorption affinity improved with increasing graphene specific surface area, more graphene carbon content, greater NOM aromatic content, and lower solution pH. Graphene sorption behavior is compared to carbon nanotubes and granular activated carbon, and high surface area graphene may possess superior sorption rates and capacities, whereas low surface area graphene may be entirely ineffective. The high surface area graphene examined here also showed selectivity for the aromatic and high molecular weight NOM fractions within measurements of specific UV absorbance and size exclusion chromatography. The results suggest that aromatic interactions significantly participate in NOM binding, but that electrostatic interactions may also influence sorption capacity depending on solution pH and graphene surface charge.
**Keywords:** Graphene; Natural Organic Matter; Sorption Processes; Freundlich Isotherm; Water Treatment.

3.2 Introduction

Dissolved natural organic matter (NOM) in drinking water sources can pose problems for water quality and treatment processes, including making contributions to disinfectant byproduct formation [1], membrane fouling [2], and undesirable taste and odors. Removal of NOM (as well as anthropogenic organic micropollutants) from water can be partially achieved through activated carbon sorption, chemical coagulation and co-precipitation, and membrane treatment. However, incomplete removal extents, slow sorption kinetics, or high operation costs has prompted the need for sorbent-based technologies that feature shorter reaction times, easier manufacture, and lower expense [3]. Consequently, development efforts in the past decade have explored carbon nanotubes (CNTs) and graphene sheets as the next-generation sorbents owing to their improved available surface areas, faster sorption rates, and size-dependent reactivities. These sorbents have been incorporated into woven mat configurations as filters or sorbents [4-8], impregnated onto membranes to enhance removal of targeted organic molecules through sorption processes [9], or used for improved biocidal properties [10].

This work investigates interactions between dissolved NOM and commercially-obtained graphene sheets in order to evaluate their potential use in water treatment technologies. Recent investigations into the fundamental interaction mechanisms between NOM and CNTs or graphene sheets has shown that sorption behavior is governed by the chemical similarities between NOM and sorbents, in ways not unlike the interactions between NOM and activated carbon [11,12]. Ideal, pristine CNTs and graphene sheets are both pure carbon with 6-member aromatic rings in hybrid sp\(^2\) electronic configuration, but with CNTs possessing a rolled tubular structure of single or
multiple walls and graphene sheets assuming an open planar shape of single or multiple layers. Laboratory-synthesized or commercially-manufactured materials commonly contain chemical impurities in the form of surface functional groups containing O, N, or H atoms made present by targeted chemical functionalization (e.g. oxidative formation of carboxylic acid on CNTs by strong acids) or as a byproduct of synthesis (e.g. surface oxidation of graphene by KMnO₄ during graphite by Hummer’s method). Dissolved NOM is comprised of a complex and chemical heterogeneous mixture of polymeric organic compounds that arise from the decomposition of plant and animal matter and contain a distribution of chemical moieties, including carboxylic and fatty acids, proteins, and aromatic and alkyl structures. Surface water or soil organic matter may be characterized chemically into aromatic-rich hydrophobic fractions and polar functional group-rich hydrophilic fractions, or categorized functionally into humic acid (HA) and fulvic acid (FA) fractions based on solubility in acid. The variety of aromatic and polar properties for both sorbates and sorbents consequently allow for several interaction mechanisms, including \(\pi-\pi\) interactions between overlapping sorbate and sorbent aromatic rings, electrostatic interactions between deprotonated acid groups of NOM and charged surface functional groups of graphene, hydrogen bonding between polar moieties in NOM and O-containing hydrophilic functionalities at graphene surfaces and general hydrophobic interactions between similar carbon structures \([5,13,14]\).

The dependence of these interaction mechanisms on sorbent properties, NOM composition, and water chemistry has been more carefully and thoroughly examined for CNTs compared to graphene. Higher CNT loadings, greater CNT specific surface area, or higher NOM concentrations lead to greater sorption extent by providing greater
surface area or driving force toward sorption equilibrium [14-21]. High solution pH may diminish sorption due to electrostatic repulsion between deprotonated acid functional groups on both NOM and CNT surfaces. Higher ionic strength promotes NOM sorption by the change in molecular configuration of NOM to be more coiled and compact, and therefore less soluble [15,21]. NOM with higher aromatic content [15,16,19] and lower polarity [17,22] tend to sorb to a greater extent presumably through improved abundance of π−π or hydrophobic interactions. Similarly, CNTs with less surface oxygen functional groups show superior NOM sorption due to less polar (and greater aromatic and hydrophobic) character [23]. However, polar functional groups of FA were observed to participate in sorption at low pH for FA [16], likely due to H-bond interactions between protonated HA functional groups and CNT surface oxygen groups. Sorption has also shown to prefer larger molecular weight (MW) sizes of NOM [15] and FA [16] but smaller MW sizes of HA [22].

However, what remains to be determined is whether NOM sorption onto graphene sheets is controlled by the same interaction mechanisms in the same manner as onto CNTs. Similar to CNTs, the graphene π aromatic system and oxide surface charges have been shown to influence HA sorption through π−π interactions and electrostatic repulsion, respectively, on graphene oxide [24], reduced graphene oxide [24], and unexfoliated graphite oxide [25]. Unlike CNTs, though, the oxygen functional groups of graphene oxide were observed by FTIR spectroscopy to directly participate in H-bonding with polar functional groups of HA [24]. The relative contributions of each sorption mechanism may therefore differ slightly between graphene sheets and CNTs owing to some chemical and structural differences. For one, graphene sheets are reported to have a
larger degree of surface oxidation (up to 50% O compared to only ~2% for CNTs) and possibly different spatial distribution of oxygen functional groups, which could lead to a greater abundance of polar surface regions at the expense of aromatic regions. The resulting additional surface charges upon functional group deprotonation could lead to stronger electrostatic repulsion interactions, less $\pi-\pi$ interactions, and greater colloidal stability. Stable graphene sheets also have open planar faces which could provide greater available surface area and more rapid sorption kinetics, compared to CNTs which readily aggregate and form interstitial spaces which could result in pore diffusion restrictions.

Finally, additional aquatic NOM, HA, and FA isolates need to be tested over a broader range of graphene types and solution conditions in order to assess graphene as the next-generation sorbents for surface water treatment applications. Beyond these two reports of HA sorption onto graphitic surfaces [24,25], additional work is needed to characterize how NOM sorption is influence by material and water chemistry. The objective of this work is to evaluate commercial graphene materials as an alternative carbonaceous sorbent for the removal of NOM from water, with a focus on determining whether the factors influencing NOM sorption onto graphene are similar to those documented for MWCNT sorbents. The predominance of the aromatic carbon rings common to both sorbents should result in similar NOM sorption behavior, but the differing graphene structure and surface chemistry may influence the sorption rates, capacities, or mechanisms. Commercial graphene powders were chosen instead of laboratory-synthesized ones because (i) they are more likely to be used in large volumes for water treatment applications due to lower cost, and (ii) they may vary in sheet size, specific surface area, and surface chemistry which may in turn influence sorption of
organic compounds [26]. In this work, sorption behavior of IHSS standard and reference organic matter from various sources were quantified within isotherm, pH-edge, and kinetic studies and compared to those of the more conventional CNT and GAC carbonaceous sorbents. Total organic carbon and UV-vis spectrophotometric measurements for a wide range of solution conditions provided insight to preferred sorption mechanisms and any sorption-induced fractionation of NOM. Through evaluating graphenes with different particle sizes and surface chemistries, it should be possible to identify key factors for selecting graphene for water treatment applications.

3.3 Materials and Methods

3.3.1 Materials

Five commercial graphene oxide powders were purchased from two manufacturers and denoted as “C” (xGnp-C-750, XG Sciences, Inc), “C500” (xGnp-C-500, XG Sciences, Inc), “C300” (xGnp-C-300, XG Sciences, Inc), “M” (xGnp-M-25, XG Sciences, Inc), and “A” (N006-010-P, Angstron Materials, Inc.). After showing no NOM sorption in preliminary experiments, graphene A was thermally treated (“A-heated”) in a 400°C oven for 1.5 h in order to vaporize possible residual organic compounds and to decompose some oxygen functional groups for improved sorption [21]. Although all graphene materials contained some surface oxidation and thus may be considered graphene oxides, they are collectively referred to as “graphene” here for consistency with manufacturers. MWCNTs were chosen in pristine form (PD15L1-5, Nanolab) and used as received. Granular activated carbon (GAC, Duchar) was washed with deionized water and dried at 100°C.
All sorbents were characterized for chemical composition by X-ray photoelectron spectroscopy (XPS) and specific surface area (SSA) by 5-point Brunauer-Emmett-Teller (BET) as described previously [26] (Table S3.1, Table S3.2, and Figure S3.1). Table S3.1 also lists average particle sizes as reported by the manufacturer. SSA values range from 26 to 771 m² g⁻¹, and carbon composition values range from 79.5 to 95.7% among all graphenes. Zeta potential was measured using a Malvern Nanosizer ZS90 for dilute aqueous suspensions of graphenes C, M, and A-heated with pH modified by small additions of 0.1 M HCl or 0.1M NaOH. Selected samples of graphene were measured by FTIR. Spectra were collected in attenuated total reflectance (ATR) mode on a Bruker Equinox55 spectrometer equipped with an MCT detector and a Bruker Platinum ATR accessory (single bounce diamond coated ZnSe optic). In all cases, the reference spectrum was the clean and empty ATR crystal. Samples were prepared by making a slurry of ~5 mg graphene solid in 0.1 mL HPLC grade ethanol and then drop coating the slurry onto the diamond ATR crystal. Successive scans were taken until ethanol evaporated and no ethanol remained in the spectrum. For all spectra, 256 co-added scans were collected at 4 cm⁻¹ resolution from 4000-400 cm⁻¹.

Suwannee River natural organic matter (SRNOM), Suwannee River humic acid standard II (SRHA), Suwannee River fulvic acid standard II (SRFA), Nordic lake natural organic matter (NordNOM), Elliott Soil humic acid standard (ESHAA), Pahokee Peat humic acid standard (PPHA), Leonardite humic acid standard (LeoHA), and Nordic lake fulvic acid reference (NordFA) were purchased from the International Humic Substance Society (IHSS) (St. Paul, MN). Here, “NOM” is used throughout this manuscript to refer to dissolved organic matter in a general sense regardless of its source and extraction.
method, and the two aquatic natural organic matter reference materials isolated by reverse osmosis will be referred to as “RO-isolated NOM” or by their specific acronyms above (SRNOM and NordNOM). NOM chemical compositions as reported by IHSS are presented in Table S3.3.

3.3.2 Sorption experiments

Batch reactors were used to perform all sorption experiments for NOM and graphene oxides in buffer solutions of 1 mM NaHCO₃ and 20 mM NaCl in deionized water (>18 MΩ-cm) with pH adjusted to 7.2 by adding small volume of 0.1 M HCl and 0.1 M NaOH. NOM stock solutions were prepared by dissolving 7 mg NOM into 20 ml buffer solution and rotating end-over-end overnight. Solutions were then filtered with 0.25 μm nylon filters followed by 0.02 μm inorganic membrane filters to remove undissolved humin and particulate matter. Because some fractions of NOM are more soluble at alkaline pH, 0.1 M NaOH was added to adjust solution pH to 9-10 at the beginning and adjust back to 7.2 after the filtration process. NOM stock was diluted with more buffer solution to desired UV absorbance or total organic carbon (TOC) concentrations and placed into glass vials with PTFE-lined caps. After addition of sorbents vials were immediately agitated by vigorous shaking for a few seconds and rotated end-over-end. Aqueous samples were taken by syringe and filtered through 0.25 μm syringe-tip nylon filters at predetermined time points. Graphene C was the most frequently utilized sorbent in batch reactors owing to its greatest SSA and superior performance with organic micropollutants [26].

Kinetic experiments with SRNOM and 0.25 g l⁻¹ graphene, MWCNTs, or GAC were performed at pH 7.2 at an initial UV absorbance of 0.2 in 100-ml glass bottles under
magnetic stirring at room temperature for 24 hours. Isotherm experiments were conducted with fixed NOM initial UV absorbances of 0.8 and varied sorbent concentrations of 0.05–1.1 g l\(^{-1}\) in buffer solution at pH 7.2 in 30-ml glass vials with PTFE lined caps rotated end-over-end at room temperature with a contact time of 24 hours. pH edges of SRNOM with an initial UV absorbance of 0.2 were generated with 0.25 g l\(^{-1}\) graphene C, M or A-heated in a pH range of 3.0–11.0 for 24 hrs.

2.3 Quantification of NOM

Concentrations of NOM were determined as total organic carbon (TOC) using a TOC analyzer (Shimadzu TOC-L CPH/CPN). A UV-Vis spectrophotometer (Shimadzu UV mini-1240) was used to measure UV absorbance at a wavelength of 254 nm, and SUVA\(_{254}\) values were calculated as this UV absorbance divided by TOC concentration (mg l\(^{-1}\)) and 0.01 m quartz cell path length. For SRNOM, different stock solutions were prepared from multiple purchased vials of the same source material and dissolved under slightly different solution conditions, causing slightly different initial SUVA\(_{254}\) values.

High-performance size exclusion chromatography (HPSEC) was conducted on NOM solutions to determine a chromatographic profile of the molecular weight distribution before and after sorption. A liquid chromatography unit (Agilent 1260 Infinity Quaternary HPLC) with an SEC column (Tosoh, TSK gel BioAssist G2SW\(_{XL}\), 7.8 mm ID × 30 cm, 5 µm particle size) and 10 mM phosphoric acid pH 6.8 eluent was used. Detection of NOM was achieved only with a UV detector set at 254 nm (as opposed to in-line organic carbon detection, and consequently chromatographic profiles represent only aromatic portions of NOM molecules). Compounds used for standard molecular weights included p-amino benzoic acid (137 Da) and the poly (styrene
sulfonate) sodium salt compounds PSS-pss 1k (1100 Da), PSS-pss 2k (1830 Da), PSS-pss 3.4k (3610 Da), PSS-pss 8k (7930 Da), PSS-pss 15k (14900 Da) from Polymer Standards Service GmbH.

3.4 Results and Discussion

3.4.1 NOM sorption kinetics

A rapid approach to equilibrium sorption was observed for SRNOM binding to graphenes C, M, and A-heated and pristine MWCNTs, whereas a slower uptake occurred for GAC (Figure 3.1). Kinetic timecourses for graphenes and MWCNTs held sharp increases at the beginning stage (<5 min), and then leveled off after one hour contact time until apparent equilibrium reached over 5 to 24 hours. Therefore, 24 hours was determined as the contact time for all subsequent equilibrium experiments. Similar fast initial uptake of NOM or NOM surrogate compounds have been reported for MWCNT suspensions [21,27], although time to equilibrium may be much longer owing to diffusion into interstitial spaces of CNT aggregates [22]. Comparatively, uptake of SRNOM on GAC was much slower within the first three hours and steadily increased in a somewhat linear fashion until 24 hours. This linear behavior is more apparent in Figure S2 which contains an unbroken linear time axis. The slower kinetics with high surface area GAC is suggestive of a pore diffusion step primarily controlling the sorption process of SRNOM onto GAC [12], and no indication of equilibrium being reached within 24 hours is recorded.

In order to better compare sorption behavior among sorbents and to further understand the sorption mechanism, commonly used kinetic models for sorbate-sorbent
reactions in aqueous solutions were applied to the kinetic data, including pseudo-first order, pseudo-second order and intraparticle diffusion models. The pseudo-second order rate law best describe the kinetics of SRNOM sorption on graphene C, M, A-heated and pristine MWCNTs with correlation coefficient $R^2>0.99$ (Figure 3.1 and Table 3.1). The equation of pseudo-second order model is $\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$, where $q_t$ (mg g$^{-1}$) is sorbed SRNOM concentration on graphene at time $t$ (h), $q_e$ is sorbed SRNOM concentration on graphene at equilibrium, and $k_2$ (g mg$^{-1}$ h$^{-1}$) is the pseudo-second order rate constant. The pseudo-second-order model assumes that sorption extent is controlled by the availability of surface sorption sites and that sorption rate is controlled by the physisorption (or chemisorption) step. These assumptions are reasonable for graphene materials that possess open planar surfaces with little diffusion limitations so long as particle aggregation is not significant. The application of pseudo-second order rate law to the sorption of NOM on graphene here is consistent with other studies of peat HA [22] and NOM surrogates [27] on MWCNT and low-molecular weight organic pollutants on graphene [26]. The pseudo-first order model did not fit SRNOM sorption onto graphenes or MWCNTs (Figure S3.2). Sorption data of SRNOM onto GAC, though, can be nicely fitted by both the pseudo-first order model ($R^2=0.99$), possibly due to the very high specific surface area that provides abundant sorption sites in this condition, and the intraparticle diffusion model ($R^2=0.97$) (Figure S3.2), likely caused by slow diffusion into pore structures.

Sorption rates are compared among all sorbents using the fitted rate constant $k_2$, the equilibrium sorption extent $q_e$, and the calculated relaxation time $t_r$, which represents the time required for sorbents sites to reach half-saturation and determined as $t_r = 1 / (k_2$.
The highest SSA sorbent, graphene C, had the shortest relaxation time. Relaxation times were on the order of minutes for all graphenes and MWCNTs but much larger (17 hours) for GAC. This $t_r$ value for sorption of SRNOM on GAC is also 30 times longer than the $t_r$ value for sorption of carbamazepine on GAC from our previous study [26], indicating that large molecular weight molecules are more hindered by pore restriction associated with GAC. Furthermore, the $k_2$ values for SRNOM on graphenes here are one to three orders of magnitude higher than those for peat humic acids on MWCNTs [22] but similar to styrene sulfonate and polystyrene sulfonates on MWCNTs [27]. Consequently, graphene materials should be considered over GAC with much less equilibration time of hours instead of days for the removal of natural organic matter within full-scale treatment operations.

Equilibrium sorption amounts $q_e$ at graphene sorbents concentration of 0.25 g l$^{-1}$ increased in the order of M < A-heated < C (Table 3.1), which is actually not the same order of BET specific area. The sorption extent of A-heated is higher than expected, possibly due to thermal treatment process which may change surface chemistry of graphene A by introducing more oxygen contained functional groups and thus promoting dispersion in solutions. The highest sorption capacity of graphene C likely results from its highest SSA. Normalizing sorption extent to surface area concentration results in similar $q_e$/SSA values within three fold differences for all graphene materials, MWCNTs and GAC (except A-heated). The observations manifest that specific surface area is a governing factor in sorption of NOM by graphitic materials and GAC.

### 3.4.2 SRNOM sorption isotherms
The observation that sorption extent could be controlled by sorbent specific surface area was more closely explored within isotherm experiments in which all graphene, MWCNT, and GAC sorbents were exposed to the same dissolved sorbate (SRNOM) at TOC concentrations varied between 18-28 mg l\(^{-1}\). After 24 hours of equilibration time, higher concentrations of dissolved SRNOM resulted in higher amounts of sorbed SRNOM in a fairly linear fashion for all sorbents held at identical mass concentrations (Figure 3.2a). Among the different sorbents, sorption extent was observed to increase with increasing sorbent SSA in the order C>C500>C300≈MWCNT>M≈A-heated. This order does not include the isotherm for GAC because it shows very little sorption despite having the highest SSA. The low sorption on GAC could be due to the slow kinetics and therefore not a equilibrium as observed in section 3.1, or due to SRNOM molecules unable to access surfaces inside GAC micropores [12] in contrast to the open planar surfaces of graphene. Virtually no sorption of SRNOM occurred on graphenes M and A-heated under these conditions.

Experimental data were best fit with the Freundlich model (Figure 3.2a), which has the equation \( q = K_F C_w^n \), where \( q \) (mg g\(^{-1}\)) and \( C_w \) (mg L\(^{-1}\)) are solid-phase and aqueous-phase concentrations of SRNOM, respectively, \( K_F \) (mg\(^{1-a}\)L\(^{n}\)/g) is the empirical constant related to sorption capacity, and \( n \) (unitless) is the Freundlich linearity index. The Freundlich model is predominantly used to describe sorption of NOM onto CNTs [15,19,21-23], likely due to the chemical heterogeneity in both NOM and graphene surfaces that leads to a distribution of both surface sites and sorbed NOM configurations. The Langmuir has described HA sorption onto MWCNTs [18], but this model and the linear partitioning model held inferior fits with our sorbents (data not shown) compared
to the Freundlich model ($0.90 < R^2 < 0.99$ for all graphenes and MWCNTs) (Table 3.2). The Freundlich model most accurately fits the data because it captures the slight upward curvature of $q$ values as $C_w$ increases, as revealed in the linearity index $n > 1$ for all sorbents with SRNOM. This behavior indicates that, at higher $C_w$ concentrations, either (i) more SRNOM molecules sorb per surface site while the number of surface sites stay constant, or (ii) more surface sites become available. To the best of our knowledge, only one other observation of enhanced nonlinear sorption has been reported for various HAs and NOMs on MWCNTs [19], and possible reasons are further discussed in section 3.4 where this behavior was observed for other sorbates.

The relationship between sorption extent and specific surface area is further characterized quantitatively through SSA-normalized isotherm model results and qualitatively through SSA-normalized isotherm data points. First, in order to quantitatively compare sorption affinities among sorbents, linear partitioning affinities $K_d$ ($1\,g^{-1}$) were calculated to avoid the problem of variable Freundlich $n$ values, where $K_d = q/C_w$ \cite{Wang-Xilong2011}. A common value of $C_w$ was chosen as 1 mg l$^{-1}$ which is close to typical TOC values of surface waters, and $q$ was determined from the Freundlich model at this $C_w$. These $K_d$ values vary over four orders of magnitude across the various sorbents and are generally higher for sorbents with larger SSA and consequently greater surface site availability (Table 3.2). When differences in sorbent SSA are taken into account by normalizing this model parameter to SSA, the resulting $K_d$/SSA values fall within a close range for all graphenes and MWCNTs, except for sorbents M and GAC. The remarkably similar values, differing only by up to a factor of four, offers a convincing indication for available surface area as the main factor that
controls sorption extent of dissolved NOM on graphene surfaces at circumneutral \( \text{pH} \) values.

A second way of illustrating the importance of available surface area is presented with all sorbed concentrations normalized to sorbent SSA \((q/\text{SSA})\) in order to compare behavior along the entire range of each isotherm (Figure 3.2b). Values of \( q/\text{SSA} \) collapse fairly well into one continuous isotherm for graphenes C, C500, C300 and A-heated and MWNCTs, providing further evidence that SSA is a primary factor and small differences in surface chemistry are less significant for a wide range of dissolved NOM concentrations under these conditions. Graphene M, however, may possess some unidentified surface or chemical property that hinders interactions with NOM. These observations on the role of SSA in controlling sorption extent is consistent with reports of HA and FA sorption onto MWCNTs improving with greater SSA \([16-18,22]\). High surface area graphene nanosheets, and similarly MWCNTs, may therefore provide greater sorption capacity and faster removal kinetics compared to conventional GAC.

### 3.4.3 Evidence for \( \pi-\pi \) interactions.

Considering graphene nanosheets and MWCNTs both assume similar Csp\(^2\) structure and both show similar surface area-dependent sorption behavior, we hypothesize the sorption mechanisms between NOM and CNTs discussed in the literature may also generally occur with graphene nanosheets, and subsequent experiments explored these mechanisms using small adjustments in NOM, graphene, or solution properties. To determine if \( \pi-\pi \) interactions between NOM aromatic groups and the graphitic \( \pi \) system are important \([15,16,18,19,23,28]\), the aromatic properties of dissolved NOM (percent aromaticity, SUVA\(_{254}\)) were closely monitored within additional sorption
isotherms between various sources of organic matter and graphene C. The isotherms of eight different dissolved IHSS-sourced NOM, HA, and FA showed fairly linear sorption behavior on graphene C under these sorbate:sorbent ratios (Figure 3.3a). Sorption extent varied moderately among the different solutes, likely owing to their differing chemical contents. The Freundlich isotherm model was again applied to quantify sorption affinity and linearity, and modeled $K_F$ and $n$ parameters (Table 3.3) were compared to measured and reported NOM chemical properties.

First, sorption affinity and linearity for the four HA types was observed to be distinct from the remaining two FA and two NOM types. $K_F$ values were consistently higher for LeoHA, ESHA, PPHA, and SRHA, indicating HAs in general may hold stronger affinities for graphene surfaces compared to FAs. This observation is consistent with greater sorption capacity reported for HA over FA with MWCNTs [15,19]. HAs generally possess greater abundances of aromatic rings, have less polar nature, and possibly lower solubilities compared to FAs and, by extension, to RO-isolated NOMs which contain both HA and FA. These properties may promote HA interactions with aromatic carbon on graphene by increasing the probability of ring $\pi-\pi$ stacking arrangements or by providing greater hydrophobic character.

Interestingly, only the four HAs held sorption linearity values $n < 1$, which, according to how the exponential coefficient of the Freundlich model is defined here, indicates incremental sorption of HA lessens as dissolved HA increases and ultimately could lead to a plateauing shape at very high HA concentrations. This isotherm behavior is typical for a continuum from preferred occupation of high-affinity surface sites to those of less affinity, and is by far the most commonly observed for dissolved NOM onto
CNTs[15,16,18,22,23] and organic micropollutants onto graphene [26,29,30]. In contrast, all two FAs (SRFA, NORDFA) and two RO-isolated NOMs (SRNOM, NORDNOM) held \( n > 1 \) values and exhibited a slight upward curve to their isotherms indicative of increased surface accumulation at higher concentrations. Increasing sorption with increasing sorbate doses could be interpreted as a surface condensation reaction that drives the formation of an insoluble phase, or a multilayer adsorption [31]. However, it is unclear how FA properties—with higher polarity, greater O content, smaller molecular weight—could lead to an insoluble, coiled FA surface precipitate. The increasing sorption may be caused by an additional interaction mechanism related to FA polarity or FA charge on weak acid groups, such as hydrogen bonding with the graphene surface [24], that become apparent only after some threshold amount of sorbed FA. A more likely interpretation, though, is that as FA molecules break up graphene aggregates and expose additional surface sites: as FA molecules sorb onto graphene, their aromatic groups orient onto the surface and polar, charged groups orient toward the solution, leading to overall higher surface charge, enhanced colloidal stability, and disaggregation.

Sorbed organic matter has been shown causes graphene and CNTs to disaggregate and settle at slower rates owing to stabilization of individual particles or smaller aggregates [17,24,32-35]. Measurements of hydrodynamic diameter, surface charge, and settling rates would help identify the effect of NOM concentration on graphene colloidal stability. Values of \( n>1 \) and \( n<1 \) were also both reported for various NOM sources sorbed onto MWCNTs, though no trend in source type was observed [19].

Second, correlations between sorption affinity \( K_F \) and NOM chemical properties point to an important contribution of \( \pi-\pi \) or hydrophobic interactions. The percent
aromatic groups, as reported by the IHSS, for all HA, FA, and RO-isolated NOM correlates fairly well with modeled $K_F$ values at equilibrium (Figure 3.4a). Greater sorption affinity is observed for organic matter with greater percent aromatic content, with the four HAs showing greatest affinity as described above. SUVA$_{254}$ is a second bulk indicator of aromatic content of organic matter, caused by the absorption of 254-nm UV light by aromatic bonds of dissolved solutes, and measurements of NOM solutions here may more accurately reflect aromaticity of our prepared solutions. $K_F$ values also generally trend with initial SUVA$_{254}$ (Figure 3.4b). The trends here are similar to those observed for NOM sorption onto CNTs [15,19] and have been attributed to a greater occurrence of $\pi-\pi$ stacking arrangements with a greater abundance of NOM aromatic content. These results support the notion that source waters with NOM of greater aromatic content may have greater removal capacity by carbonaceous sorbents [15].

Third, the aromatic character of the sorbents may also influence sorption extent, if aromatic $\pi-\pi$ interactions or hydrophobic interactions are indeed important. The $K_F$/SSA values from the isotherm experiments in Table 3.2 positively correlate with the graphene Csp$^2$ content (Figure 3.4c) and negatively correlate with surface oxygen percentage (Figure 3.4d). These trends suggest that aromatic properties of graphene can partly control sorption in a similar way as the aromatic content of NOM. A greater availability of graphene benzene rings provides a greater chance for $\pi-\pi$ stacking and generally greater hydrophobicity for NOM sorbents. Correspondingly, more O content caused by surface O functional groups may diminish $\pi-\pi$ interactions by discontinuing the repeating benzene structures or by withdrawing $\pi$ electron density (should O groups be electron-withdrawing, such as carboxyl acids, which were detected in XPS spectra in
Figure S3.1). The role of surface O groups on MWCNTs has been examined [18,23], and these reports suggest less sorption on oxidized MWCNT is partly due to less hydrophobic and aromatic surface area.

3.4.4 Aromatic fractionation.

The importance of aromatic interactions is further supported by observing the aromatic fraction of organic matter being preferrably sorbed onto graphene over the non-aromatic fraction. Solution SUVA$_{254}$ values decrease after organic matter sorption to graphene C for all HA, FA, and RO-isolated NOM types (Figure 3.5), indicating the organic matter remaining in solution has become somewhat depleted in aromatic content and surface-bound organic matter is aromatically enriched. If aromatic and non-aromatic fractions sorbed simultaneously and equally, no change in SUVA$_{254}$ values would have been observed. A simmilar preference for the aromatic fraction of FA with MWCNTs has been reported using E2/E3 absorbance ratios (250 nm/ 365 nm) [16].

Figure 3.5 shows greater sorption extent leads to greater decrease in SUVA$_{254}$ values for all eight NOM types, albeit in a nonlinear fashion. A similar trend is also observed for SRNOM sorption onto other graphenes and MWCNTs but not GAC (Figure S3.3). Little change in SUVA$_{254}$ is observed during the first ~30% of TOC removed, indicating the aromatic and non-aromatic fractions sorb fairly equally at low sorbate coverages, probably due to an abundance of surface site availablity for both fractions. A stronger preference for the aromatic fraction is then exerted between ~30 to ~80% TOC removed as shown by a more rapid decrease in SUVA$_{254}$ values. This could be due to (i) aromatic fractions forming stronger, more preferable binding arrangements compared to non-aromatic fractions as all surface sites become scarcer, or (ii) the surface sites that
prefer non-aromatic fractions have been exhausted and no longer remove this fraction from solution. Regarding option (ii), it is noted that the non-aromatic NOM fraction could possess more polar, hydrophilic properties that bind by mechanisms other than $\pi-\pi$ stacking, such as electrostatic interactions or H-bonding involving surface O functional groups that are limited in number. In fact, when graphene contains a high abundance of surface O groups, these groups have been shown to interact with NOM polar groups (hydroxyl, carboxyl, and ketone) within FTIR spectra, and when graphene O groups are absent, only $\pi-\pi$ interactions were indicated [24]. It is therefore possible that graphene surface chemistry could control sorption extent of the aromatic and polar fractions of dissolved NOM, and studying aromatic fractionation with graphene oxides with a wider range of O abundance could confirm this hypothesis. Finally, the aromatic fraction is completely sorbed after 80-90% TOC removal, and any remaining dissolved organic matter possesses no measurable UV$_{254}$ absorbance. This fractionation based on NOM aromatic properties could have important implications for disinfectant byproduct formation whose speciation can be dependent on relative amounts of hydrophobic and hydrophilic fractions present during chlorination treatment [36]. Any remaining non-sorbed, non-aromatic fraction of NOM may require additional removal such as with higher graphene doses or a more polar sorbent with required selectivity.

3.4.5 Size fractionation.

While SUVA$_{254}$ measurements provide a bulk indication of total aromatic fractionation, SEC-UV was used to examine whether the aromatic fraction also fractionates by molecular size during sorption onto graphene surfaces. This was achieved by separating dissolved organic matter by size within an SEC column and profiling the
abundance of UV-absorbing (aromatic) molecules over time. The use of this technique has shown that MWCNTs may have preference for the larger molecular weight fractions of standard SRHA, SRFA, and SRNOM [15], but others reported only a temporary (< 5 hours) fractionation of low molecular weight HA molecules extracted from peat soil, which was attributed to preferential access of smaller molecules into interstitial spaces of MWCNT aggregates [22]. The pore sizes in activated carbon are also thought to restrict access only smaller sizes of NOM, although top exposed surfaces may preferentially sorb larger MW [12,37]. Considering graphene’s planar structure with abundant exposed surfaces and few pore spaces, we hypothesized a size fractionation preferring larger OM molecular weights would occur during sorption.

Preferential sorption of the higher molecular weight fractions of SRHA, SRFA, and SRNOM to graphene C was indeed observed in HPSEC-UV chromatograms (Figure 3.6a). Prior to sorption, nearly all UV-active sizes were about 10^2 Da or greater, with SRHA containing higher MW sizes than SRFA and SRNOM. After equilibration with graphene C, chromatograms show the remaining dissolved UV-active fraction decreased throughout all MW sizes. Moreover, larger MW sizes (earlier elution times) had a greater extent of removal, and sizes greater than ~10^{3.5} Da were completely removed. Similar size fractionation was also observed in HPSEC-UV analysis performed with SRNOM and other sorbents including graphenes C300, C500, M, and A-heated, and MWCNTs, though to a far less extent for GAC, possibly due to pore restrictions described above (Figure 3.6b). Preference for the largest MW sizes might be explained by their larger abundance of aromatic groups as indicated by higher UV absorbance and graphene’s preference for aromatic groups as described above. High surface area
graphitic sorbents such as graphene and MWCNTs could therefore be utilized for preferential removal of aromatic and high MW fractions of NOM in source waters, provided sufficient nonporous surface exposure is ensured.

3.4.6 Evidence for electrostatic interactions

The contribution of electrostatic interactions to NOM sorption onto carbonaceous surfaces is typically explored by varying solution pH, which alters the protonation and hence charge of weak acid groups on both dissolved organic matter and sorbent surfaces. As pH increases, the deprotonation of acid groups in SRNOM \[38\] and on graphene surfaces \[32\] leads to increased negative charge for both sorbate and sorbents. Over the pH range of 2 to 10, the three types of graphene (C, M, and A-heated) were found to always possess negative surface charge, here approximated by zeta potential (Figure 3.7a), and to gradually decrease in surface charge with increasing pH. The similar zeta potential values for the three different graphenes is fairly consistent with their similar percent carboxylic contents as measured by XPS (Table S3.2), which is presumed to be the primary surface group that deprotonates in this pH range.

The removal of SRNOM as measured by dissolved TOC loss by all three graphenones is consequently pH-dependent (Figure 3.7b), with less removal observed under more alkaline conditions. This observation is consistent with previous studies for HA sorption on MWCNTs \[17,18\], SRNOM on MWCNTs \[15\], FA on MWCNTs and activated carbon \[16\], and HA on graphene oxide and reduced graphene oxide \[24\]. Among these studies, the effect of pH is primarily attributed to electrostatic repulsion between negatively-charged surfaces and negatively-charged dissolved NOM, or between surface-bound NOM and dissolved NOM \[15-18\]. Relatedly, less NOM mass may sorb
due to NOM molecules spreading out and occupying more surface space per mass as
NOM becomes uncoiled and more stabilized by charge presence [21]. Electrostatic
repulsion reasonably explains the four- to seven-fold decrease in sorption extent among
the three graphenes. Graphene C has also demonstrated similar pH-dependent behavior
consistent with electrostatic repulsion and attraction with organic probe compounds with
negative or positive charges respectively [26], as has other graphene oxides [39,40].

Consistent with the influence of SSA described in section 3.2, the order of
SRNOM sorption extent at all pH values is the same as their order of SSA (C>A-
heated>M). The near lack of SRNOM sorption for graphene M observed in the pH 7.2
isotherm (Figure 3.2) can now be partly explained by an unsuitably high pH for this
sorbent, as sorption is negligible at all pH >7 but increases under acidic conditions. This
shows that graphenes prepared by different manufacturing processes may be applicable
as sorbents only in certain operating conditions, and care must be used in material
selection. For water treatment operations, pH can vary between 6 and 10 depending on
alkalinity, and graphenes like M with low surface area and little NOM affinity at in this
pH range.

Previous studies also discuss that mechanisms involved in improving sorption at
low pH onto CNTs could include (i) greater aromatic and hydrophobic interactions as
protonation neutralizes surface and NOM charges and possibly leads to more coiled and
less soluble NOM molecules, and (ii) greater polar interactions via formation of H-bonds
between protonated NOM functional groups and O or benzene groups on graphene
surfaces [16-18]. Using the aromatic fractionation of dissolved NOM as a proxy for
aromatic or hydrophobic interactions, SUVA$_{254}$ were recorded over the pH range (Figure
3.7c), and their values changed dramatically for the each sorbent. Graphenes C and A-heated showed preference for aromatic fractions at low pH as SUVA$_{254}$ values decreased, consistent with greater hydrophobic interactions described above or improved $\pi-\pi$ stacking. A preference for aromatic groups at low pH was also reported for FA and MWCNTs [16]. However, SRNOM with graphene M showed an increase in SUVA$_{254}$ values at low pH as the aromatic fraction preferably remains dissolved, and this suggests graphene M is more capable of forming bonds with more hydrophilic or aliphatic fractions of SRNOM compared to the aromatic fraction. This unusual non-aromatic fractionation for graphene M might be caused by an unidentified, distinct surface chemistry difference, but no trend in SUVA$_{254}$ values or sorbed concentrations with percent O abundance or surface O group abundance (via XPS spectra) was found that could explain why graphene M would behave so differently. One possible explanation could be graphene M, with the largest sheet size and low O abundance, inadvertently agglomerates in suspension by $\pi-\pi$ stacking, covering up a large portion of predominantly aromatic surfaces and leaving predominantly polar, O-bearing edge surfaces which might prefer polar, non-aromatic NOM groups. Additional measurements on agglomeration sizes and rates and electrostatic properties [32] may further explain differences in graphene affinities with NOM.

Polar interactions specific to each sorbent might also be revealed by further use of UV/vis spectrophotometric absorbance sensitive to NOM polar functional groups. Others have used the E2/E3 or E4/E6 ratios to track aromatic and polar fractionation respectively [16,19]. E4/E6 is an indication of polar group abundance for dissolved NOM, defined as the ratio of absorbance at 465 nm to that at 665 nm. If E4/E6 values of dissolved NOM
decrease after sorption, the remaining NOM has lower polarity than before sorption, and the sorbent preferably binds with the more polar NOM molecules, a behavior that has been observed for FA sorption onto MWCNTs [16]. Here, E4/E6 values were monitored in additional sorption experiments between SRNOM and graphenes C, M, and A-heated at pH 5.1 and 7.1. Higher initial SRNOM concentrations were used (~45 mg l\(^{-1}\)) due to its low visible light absorbance, and neutral and acidic conditions were chosen instead of alkaline pH where little sorption occurred for M and A-heated. SRNOM E4/E6 values after sorption by graphene C decreased for both pH 5.1 and 7.1, which indicates a preference for the polar fraction of NOM (Table 3.4). In contrast, E4/E6 values for M and A-heated were all higher than values before sorption. For these sorbents, the sorbed NOM fraction has less polarity than the initially dissolved SRNOM, suggesting a preference for non-polar molecules. For each sorbent, the difference between E4/E6 values before and after sorption were similar for pH 7.1 and 5.1, indicating only slight changes in sorption preference as pH decreases.

The observations of aromatic fractionation (SUVA measurements) and polarity fractionation (E4/E6 measurements) taken together thereby sort the three graphenes into three separate affinity classifications for SRNOM sorption at neutral and acidic pH. Graphene C prefers both aromatic fraction (based on decreasing SUVA) and a polar fraction (based on decreasing E4/E6). Both fractions could possibly be accommodated by C due to its surface aromaticity available for aromatic interactions as well as its large percentage of surface O atoms available for polar interactions (e.g. H bonding) (Table S3.1). Graphene A-heated held affinity for the aromatic fraction and a non-polar fraction. This is consistent with A-heated having the greatest carbon and lowest O elemental
compositions. Finally, graphene M prefers the non-aromatic fraction and the non-polar fraction. This could be explained by graphene M removing only non-polar, aliphatic molecules and leaving the more aromatic and more polar molecules remaining in solution. Our results suggest that graphene powders synthesized by different production processes may result in variable NOM fractionation behavior in aqueous suspensions.

Additional information on specific bonding mechanisms could possibly be obtained using FTIR measurements that probe interactions between sorbed NOM and surface O groups. Previous studies [24] have shown shifts in FTIR peaks for laboratory-synthesized graphene oxides after sorption of HA, as well as shifts in peaks for sorbed HA, which are interpreted as those functional groups participating in bonding. ATR-FTIR measurements on graphenes C, M, and A-heated, however, revealed no observable functional groups similar to graphene oxides (Figure S3.4). Additional SRNOM sorption experiments with higher SRNOM concentrations (40 mg l$^{-1}$ TOC) at pH 3, where sorption extent is highest and SUVA$_{254}$ values the most different, also did not reveal indications of sorbed SRNOM peaks in ATR-FTIR spectra. It is likely the sorbed SRNOM amount is below observable limits, and surface oxygen functional groups were possibly localized in platelet edges less in contact with the measurement surface. Carbonaceous sorbents with greater surface oxygen abundances such as graphene oxide may allow clearer inspection of organic matter – sorbent interactions.

3.8. Time-dependent aromatic and size fractionation

Considering the aromatic and size fractionation observed here after 24 hours and the transient size fractionation reported for NOM and MWCNTs [22], it is necessary to characterize fractionation kinetics between NOM and graphene in order to determine
whether fractionation occurs simultaneously and permanently with TOC removal. Reaction kinetics were determined for SRNOM with graphene C by monitoring TOC concentrations (Figure 3.8a), bulk SUVA$_{254}$ values (Figure 3.8b), and size-dependent UV$_{254}$ values over time (Figures 3.8c and 3.8d). Similar to Figure 3.1, the majority of dissolved TOC was removed within about 30 minutes and reached equilibrium concentration near one hour. Both bulk SUVA$_{254}$ values (measured spectrophotometrically in quartz cuvettes) and size-dependent UV$_{254}$ values (measured at selected sizes in HPSEC-UV chromatograms) showed disappearance in aromatic and size fractions concurrent with TOC concentrations. In HPSEC-UV chromatograms, three MW sizes were chosen within the larger, medium, and smaller ranges corresponding to absorbance peaks at elution times of 7.2, 8.8, and 10.7 minutes. The largest size fraction held the greatest UV$_{254}$ absorbance, showed the biggest decrease in UV$_{254}$ values, and may have taken slightly longer time to reach equilibrium values. Virtually no uptake of the smallest MW compounds occurred, possibly due to their presumably more aliphatic composition and therefore less inherent surface affinity or due to being out-competed for surface sites by larger MW molecules. No desorption of any MW size was observed, in contrast to observations NOM on MWCNTs [22], indicating that NOM remains firmly bound to graphene surfaces under the suspension conditions. This could be due to graphene’s planar structure as opposed to MWCNT bundles which contain pores which may briefly restrict access to low MW sizes [22].

The time-dependent MW size behavior confirms graphene’s selectivity for aromatic-rich, high MW fractions of NOM occurs rapidly in suspension without significant desorption. Interestingly, within kinetic experiments with other sorbents,
SUVA$_{254}$ values of dissolved SRNOM were observed to decrease over time only for MWCNTs (Figure S3.5). Graphenes M and A-heated, as well as GAC, showed no significant preference for aromatic fractions at pH 7.2 over 24 hours. These SUVA$_{254}$ values correspond to the TOC concentrations in Figure 3.1 which shows some TOC removal, and the lack of any changes in dissolved aromatic content indicates these sorbents may not selectively sorb different NOM fractions in the manner of graphene C. These results further illustrate the varying affinities for NOM by different graphene surfaces.

### 3.5 Conclusions

Commercial graphene powders can be obtained with a variety of particle sizes, physical properties, and surface chemistries, and consequently only certain powders may be suitable for targeted solute removal via sorption processes. High-surface area graphene powders (e.g. graphene C) may exhibit superior sorption rates and capacity for dissolved NOM removal compared to MWCNTs and GAC, with >90% of TOC removal occurring within minutes, whereas low-surface area graphene held little to no NOM removal under certain water chemistry conditions. NOM sorption extent is influenced by graphene surface area, surface charge, and aromatic content. NOM appears to interact with graphene surfaces according to similar mechanisms as reported for MWCNTs, primarily by aromatic interactions. NOM sorption was improved with greater graphene aromatic content and higher NOM aromaticity, and the aromatic and high-molecular weight fractions of dissolved NOM were preferably retained by graphene C surfaces.
Lower solution pH, and consequently less negative graphene surface charge and NOM polarity, improved sorption presumably by lessening electrostatic repulsion.

In practice, graphene specific surface area and surface functionality should be considered when selecting powders for use in purification technologies such as membranes. Additional spectroscopic measurements are needed within broader investigations involving multiple graphene types in order to identify which surface functional groups are most responsible for interactions with NOM. Knowledge of the most reactive chemical groups could be used to design graphene surfaces for improved sorption of NOM and organic micropollutants. The nature of dissolved NOM in raw waters should be determined as well, because NOM with low aromaticity may require a sorbent selective for the more hydrophilic fraction in addition to the aromatic-selective graphene.

Acknowledgments

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Appendix B. Supplementary data

Supplementary data associated with this article can be found in the end of the dissertation.
LIST OF TABLES

Table 3.1 Values of fitted parameters for the pseudo-second-order kinetic model of SRNOM sorption on graphene oxides (C, M, and A-heated), and granular activated carbon (20 mM NaCl, 1 mM NaHCO₃, pH 7.2). $R^2 > 0.99$ for all model simulations.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbent Concentration g l$^{-1}$</th>
<th>$t_r$ h</th>
<th>$k_2$ g mg$^{-1}$ h$^{-1}$</th>
<th>$q_e$ mg g$^{-1}$</th>
<th>$q_e / $SSA mg m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.25</td>
<td>0.052</td>
<td>2.03</td>
<td>9.46</td>
<td>0.012</td>
</tr>
<tr>
<td>M</td>
<td>0.25</td>
<td>0.012</td>
<td>28</td>
<td>2.98</td>
<td>0.040</td>
</tr>
<tr>
<td>A-heated</td>
<td>0.25</td>
<td>0.297</td>
<td>0.69</td>
<td>4.92</td>
<td>0.190</td>
</tr>
<tr>
<td>GAC</td>
<td>0.25</td>
<td>17.15</td>
<td>0.002</td>
<td>29.7</td>
<td>0.025</td>
</tr>
<tr>
<td>MWCNT</td>
<td>0.25</td>
<td>0.122</td>
<td>1.10</td>
<td>7.46</td>
<td>0.026</td>
</tr>
</tbody>
</table>
Table 3.2 Freundlich model parameters for SRNOM sorption on graphene oxides (C, C500, C300, M, and A-heated), pristine multiwalled carbon nanotubes, and granular activated carbon at pH 7.2.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>SSA (BET) ((m^2 \cdot g^{-1})^a)</th>
<th>(R^2)</th>
<th>(n)</th>
<th>(K_F^a)</th>
<th>(K_d^c)</th>
<th>(K_d/\text{SSA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>771</td>
<td>0.96</td>
<td>1.13</td>
<td>5.48</td>
<td>5.48</td>
<td>0.007</td>
</tr>
<tr>
<td>C500</td>
<td>746</td>
<td>0.98</td>
<td>1.11</td>
<td>4.62</td>
<td>4.62</td>
<td>0.006</td>
</tr>
<tr>
<td>C300</td>
<td>271</td>
<td>0.96</td>
<td>1.13</td>
<td>2.25</td>
<td>2.25</td>
<td>0.008</td>
</tr>
<tr>
<td>M</td>
<td>74</td>
<td>0.95</td>
<td>2.86</td>
<td>0.002</td>
<td>0.002</td>
<td>0.00003</td>
</tr>
<tr>
<td>A-heated</td>
<td>26</td>
<td>0.90</td>
<td>1.76</td>
<td>0.05</td>
<td>0.05</td>
<td>0.002</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>292</td>
<td>0.99</td>
<td>1.37</td>
<td>1.39</td>
<td>1.39</td>
<td>0.005</td>
</tr>
<tr>
<td>GAC</td>
<td>1181</td>
<td>0.86</td>
<td>1.34</td>
<td>0.47</td>
<td>0.47</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

\(^a\) SSA values for graphene C and M are taken from Cai and Lares-Casanova (2014) [26].

\(^b\) All Freundlich modeling was performed on data with units of dissolved sorbate concentration in mg l\(^{-1}\) and a sorbed concentration of mg g\(^{-1}\).

\(^c\) The linear partitioning affinity coefficient \(K_d\) was calculated using 1 mg l\(^{-1}\) dissolved sorbate concentration and sorbed concentration in mg g\(^{-1}\) determined by the Freundlich model.
Table 3.3 Freundlich model parameters for sorption of various NOM types with graphene C at pH 7.2.

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>% Aromatic</th>
<th>n</th>
<th>$K_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LeoHA</td>
<td>58</td>
<td>0.78</td>
<td>13.0</td>
</tr>
<tr>
<td>ESHA</td>
<td>50</td>
<td>0.77</td>
<td>9.93</td>
</tr>
<tr>
<td>PPHA</td>
<td>47</td>
<td>0.75</td>
<td>9.99</td>
</tr>
<tr>
<td>SRHA</td>
<td>31</td>
<td>0.55</td>
<td>7.76</td>
</tr>
<tr>
<td>NORDFA</td>
<td>31</td>
<td>1.23</td>
<td>3.46</td>
</tr>
<tr>
<td>SRNOM</td>
<td>23</td>
<td>1.13</td>
<td>5.48</td>
</tr>
<tr>
<td>SRFA</td>
<td>22</td>
<td>1.18</td>
<td>3.12</td>
</tr>
<tr>
<td>NORDNOM</td>
<td>19</td>
<td>1.75</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Table 3.4 Values of solution E4/E6 recorded before and after sorption of SRNOM to graphenes C, M, and A-heated at pH 5.1 and 7.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4</td>
<td>1.5</td>
<td>-2.5</td>
<td>6</td>
<td>4</td>
<td>-2</td>
</tr>
<tr>
<td>M</td>
<td>4</td>
<td>12</td>
<td>+8</td>
<td>6</td>
<td>14</td>
<td>+8</td>
</tr>
<tr>
<td>A-heated</td>
<td>4</td>
<td>7</td>
<td>+3</td>
<td>6</td>
<td>11</td>
<td>+5</td>
</tr>
</tbody>
</table>
Figure 3.1 Kinetic profile of SRNOM sorption on different graphene sorbents (C 0.25 g l\(^{-1}\), red open diamonds; M 0.25 g l\(^{-1}\), green open circles; A-heated 0.25 g l\(^{-1}\), blue filled triangles), MWCNTs (0.25 g l\(^{-1}\), pink open triangles), and GAC (0.25 g l\(^{-1}\), black open squares). The solid lines are pseudo-second-order kinetic model simulations. Experimental conditions: initial SRNOM UV absorbance 0.2, TOC concentration range 6.2 to 13.3 mg l\(^{-1}\), pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\), reaction time 24 hours.
Figure 3.2 (a) Sorption isotherms of SRNOM on graphene C (red open diamonds), C500 (red dotted circles), C300 (red open triangles), M (green open circles), A-heated (blue filled triangles), pristine MWCNT (pink inverted open triangles), and GAC (black open squares). Solid lines are Freundlich model simulation. (b) Normalize sorption data on various sorbents to SSA. Experimental conditions: 0.05 to 1.1 g L$^{-1}$ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours.
Figure 3.3 Sorption isotherms of graphene C with varied sorbates including, from left to right, LeoHA (green dotted circles), ESHA (red open triangles), SRNOM (red open diamonds), PPHA (black filled circles), SRHA (blue open circles), NordFA (black open squares), SRFA (green dotted squares), and NordNOM (blue dotted diamonds). Solid lines are Freundlich model simulation. Experimental conditions: 0.05 to 1.1 g L$^{-1}$ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours.
Figure 3.4 (a) Linear relationship between Freundlich constant $K_F$ with percent aromatic content of various NOM types. (b) Linear relationship between Freundlich constant $K_F$ related to sorption capacity with initial SUVA$_{254}$ of various NOM types. (c) Linear relationship between SSA-normalized $K_F$ and Csp$^2$ percentage for various graphene materials except for graphene C. (d) Linear relationship between SSA-normalized $K_F$ and O percentage for various graphene materials except from graphene C. Data for graphene C was not included in (c) and (d) due to its great difference from the trend.
Figure 3.5 SUVA$_{254}$ values for sorption of varied natural organic matter types onto graphene C from the isotherm experiments in Figure 3.3. Experimental conditions: 0.05 to 1.1 g l$^{-1}$ graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours. NOM in legend are listed in order of highest to lowest initial SUVA$_{254}$ values.
Figure 3.6 (a) HPSEC chromatogram for SRNOM, SRHA, SRFA before and after 24 hours sorption with graphene C before and after reaction. Experimental conditions: graphene C mass 8 mg, volume 11 ml, initial SUVA$_{254}$ 0.78, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours. (b) HPSEC chromatogram for SRNOM before and after 24 hours with various sorbents. Experimental conditions: sorbent mass 8 mg, volume 11 ml, initial SUVA$_{254}$ 0.78, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours.
Figure 3.7 (a) Zeta potential of graphene C (red diamonds), A-heated (blue triangles), and M (green circles). Experimental conditions for a: 0.1 g l$^{-1}$ graphene in 5 mM NaCl. (b) Effect of pH on SRNOM sorption by graphene C (red diamonds), A-heated (blue
triangles) and M (green circles). (c) SUVA at 254 nm for sorption of SRNOM with graphene C (red diamonds), A-heated (blue triangles), and M (green circles) at pH range of 2 to 12. Experimental conditions for b and c: 0.25 g l\(^{-1}\) graphene and initial SRNOM concentration of 5.6 to 6.5 mg l\(^{-1}\) TOC, initial UV absorbance 0.2, in buffer solution 1 mM NaHCO\(_3\) and 20 mM NaCl, reaction time 24 hours.
Figure 3.8 (a) Kinetics of dissolved TOC concentrations for SRNOM exposed to 0.25 g l$^{-1}$ graphene C at pH 7.2 in 20 mM NaCl and 1 mM NaHCO$_3$. (b) Bulk SUVA$_{254}$ values of dissolved SRNOM in samples in part (a). (c) UV absorbance values (measured as difference between peak value and baseline value) for the three UV-absorbing peaks (at elution times 7.2, 8.8, and 10.7 min) in HPSEC-UV chromatograms in part (d). (d) HPSEC-UV chromatograms obtained for selected time points in part (a).
Chapter 4  Ethylenediamine Functionalized Graphene: Synthesis and Application in Charged Contaminants Removal

4.1 Abstract
The functionalization of graphene in water treatment applications has been discussed for the first time. A novel ethylenediamine functionalized graphene (ED-G) with positive charge on the surface has been synthesized in our laboratory. The sorption capacity of ED-G for negative charged ibuprofen, positive charged atenolol, and neutral compound carbamazepine was tested, and the isotherm data confirmed the preference for negatively-charged ibuprofen over atenolol and carbamazepine. Competitive sorption experiments showed that ibuprofen is consistently preferred over atenolol over a wide range of concentrations, and the presence of other negative-charged compounds can suppress the sorption of ibuprofen. Therefore, graphene oxide with amine functionalization to hold positive charges can be an effective material for negative charged micropollutants in water systems.

Keywords: Graphene; Positive Graphene; Amine Functionalization; Sorption Processes; Freundlich Isotherm; Water Treatment.

4.2 Introduction

Graphene, a novel and prospective material with carbon atoms arrayed in honeycomb structure, has become a most intensively studied substance in material science [1]. As the issue of salience of water pollution is getting higher during the past decades, environmental research is exploring graphene-based carbonaceous nanomaterials for their employment in water treatment technologies. Graphene has very high specific surface area (theoretical 2620 m²g⁻¹, modified up to 3100 m²g⁻¹, but in practice <100 m²g⁻¹) and remarkable structural and mechanical properties [2], making it a suitable candidate as a sorbent or reactive surface for water pollutants. Graphene can be applied as sorbents, high-flux membranes, composite filters, antimicrobial agents, and environmental sensors in environmental applications [3].

Graphene-based materials have been investigated as sorbents for the removal of synthetic organic pollutants and natural organic matter from water as a preferred alternative to conventional carbonaceous materials. Graphene-based materials have demonstrated excellent sorption ability for the removal of organic pollutants including dyes (methyl blue, natural red, rhodamine B, and methyl orange) [4]; heavy metals (Pb, Cd, Cr and Hg) [5-7], aromatic compounds (tetracycline and naphthalene) [8], pesticides [9], and algal toxins [10]. Graphene oxides and reduced graphene oxides have been studied for their favorable sorption capacity of humic acid [11,12] and a variety of natural
organic matter [13]. Comparing to traditionally used activated carbon, graphene can offer higher capacities and faster equilibration over a wide pH range, due to more homogeneous sites, less pore diffusion, and rapid π-π electron doner-acceptor (EDA) kinetics [3]. The presence of covalently attached oxygen bearing functional groups in graphene oxides such as hydroxyl, epoxy and carboxyl groups can change the wettability of material surface, improve stability, provide H bond sites and especially, provide a pathway for further surface functionalization to design hybrid graphene based nanostructure for potential applications [14].

Functionalization of graphene sheets is crucial to make graphene processable and tunable with new chemical, electronic and optic properties to reach graphene’s full potential [15,16,17]. Graphene can be functionalized at the basal plane and the edges via covalent and nocovalent modifications [1,17,18]. The main purposes of graphene functionalization are (i) to open up the band gap for nanoelectronic applications and (ii) to improve the dispersibility of graphene in water or in organic solvents for the formation of nanocomposite materials with graphene [1,18,19]. Englert et al. have developed for the first wet chemical bulk 4-tert-butylphenyl functionalized graphene, which successfully prevents reaggregation while providing solubility in organic solvents [20,17]. Stable and water-soluble graphene sheets with high dispersibility have also been achieved by the functionalization via 1,3-dipolar cycloaddition [21], a single-step sonochemical method with polystyrene[22], and 1-pyrenebutyrate [23,24]. Besides, Liu et al. have designed sulfated graphene oxide (GO-OSO$_3$H) with –OSO$_3$H attached to reduced GO basal plane and –COOH along with the edges, and GO-OSO$_3$H has demonstrated to be a great hole extraction layer for polymer solar cell in energy
applications [25,26]. Pham et al have explored a strategy for the covalent functionalization of graphene with polyglycerol to greatly improve the dispersibility of the hybrid nanostructure, and most importantly provide a suitable template for anchoring magnetic nanoparticles [14]. Singh et al found that amine-modified graphene as a safer alternative to graphene oxide (which possesses an abundance of oxygen groups) for biomedical applications [27]. The investigation of synthetic methodology of functionalized graphene lays the foundation of a new chemistry of graphene and graphene based materials with the addition of specific functionalities and new properties for different science and technology applications [16].

Many investigations have studied various synthesis methods of amine functionalized graphene or carbon nanotube with better electronic, mechanic, nanocatalytic, and biomedical properties through chemical doping and modifications [27,28]. Park et al., Qiu et al. and Singh et al. [27,29,30] all synthesized amine-functionalized graphene or amine MWCNTs first by acyl-chlorination reaction by graphene oxides or acid-treated MWCNTs and thionyl chloride (SOCl₂) followed by amidation process with ethylenediamine or a mixture of sodium azide and dimethylformamide (DMF). Sydlik and Swager [31] first synthesized Johnson-Claisen functionalized graphene (CG2) in strong basic conditions with primarily carboxylic acid functionalities and highly negative charges on the surface, and then CG2 reacted with oxalyl chloride in dioxane with the presence of DMF, and eventually achieved propargyl amide graphene (Prop-AG) and dimethylaminopropyl amide (D-AG) with propargylamine and 3 (dimethylamino)-1-propylamine, respectively. Zhang et al. [28] invented a simple and effective solvothermal process to synthesize amino-functionalized
graphene from graphene oxide using only ammonia solution in autoclave at 200 °C for 12 hr.

However, beyond abovementioned applications, there is very limited study on the employment of functionalized graphene in environment and water treatment related technologies. From our previous study, we found that most commercial available graphene or graphene-based nanomaterials in the market are negatively charged on the surface in aqueous suspensions at circumneutral pH due to the presence of oxygen-bearing functional groups such as carboxylic and hydroxyl [32]. Also, as electrostatic interaction between the charges on sorbents and sorbates is one of the most important governing factors for sorption capacity on graphene oxides, these negatively charged graphene surfaces can influence the sorption extent of charged organic compounds. The sorption of positive charged compounds can be enhanced by negative charge graphene, but sorption of negatively charged compounds are diminished. Therefore, it will be beneficial to introduce positive charged graphene from chemical functionalization into sorption reaction targeting on the better removal efficacy of a wide range of negatively charged micropollutants and natural organic matters in water systems. In our work, we synthesized ethylenediamine-functionalized graphene (ED-G) through chlorination and amidation processes and test the material in laboratory prepared water samples for the removal of three endocrine disrupting compounds with different charges, and competitive sorption among five negatively charged organic and inorganic compounds. We expect that our work could lead a new application of functionalized graphene for contaminants removal.
4.3 Experimental Method

4.3.1 Material Synthesis

Graphene oxide (GO) was prepared from 6 g of graphite powder (mineral carbon, Fisher Scientific) using a modified Hummers method (Xu, ref), and then dried in fume hood without any exfoliation. Dried chunks of graphene oxide were grinded by marble mortar and pestle, and sieved by U.S.A standard sieve (150 microns, Humboldt) to very fine powders. 40 ml thionyl chloride (SOCl₂, 99+, Alfa Aesar) was added to dry GO powder in a 100 ml pyrex glass bottle with a screw cap to perform the acyl-chlorination reaction, an intermediate process for the final amidation process. SOCl₂ reacted with GOs at 70 to 80 ºC in fume hood while the reactor was stirred on a stirring machine with heating function for 24 hours (Cole Parmer Instrument Company). The screw cap of the reactor bottle was taken off during the reaction to enable volatilization and drying of SOCl₂. The leftover of SOCl₂ in graphitic powder was removed by vacuum filtration using PVDF membrane filter papers (Millipore GVWP04700 Durapore® hydrophilic membrane, 0.22 µm) in a Buchner funnel, and then rinsed off by excess volume of methylene chloride (>99%, anhydrous, ACROS Organics™). We added ethylenediamine to acyl-chlorinated graphene in pyridine without any pre-washing at our first try, but this will lead graphene particles forming a paste with limitation of accessible surface area.

After dried by low heat, acyl-chlorinated graphene powder was suspended in 40 ml ethylenediamine (>99%, ACROS Organics™) in a glass bottle while stirring at 80 ºC to 100 ºC for 48 hours, followed by repeated washing with methanol and deionized water, and then suspended in 300 ml deionized water. The amine–functionalized graphene suspension was exfoliated by sonication with 1 gallon ultrasonic cleaners (FS-30, Fisher Scientific) for 3 hours and ultrasonic probe for 15 mins. Dry powder of amine-functionalized graphene was obtained by heating the suspension in the oven at 50 ºC for 24 hours.
Amine-functionalized graphene was characterized for chemical composition by X-ray photoelectron spectroscopy (XPS) as described in Table X and specific surface area (SSA) by 5-point Brunauer-Emmett-Teller (BET) as of 14.4 m² g⁻¹. Transmission electron microscopy (TEM) was performed with a Jeol JEM-1010 instrument. X-ray Diffraction (XRD) was performed with a Rigaku Ultima IV instrument with CuKα radiation (to be done). Zeta potential was measured using a Malvern Nanosizer ZS90 for dilute aqueous suspensions of 0.1 g l⁻¹ in 5 mM NaCl with pH modified by small additions of 0.1 M HCl or 0.1 M NaOH.

4.3.2 Sorption Experiments

All sorption experiments for amine-functionalized graphene were performed with batch reactors in buffer solutions of 1 mM NaHCO₃ and 20 mM NaCl in deionized water at pH 7.2 adjusted by 0.1 M NaOH and HCl. Organic compounds (Ibuprofen, atenolol, carbamazepine, acetaminophen, salicylate) stock solutions were prepared in methanol, except that NOM stock solutions were prepared in buffer solutions of 1 mM NaHCO₃ and 20 mM NaCl with filtration process, and the inorganic solute, sodium acetate stock solution was prepared in deionized water. Initial samples were prepared by adding spike volumes of stock solutions into buffer in 30-ml glass vials with PTFE-lined caps. After the addition of weighted amine-functionalized graphene powders, glass vials were immediately agitated by vigorously shaking to promote graphene suspension, and then placed on rotator disk end-over-end for 20 min reaction time. Final samples were syringed by 0.25 µm syringe-tip PTFE filters.

pH edges of ibuprofen, atenolol and carbamazepine with initial concentration 80~90 mg l⁻¹ were generated with 0.5 g l⁻¹ amine-functionalized graphene in a pH range 3~11. Isotherm experiments were conducted at different sorbate initial concentration (CBZ and AT 5 ~ 200 mg l⁻¹, IBU 5 ~ 100 mg l⁻¹) by 1 g l⁻¹ amine-functionalized graphene at pH 7.2. Competitive sorption of ibuprofen and atenolol were performed with equal initial molar concentration of 20-480 µmol l⁻¹ in dual sorbate reactors and 1 g l⁻¹ amine-functionalized graphene. Competitive sorption of
ibuprofen and other selected negatively charged compounds, including natural organic matter, salicylate, sodium acetate and acetaminophen, on 0.5 g l\(^{-1}\) amine graphene in dual sorbate systems were conducted and compared with single solute system with ibuprofen alone.

### 4.4 Results and Discussion

#### 4.4.1 Material TEM and XPS Analysis

The surface functionalization process resulted in a fine black powder obtained upon drying and sieving. The powder consisted of nanosheets a few microns wide and a few layers thick as indicated in TEM images (Figure 4.1), indicating exfoliation by sonication did create individual particles. XRD patterns (if we get it) show signals indicating the presence of both graphene and graphite, which correspond to the nanosheets and the presence of larger, multilayer particles resembling graphite, respectively. Further sonication could lead to more complete exfoliation, but care must be taken to prevent oxidative damage to nanosheets during prolonged sonication. The specific surface area (SSA) of dried powder was found to be 14.4 m\(^2\) g\(^{-1}\). This value is comparable to Angstron Materials (N006-010-P) commercial graphene oxide powders with micron-sized particles but far less than the high surface area graphene oxides with much smaller particle sizes [32]. The low SSA is likely due to the larger particle size compared to the commercial nano-sized powders, and possibly due to the presence of some unexfoliated graphite that “hides” surface area as graphene sheets remain stacked upon each other.

Ethylenediamine was observed on graphene surfaces within XPS spectra based on the presence of an N peak (Figure 4.2). Nitrogen was observed within a broad scan and
found to be 6.7% of the elemental composition, with C as 66.4% and O as 21.5%, and trace (5.4%) Al likely from the sample support. There was no evidence of any remaining surface-bound chloride after reaction, meaning the amidation process removed all chloride and replaced them with ED. High resolution spectra were recorded for the C, O, and N energy ranges (Figure 4.2). Fitted model parameters are listed in Table 1. The surface-bound ethylenediamine could be modeled with three model peaks that are commonly observed for amine groups and for surface-bound ethylenediamine specifically[33]. The amine peak (N-C) corresponds to the terminal C-NH2 group, and the amide peak (N-C=O) corresponds to the C, HN=C=O bond connecting the ethylenediamine molecule to a formerly carboxyl surface group. The proportions of these peak areas is approximately 1:1 which correlates well with the expected abundance of each group, as each ethylenediamine molecule contains one of each. The presence of the amide group confirms the formation of the covalent N-C bond at the graphene surface. The N-C and N-C=O groups were also included in the modeled C1s spectra, although at an abundance ratio of 2:1. This different proportion could be due to uncertainty caused by overlapping larger peaks and their low peak areas close to the modeled baseline. A third, smaller peak in the N1s spectra resembles that of quaternary amines. Keen et al [33] interpreted this feature as an indication of an ion pair formation between surface carboxyl groups and sorbed ethylenediamine molecules which were not washed away by ethanol and water. Other surface oxygen groups observed were carboxyl, hydroxyl, and carbonyl groups which are typical for graphene oxides [13,32]. C1s spectra revealed the carbon nature to be primarily aromatic (C=C) with some aliphatic content (C-C).
4.4.2 Effect of pH

Ethylenediame has a $pK_a_1$ of 6.9 and $pK_a_2$ of 9.9, where one N group is positively charged at $pH < 9.9$. Exfoliated, suspended graphene oxide typically contains negative charges in this $pH$ range due to the deprotonation of primarily carboxylic groups. The surface-bound ethylenediamine provided a net positive surface charge when suspended in water at circumneutral and acidic $pH$ as revealed by zeta potential measurements of ED-G in aqueous suspensions (Fig. 3a). Zeta potential measurements of ED-G showed that below the $pH$ zero point of charge ($pH_{zpc}$) of 8.1, the surface charge of functionalized graphene is positive, otherwise, it is negative charged. ED-G becomes negative at higher $pH$ due to deprotonation of amine groups, the remaining carboxylic groups and hydroxyl groups, those oxygen- and hydrogen-bearing functional groups. The two amine groups on free ED molecules have $pK_a$ values of $\sim 6.9$ and $\sim 9.9$, allowing a doubly positively charged molecule at $pH < 6.9$ where both amines are fully protonated $\text{--NH}_3^+$, a singly positively charged molecule predominantly at $6.9 < pH < 9.9$ where one amine deprotonates to $\text{--NH}_2$, and a neutral molecule a $pH > 9.9$ after both amines deprotonate.

The amidation procedure is assumed to bind ED to surface oxygen sites such as carboxylic groups, as detailed in prior reports of CNT amidation[29], resulting in the formation of an amide group. The N atom in the amide is expected to no longer participate in acidity reactions within the $pH$ range of interest owing to the strong electron-withdrawing carbonyl group that disrupts the lone pair of electrons on the neighbor N by resonance. The terminal amine group $pK_a$ is far less affected and provides the positive surface charge at circumneutral $pH$. Additional surface O groups could also
be providing negative charge simultaneously, and their roles could be further diminished by their removal, such as by reduction with hydrazine or sodium hydroxide.

The altered surface charge should influence the sorption extents of charged organic molecules. Comparing to commercial graphene materials we tested in our previous study [32], which are mostly negative charged over the entire pH range of 2 to 11, ED-G with positive charge under pH 8 on the surface will behave quite differently when they react with charged contaminants in water systems. Positive charged atenolol (pKa=9.43), negative charged ibuprofen (pKa=4.91) and neutral compound carbamazepine were investigated for their interactions with ED-G in aqueous solutions. The molecular structures of those three compounds are displayed in Figure 4.2b, and speciation diagrams showing distribution of charged and neutral species are provided in Figures 4.2c and 4.2d. The pH edge results showed that the sorption of ibuprofen by ED-G was greatly enhanced under ED-G’s pH \(_{zpc}\) 8.1 due to electrostatic attraction between the positively charged ED-G and the negatively-charged IBU. Above pH 8.1, the sorption capacity of ibuprofen leveled off due to electrostatic repulsion as both ibuprofen and ED-G become negatively charged. The sorption of IBU did not continuously drop as graphene charge becomes more negative at pH>8.1, probably due to strong p-p interactions between the benzene ring of IBU and the benzene rings of graphene.

The sorption capacity variation over the entire pH range for the positive charged compound atenolol on ED-G was the opposite of what we observed for ibuprofen. The sorption of atenolol was greatly inhibited at acidic pH due to electrostatic repulsion between the positively charged atenolol and ED-G surfaces. When pH increased from 4, the positive charges on ED-G gradually decreased as shown from Figure 4.2(a), the
sorption of atenolol was slightly increased because the intensity of molecular repulsion force between sorbent and sorbate was weakened. Until after pH 8, the increasing trend was level off because the charge of ED-G started to turn into negative, and at the same time, the charge of atenolol gradually turned into neutral. Overall, the pattern of consistently better removal of the negative ibuprofen over the positive atenolol is in contrast to observations of these two compounds during sorption onto negatively charged graphene oxide [32]. In that study, atenolol sorption was greater than that of ibuprofen at alkaline pH due to electrostatic attraction between positively charged atenolol and negative graphene oxide. Here, the negative charge of ED-G at pH near 10 does improve sorption of atenolol but not in sufficient amount to surpass the neutral ibuprofen.

The sorption of neutral compound carbamazepine did not changed too much over the entire investigated pH range because it is in dependent of electrostatic interactions. pH-invariant behavior of carbamazepine was also observed on negatively-charged graphene oxide surfaces [32], indicating that electrostatic interactions have little influence on the sorption of neutral compounds for both negatively and positively charged graphene surfaces. These results suggest that positively-charged graphene surfaces could be used for the sorption of both negatively-charged and neutral organic compounds.

4.4.3 Sorption Capacity

Sorption isotherms were performed on ED-G using the three sorbents to better test the sorbate preferences of ED-G over a wider range of solute concentrations. Sorption was performed at pH 7.2 to ensure primarily negative charge to ibuprofen, primarily positive charge to atenolol, and an overall positive charge to ED-G. Sorption data of
ibuprofen, atenolol and carbamazepine showed increased sorption with increased aqueous sorbate concentrations, and the patterns were best fitted with Freundlich model, which has the equation $q = K_F C_w^n$, where $q$ (µmol g$^{-1}$) and $C_w$ (mmol L$^{-1}$) are solid-phase and aqueous-phase concentrations of the sorbates, respectively, $K_F$ (µmol mmol$^n$ L$^n$/g) is the empirical constant related to sorption capacity, and $n$ (unitless) is the Freundlich linearity index. The $K_F$ values for ibuprofen, carbamazepine and atenolol are 291.12, 128.53 and 100.05, respectively. Figure 4.3 showed that the sorption capacity of negative charged ibuprofen is higher than the neutral compound carbamazepine at high concentration range, and the sorption extent for carbamazepine levels off earlier than ibuprofen due to a stronger nonlinearity behavior. If we continue to increase the initial concentration of tested samples, the trend is predictable that the sorption extent of ibuprofen should be much higher than the sorption extent of carbamazepine, but these experiments are precluded by ibuprofen solubility limit in water. At low concentration range, it's possible that the sorption mechanisms are quite different between ibuprofen and carbamazepine with ED-G. pi-pi interaction between benzene rings in the compounds and ED-G surface pi electron structures may become the one of the more important mechanism than electrostatic interaction governing the sorption extent. Carbamazepine with two benzene rings in its molecular structure could more actively promote pi-pi interactions than ibuprofen with only one benzene ring in its structure. However, at higher concentration range, as charges increases with greater compound concentration, electrostatic interaction exceed pi-pi interaction becoming the most important mechanism governing sorption extent. The positive charged compound atenolol has the lowest sorption capacity of the three contaminants due to electrostatic repulsion.
Mestre et al. discussed the sorption of ibuprofen by activated carbon, CAC and CPAC prepared with different methods [34]. The experimental data in their study was best fitted with Langmuir model. Since our sorption data with ED-G for the sorption of ibuprofen can also be fitted with Langmuir model, a comparison between normalized $q_m$ (mg g$^{-1}$) by SSA was performed. The results showed that $q_m$/SSA for ibuprofen sorption by ED-G is 17~40 times higher than $q_m$/SSA for CAC and CPAC, which suggested to us that positive charged ED-G greatly enhanced the sorption of negatively charged compounds.

4.4.4 Competitive Sorption

While positive ED-G clearly exhibits greater sorption extent for the negatively charged ibuprofen compared to the positively charged atenolol, we sought to test whether ED-G’s preference for ibuprofen continued during competitive sorption. Waters containing organic micropollutants typically possess multiple compounds, and competitive sorption can be an important factor that limits sorption extent of any compound onto sorbent surfaces. Initial samples with same molar concentrations of negative charged ibuprofen and positive charged atenolol were tested to investigate competitive sorption of those two compounds simultaneously on ED-G. First, ibuprofen was preferably sorbed to a greater extent compared to atenolol for all solute concentrations (Figure 4.4), confirming the role of electrostatic attraction between ibuprofen and ED-G. Positive ED-G will still sorb some positive atenolol despite stronger preference for ibuprofen. Second, the presence of dual sorbates did diminish the sorption extent for each compound compared to sorption in single-sorbate experiments (indicated as model lines in Figure 4.4). Comparing to Freundlich sorption isotherm model with
ibuprofen only and atenolol only on ED-G, it is found that at low concentration (< 20 mg l\(^{-1}\)), competitive sorption data points almost overlapped with the sorption models of non-competitive sorption for both ibuprofen and atenolol, possibly because abundant sorption sites are available to be taken by limited amount of sorbates. However, as the concentration of ibuprofen and atenolol increased, they would start to compete with each other for the sorption sites on the surface of ED-G, so both of their sorption extents were impeded at conditions with high concentration. This behavior provides some insight to the relative importance of different solute-sorbent interaction mechanisms. ED-G therefore can still sorb positively-charged compounds despite having a clearer preference for negatively-charged compounds in mixed solutions. Other interactions, such as p-p interactions and general hydrophobic interactions, still cause surface binding for atenolol. Electrostatic interactions may therefore influence sorption extent, but they are not the sole interaction mechanism. The sorption amount of ibuprofen is still much more than that of atenolol during the competitive sorption test due to the attraction between its negative charge and the positive charge on ED-G. Therefore, it could be concluded that positive charged material ED-G could enhance the sorption of negative charged contaminants in water systems.

Because source waters with organic micropollutants may also contain naturally-occurring organic molecules or other micropollutants with negative charge, the ability for ED-G to still remove a negatively-charged EDC present with mixtures of other negatively-charged compounds were tested. Competitive sorption between ibuprofen and other negative charged organic compound, including natural organic matter (NOM), acetaminophen, salicylate, and acetate on ED-G was also studied in aqueous solutions at
pH 7.2. These dissolved compounds all possess negative charge at this pH and represent a wide range of molecular sizes from 59 Da to several thousand Da. Results were compared to non-competitive sorption with ibuprofen only. It is found that acetate anions do not compete with ibuprofen for the sorption sites on the surface of ED-G, and sorption extent for ibuprofen is similar with or without acetate. However, NOM, acetaminophen, and salicylate can compete for the surface sites on ED-G to impede the sorption of ibuprofen to different degrees, and less ibuprofen sorption was observed at all initial concentrations. These three compounds likely sorbed to ED-G due to both their negative charge and their aromatic character, unlike acetate which is aliphatic. However, sorption extent of the 50 mg L-1 competitive sorbates was not determined due to interference of ibuprofen on NOM measurements by total organic carbon analysis and acetate analysis by anion chromatography. Interference by acetaminophen and salicylate with ED-G were stronger than those by NOM at pH 7.2. NOM sorption to graphene is mainly controlled by NOM aromatic content and is enhanced at acidic pH [13]. NOM sorption onto micron-sized graphene can be very low at circumneutral pH depending on graphene size and surface chemistry [13], and low sorption here could explain the minimal interference on ibuprofen sorption. The sorption of ibuprofen decreases by 25-95% when a high concentration of salicylate or acetomenophen is present. This suggests that organic anions of similar structure can strongly suppress sorption extents. However, even high concentrations of natural organic matter only partly diminishes ibuprofen sorption.

4.5 Conclusions

Graphene functionalized with ethylenediamine was synthesized for the first time from graphite oxide by an amidation process followed by sonicated exfoliation. The resulting
product was in the form of micron-sized sheets that appeared to be a few graphene layers thick. The functionalized ethylenediamine molecules provided a net positive surface charge when the graphene was suspended in water, and this material was tested for its ability to preferably sorb negatively-charged organic micropollutants, with ibuprofen as a test compound. The general hypothesis that a positively-charged graphene-based sorbent would improve sorption of negatively-charged ibuprofen—as compared to negatively-charged graphene oxide—was confirmed. The positive charge of graphene surfaces also lessened the sorption of atenolol, a positively-charged micropollutant. Isotherm data confirmed the preference for negatively-charged ibuprofen over atenolol and carbamazepine, a neutral molecule of similar molecular weight. Competitive sorption experiments showed that ibuprofen is consistently preferred over atenolol over a wide range of concentrations, and the presence of other negative-charged compounds can suppress the sorption of ibuprofen. Our results show that graphene oxide modified to hold positive charge may be a useful material for targeted removal of negatively charged micropollutants. To treat source waters with mixtures of micropollutants with a variety of physicochemical properties, a mixture of both positive-graphene and negative-graphene may be preferred in order to maximize removal of all types of compounds. The effect of surface functionalization also needs to be examined for the removal of natural organic matter from drinking water, which may be a precursor to disinfectant byproducts. Further experimentation is needed with both ED-functionalized and pristine graphene to determine if ethylenediamine functionalization can improve the sorption of negatively-charged NOM under typical water treatment conditions.
Table 4.1 X-ray photoelectron spectroscopy fitted model parameters for ethylenediamine-functionalized graphene oxide.

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**Figure 4.1** TEM images of ethylenediamine-functionalized graphene oxide after exfoliation by sonication followed by drying.
**Figure 4.2** XPS spectra of ethylenediamine-functionalized graphene oxides. Fitted model parameters appear in Table 4.1.
Figure 4.3 (a) Zeta potential of amine graphene. Experimental conditions for a: 0.1 g l\(^{-1}\) graphene in 5 mM NaCl. (b) Effect of pH on the positive charged sorbate atenolol (AT, pK\(_a\) 9.4), the negative charged sorbate ibuprofen (IBU, pK\(_a\) 4.9), and the neutral sorbate carbamazepine (CBZ). Experimental conditions: 0.5 g l\(^{-1}\) amine graphene and initial sorbate concentrations of 80-90 mg l\(^{-1}\) in a buffer solution of 1 mM NaHCO\(_3\) and 20 mM NaCl. (c) Speciation diagram of IBU and AT. Positive species (red line), neutral species (blue line) and negative species (green line) coexist in the solution with varied percentages for pH from 2 to 12.

Figure 4.4 Sorption isotherms of amine graphene with varied sorbates including carbamazepine (red open diamonds), ibuprofen (blue filled triangles), and atenolol (green open circles). Solid lines are Freundlich model simulations. Experimental conditions: 1 g l\(^{-1}\) graphene, initial concentration of CBZ and AT 5 ~ 200 mg l\(^{-1}\), initial concentration of IBU 5 ~ 100 mg l\(^{-1}\), pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\), reaction time 20 min.
Figure 4.5 Competitive sorption of ibuprofen (blue filled triangles) and atenolol (green open circles) at equal initial molar concentrations in dual sorbate reactors with amine graphene. Dotted lines are Freundlich models of single solute sorption of ibuprofen (blue) and atenolol (green) from Figure 3. Experimental conditions: 1 g l$^{-1}$ graphene, initial concentration of ibuprofen and atenolol ~20-480 µmol/L, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 20 min.

Figure 4.6 Competitive sorption of ibuprofen onto amine graphene in dual sorbate systems with other selected negatively charged compounds including sodium acetate (black open square), NOM (pink dotted circle), acetaminophen (red open diamond), and salicylate (green open circle), compared to ibuprofen alone (blue filled triangles). Experimental conditions: 0.5 g l$^{-1}$ graphene, initial concentration of ibuprofen ~10-60 mg l$^{-1}$, initial concentration of NOM 22 mg l$^{-1}$ TOC, initial concentration of salicylate, sodium acetate, and acetaminophen 50 mg l$^{-1}$, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 20 min.
Chapter 5  Facile Synthesis and Reuse of Magnetic Black Carbon Magnetite (BC-Mag) for Fast Carbamazepine Removal

5.1 Abstract

Magnetic carbonaceous materials are needed to enable materials regeneration and reuse for improved sorption-based water technologies. In this study, we employed a facile method to synthesized black carbon magnetite (BC-Mag) for contaminants removal. Sorption kinetic included a very fast initial uptake and equilibrium can be reached within only minutes. Sorption extent of carbamazepine follows the Freundlich model best. Increasing solution pH leads to a decrease in surface charge due to deprotonation of oxygen- and hydrogen-bearing functional groups. A drop of sorption extent of carbamazepine was only observed at very basic water conditions, other than that, the sorption amount remained at the same level between pH 2~10. BC-Mag can be reused for the sorption of carbamazepine up to six times without significant loss of sorption extent.

Keywords: Graphene; Black Carbon Magnetite; Sorption Processes; Freundlich Isotherm; Water Treatment.

Abbreviations: BC-Mag = Black Carbon Magnetite. BET = Brunauer-Emmett-Teller. XPS = X-ray photoelectron spectroscopy. CBZ = carbamazepine.
5.2 Introduction

Water and wastewater treatment strategies often employ adsorption technologies for the removal of organic, inorganic, and metallic pollutants. Carbonaceous sorbents hold strong affinities for organic micropollutants owing to their strong abilities to form hydrophobic and aromatic interaction. Recent advances in carbonaceous sorbents have been to incorporate nanotechnologic features and fine-tuning of carbon surfaces for enhanced reactivity. Nanometer-sized features of carbon sorbents can provide significantly high specific surface areas and chemically tunable surfaces (Csp$^2$, Csp$^3$, or functional groups) available for contaminant sorption. The graphene structure in the form of carbon nanotubes and graphene nanosheets have shown particularly superior performance compared to activated carbon for the removal of organic micropollutants. More disordered forms of carbon that have been evaluated as alternative sorbents include biochar, coal and soot.

Nano-sized amorphous carbon has also been formed on surfaces of magnetic iron oxide nanoparticles for manipulation within test waters using a magnetic field. These particles typically contain a core-shell structure where the exposed carbon shell provides available sorption sites and the protected iron oxide core (typically magnetite, Fe$_3$O$_4$) is sensitive to applied magnetic fields. This combination of physical properties allows retrieval of the nanoparticles for regeneration and reuse. Carbon-coated magnetic iron oxides are typically formed within hydrothermal conditions where dissolve organic molecules (e.g. glucose) becomes charred upon pre-formed nanomagnetite particles [1]. The result is typically a coating of amorphous carbon (as opposed to ordered graphite-
like sheets) upon 10-50 nm sized iron oxide cores. Repeated washing of the particles with alcohol and water is required to remove unbounded charred compounds, and so far allowable mass production is low due to low concentrations of nanoparticles and dissolved glucose.

The purpose of this report is to evaluate magnetic black carbon particles as a sorbent for the removal of trace organic micropollutants in water. Black carbon is nanometer-sized particles of pure carbon (typically <20 nm) commercially available in powdered form. These nanoparticles typically hold very high surface areas that, if exposed to the solution phase, could provide surface sites for rapid and extensive sorption of organic molecules. Synthesize of black carbon attached to magnetic iron minerals has been reported to occur around 1000 °C, and higher temperatures can lead to dissolution of carbon within the iron oxide and reprecipitation as an amorphous exterior coating upon cooling [2]. The synthesis of black carbon magnetic particles is suited for product yields of several grams after processing within tube furnaces, and no post-washing is required due to the annealing of loosely-bound organic molecules. This synthesis route may prove to be less resource- or time-intensive compared to hydrothermal synthesis.

Graphene, carbon nanotube, black carbon and other traditional carbonaceous sorbents have great sorption performance to remove most contaminants from water systems, however, all those materials are hard to be retrieved and reused. One way to enable the particles retrievable is to synthesize magnetic graphitic nano particles in that way the used particles could be easily retrieved by magnet and regenerated by organic solvents. Chandra et al. developed magnetite-graphene hybrids via a chemical reaction, and results showed that the composites can remove arsenic near completely within ppb
level [3]. Zhu et al. reported a facile thermodecomposition process to synthesize magnetic graphene nanocomposites for fast chromium removal [4].

Carbamazepine, a widely used anticonvulsant for the treatment of epilepsy, is one of the 11 most frequently detected endocrine disrupting compounds in water systems [5]. It is marginally soluble in water (~200 mg l⁻¹) which allows studying a range of concentrations, and recalcitrant to be removed. Carbamazepine can keep as untransformed and pass through all conventional water treatment processes and advanced processes such as membrane bioreactors. The advanced oxidation process (AOP) can be used to break down and transform carbamazepine; however, the formation of unknown byproducts has been a big concern. Therefore, sorption processes and techniques using graphene based nanomaterials could be employed to produce favorable carbamazepine removal efficiency.

This work synthesized a novel graphene based nanomaterials, black carbon magnetite (BC-Mag), which introduced magnetite elements into black carbon to make the sorbents magnetic. Sorption rates and capacity were tested with carbamazepine by BC-Mag under different buffer conditions. The recovery of carbamazepine and the regeneration of BC-Mag were evaluated for practical considerations.

5.3 Methods

5.3.1 Material synthesis and characterization

3 g Hermatite and 1.45 g black carbon powders were used as the starting materials for the synthesis of black carbon magnetite (BC-Mag). After putting those weighed materials in a 50 ml falcon tube, they were vigorously vortex for 30 minutes, and then
rotated end-to-end overnight for 24 hours to achieve a good mixing. The mixture was heated at 1000 °C in a furnace at heating rate of 3 °C per minute, and kept for 2 hours at temperature within a nitrogen atmosphere. BC-Mag was characterized for physical and chemical properties prior to use. Specific surface area (SSA) was measured by 5-point Brunauer-Emmett-Teller (BET) analysis following degassing at 80°C using a Quantachrome Nova 2200e instrument. Transmission electron microscopy (TEM) was performed with a Jeol JEM-1010 instrument. X-ray Diffraction (XRD) was performed with a Rigaku UltimaIV instrument with CuKα radiation. Zeta potential was measured using a Malvern Nanosizer ZS90 for dilute aqueous suspensions of 0.1 g l⁻¹ in 5 mM NaCl with pH modified by small additions of 0.1 M HCl or 0.1M NaOH.

5.3.2 Sorption experiments

All sorption experiments for carbamazepine and BC-Mag were conducted in batch reactors containing buffer solution of 20 mM NaCl and 1 mM NaHCO₃ in deionized water (>18 MΩ-cm) with small additions of 0.1 M HCl or 0.1 M NaOH to set solution pH. Carbamazepine stock solutions were prepared in methanol, and spike volumes were kept below 0.1% of reactor volumes to minimize cosolvent effects. Carbamazepine was first spiked to buffer solution, and initial samples were taken at the beginning. Reaction was initiated by addition of BC-Mag and immediately agitated. To separate the solid phase of BC-Mag and the aqueous phase of the solution after reaction, a strong magnet was used to assist. Aqueous samples were taken at predetermined time points by filtering through 0.2 micron PTFE syringe-tip filters. The amount of carbamazepine sorbed was determined by difference between initial and final concentrations and normalized to mass of graphene added.
Kinetic experiments with carbamazepine at an initial concentration of 90 mg l\(^{-1}\) and BC-Mag at an initial concentration of 0.5 g l\(^{-1}\) were performed at pH 7.2 in 100-ml glass bottles under magnetic stirring at room temperature for up to 24 hours. Isotherm experiments with carbamazepine at initial concentrations of 5-200 mg l\(^{-1}\) and 1.0 g l\(^{-1}\) of BC-Mag were carried out at pH 7.2 within 30-ml glass vials with PTFE lined septa rotated end-over-end at room temperature with a contact time of 20 min. The solution pH remained at 7.2 ± 0.2 after completion of experiment. pH edges of carbamazepine were generated in a pH range of 3.0 – 11.0 with an initial concentrations of 80 mg l\(^{-1}\) and 0.5 g l\(^{-1}\) BC-Mag for 20 minutes.

5.3.3 Desorption and regeneration

Recovery experiments were performed with repeated retrievals of BC-Mag and washings and further use. Carbamazepine at an initial concentration of 10 mg l\(^{-1}\) was first sorbed to BC-Mag at a concentration of 1 g l\(^{-1}\) in 10 ml of buffer solution within 30-ml glass vials for 20 minutes. After reaction, solids of BC-Mag were separated by the magnet within 5 minutes of precipitation and attachment. 1 ml of supernatant was carefully sampled with 0.2 micron PTFE syringe-tip filters, and the other 9 ml of supernatant was damped into a waste bottle and replaced with 10 ml ethanol (95+% pure, anhydrous, denatured with up to 5%v/v ether, Acros) as desorbent to promote recovery of carbamazepine and regeneration of BC-Mag. The suspension was quickly shaken and vortexed for 30 seconds and then placed on rotator disk for 5 minutes. Solids were separated using magnet, and the supernatant was sampled using 0.2 micron PTFE syringe-tip filters for HPLC measurement of carbamazepine recovery. After the removal of the supernatant of ethanol, the damp BC-Mag powders were heated at 50 °C in the
oven for 30 minutes until dried. A reuse cycle started by the injection of 10 ml fresh 10 mg l\(^{-1}\) carbamazepine stock solution into the glass vial with dried BC-Mag, and vigorously vortex the suspension for 30 seconds. Then the glass vial was placed on the rotator disk for 20 minutes contact time, and the following experimental procedures will follow above-mentioned steps. A total of five regeneration steps were carried out. Sorbed carbamazepine mass was determined by calculating the change in concentrations before and after each step, and carbamazepine recovery percentage was calculated through dividing the measured carbamazepine concentration in ethanol by the sorbed carbamazepine mass. The sorption percentage of carbamazepine in every step was calculated by dividing the change in concentrations before and after each step with the initial concentrations.

### 5.3.4 Quantification of carbamazepine

Concentrations of carbamazepine were analyzed by high performance liquid chromatography (HPLC) (Agilent 1260 Infinity Quaternary LC) with a UV detector using a 4.6 x 50 mm ODS Hypersil C18 column (Thermo Scientific) with injection volume of 10 µL, 40% acetonitrile and 60% HPLC grade water as eluent, flow rate of 1 ml/min, and wavelength of UV absorbance of 220 nm.

### 5.4 Results and Discussion

#### 5.4.1 Characterization of Black Carbon Magnetite

The heat treatment of hematite and black carbon at 1000 ℃ resulted in a fusion of the particles and a phase transformation of the iron oxides (Figure 5.1). TEM images
revealed the presence of ~10 nm black carbon particles accumulated near surfaces of the ~50-100 nm sized iron minerals. The heat treatment did not significantly transform the black carbon particles in size or identity; such transformation (e.g. dissolution of carbon into the iron oxides, volatilization) usually occurs at higher temperatures. The high temperature reaction did result in transformation of most of the parent hematite into a mixture of more reduced iron minerals including magnetite (Fe₃O₄) and zero-valent iron (Fe(0)), as revealed in an XRD pattern (Figure 5.2). Reflections were compared to locations for mineral standards as provided in standard powder diffraction file cards. The reduction of Fe (III) in hematite to Fe (II) in magnetite and Fe(0) was possible at high temperature with elemental carbon as an electron source and without oxygen in the gas stream. Because some hematite reflections overlap with magnetite, it is possible some hematite was not transformed fully. The black carbon is mostly graphitic in nature, as indicated by the graphite reflections present in the XRD pattern. It is possible some of the magnetite contains maghemite (γ-Fe₂O₃) because standard reflections of these minerals are indistinguishable. The BC-mag particles were easily retrievable from aqueous suspension using a strong magnet, and this observation supports the identification of magnetite and Fe (0) owing to their significantly larger magnetic susceptibility values compared to that of hematite, which is not attracted to magnets.

5.4.2 Sorption rates and capacity

The kinetic data of carbamazepine sorption on black carbon magnetite shows a very fast uptake at the beginning and a quick process to reach the equilibrium (Figure 5.3). The pseudo-second order rate law best describe carbamazepine sorption on BC-Mag with correlation coefficient $R^2>0.999$. The equation of pseudo-second order model
is \( dq_t / dt = k_2 (q_e - q_t)^2 \), where \( q_t \) (mg g\(^{-1}\)) is sorbed carbamazepine concentration on BC-Mag at time \( t \) (h), \( q_e \) is sorbed carbamazepine concentration on BC-Mag at equilibrium, and \( k_2 \) (g mg\(^{-1}\) h\(^{-1}\)) is the pseudo-second order rate constant. The pseudo-second-order model assumes that sorption extent is controlled by the availability of surface sorption sites rather than the sorbate concentration in the solution, and chemisorption is the rate controlling step. Sorption rates parameters are calculated as listed in Table 5.1, which including the fitted rate constant \( k_2 \), the equilibrium sorption extent \( q_e \), and the calculated relaxation time \( t_r \), which represents the time required for sorbents sites to reach half-saturation and determined as \( t_r = 1 / (k_2 q_e) \). The fast sorption of carbamazepine on BC-Mag was reflected through the high \( k_2 \) value, and small \( t_r \) value which equals to only 4.32 seconds for BC-Mag sorption sites to reach half salturation. This relaxation time is one of the smallest of any sorbent tested in all of your studies. Those values were 0.36-147.6 seconds. This material may represent the fastest sorbent for EDCs, superior to most of other graphene and 500 times faster than traditional GAC. The very fast sorption kinetics may be due to high specific surface area exposed in solution.

The common used isotherm models, Freundlich model and Langmuir model, have been applied to the experimental data from isotherm study, and the results showed that both of the two models can fit the data but Freundlich model had a higher correlation coefficient \( R^2 \) of 0.95 than \( R^2 \) of 0.82 for Langmuir model. This would suggest us heterogeneity sorption instead of homogeneous sorption is dominant in the sorption of carbamazepine on BC-Mag because surface functional groups and magnetite composites make the sorption sites on BC-Mag a wide distribution for different sorbates not having all the same affinity as suggested by Langmuir model. By comparing to the sorption
capacity of carbamazepine by different commercial graphene and CNTs from our previous study [6], it is found that graphene C has the highest value due to its very high specific surface area, and the $K_F$ value of BC-Mag is only comparable to graphene M standing in the middle level. However, it is two times higher than conventional GAC with much lower specific surface area.

5.4.3 Effect of solution pH

Over the pH range 2 to 12, BC-Mag was always found to have very negative surface charges, which even much more negative (-52.7 mV at pH 10.5) than what we observed for graphene C earlier. The negative charge was cause by deprotonation of surface functional groups such as carboxyl, hydroxyl and phenol groups as pH increases. As more negative charges will repulse each other more strongly, the suspension of BC-Mag should behave more stable than others. By varying pH from 2 to 10, the sorption of carbamazepine didn’t change because carbamazepine is a neutral compound and no electrical repulsion or attraction involved. However, at the very basic pH 10.5, the sorption has been slightly decreased which might because the surface of BC-Mag has very negative charges, and as pH increased, much more hydroxyl groups generated in the solution, and they might compete with the sorbate carbamazepine [4], or impeded the sorption of carbamazepine on BC-Mag due to the repulsion of the hydroxyl groups and the very negative surface charges on BC-Mag.

5.4.4 Recovery of carbamazepine and regeneration of BC-Mag

To evaluate the stability and possibility of reuse of BC-Mag as sorbent in order to reduce the cost of sorption procedures and recovery of contaminants from wastewater, repeating applications for 6 steps of BC-Mag sorption experiments has been performed.
The separation of solid phase and liquid phase in each step has been much easier resulting from the magnetism of synthesized magnetic sorbent BC-Mag with the help of a strong magnet. Sorption efficiencies of carbamazepine on BC-Mag were shown in the bar graph of Figure 5.7. It was as high as 85% for the first run, then dropped to 70% and kept stable for the following four runs, and dropped to 65% at the last run. The decrease of removal efficiency is possibly due to a fraction of carbamazepine remained firmly bounded on the surface sites of BC-Mag and resisted to desorb even with ethanol. Also, it has been observed that during the process of BC-Mag separation from carbamazepine solution after sorption and washing processes with ethanol, a small portion of particles have been lost because they have weak or no magnetism and they couldn’t be attracted by the magnet but damped with liquid. The efficiency of carbamazepine recovery was also presented in Figure 5.7. with dots and line, and it keep stable as high as average 85%, which indicated ethanol as an effective eluent to extract carbamazepine. Also, a slightly increase of carbamazepine recovery percentage may due to the desorption of the originally firmly bounded molecular because of six times of washing by ethanol.

5.5 Conclusions

The study demonstrated fast removal of carbamazepine with high capacity from water within minutes to reach sorption equilibrium by BC-Mag. Sorption extent of carbamazepine was hardly influenced by pH in the range of 2.0 ~10.0. Due to a fairly negative surface charge on BC-Mag at pH over 10, the sorption of carbamazepine was impeded. Besides, the sorbed carbamazepine could be efficiently desorbed in ethanol with an average recovery percentage 85%, and the used BC-Mag could be easily
separated from liquid solution with the aid of magnet and reused at least 6 times with removal efficiency higher than 65%. In practical, BC-Mag can be an effective sorbent for carbamazepine removal from water. The reuse and regeneration of BC-Mag will help to save cost in sorption processes. With a much faster sorption rate and higher sorption capacity comparing to conventional activated carbon, and the possible new properties of reusability, BC-Mag can serve as an alternative to conventional sorption materials in modern water treatment applications.
LIST OF TABLES

Table 5.1 Pseudo-second-order kinetic model parameters of carbamazepine sorption on BC-Mag. $R^2 > 0.99$ for all model simulations.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorbent Concentration g l$^{-1}$</th>
<th>$t_r$ h</th>
<th>$k_2$ g mg$^{-1}$ h$^{-1}$</th>
<th>$q_e$ mg g$^{-1}$</th>
<th>$q_e$ / SSA mg m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-Mag</td>
<td>0.5</td>
<td>0.0012</td>
<td>24.8</td>
<td>33.6</td>
<td>?</td>
</tr>
</tbody>
</table>

Table 5.2 Isotherm parameters for fitted Freundlich and Langmuir isotherm models of carbamazepine sorption on BC-Mag.

<table>
<thead>
<tr>
<th>Freundlich isotherm</th>
<th></th>
<th>Langmuir isotherm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_F$ a</td>
<td>5.8</td>
<td>$K_L$(1 mg$^{-1}$)</td>
<td>0.05</td>
</tr>
<tr>
<td>$n$</td>
<td>0.33</td>
<td>$q_{max}$ (mg g$^{-1}$)</td>
<td>31.8</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.95</td>
<td>$R^2$</td>
<td>0.82</td>
</tr>
</tbody>
</table>

a All Freundlich modeling was performed on data with units of dissolved sorbate concentration in mg l$^{-1}$ and sorbed sorbate concentration of mg g$^{-1}$.
LIST OF FIGURES

Figure 5.1 TEM image of BC-Mag particles synthesized at 1000 °C. Electron-dense regions are iron minerals, and lighter particles are black carbon. Scale bar is 100 nm.

Figure 5.2 XRD pattern of BC-Mag particles synthesized at 1000 °C. M = magnetite, H = hematite, Fe(0) = iron metal (alpha form), Gr = graphite.
**Figure 5.3** Time profile of carbamazepine sorption on black carbon magnetite 0.5 g l\(^{-1}\), solid lines are pseudo-second order kinetic model simulation.

**Figure 5.4** Sorption isotherms of carbamazepine on black carbon magnetite. Red solid line is Freundlich model simulation, and black dotted line is Langmuir model simulation. Experimental conditions: 1.0 g l\(^{-1}\) graphene, pH 7.2, 20 mM NaCl, 1 mM NaHCO\(_3\).
Figure 5.5 Zeta potential of black carbon magnetite compared to graphene C [7]. Experimental conditions for a: 0.1 g l$^{-1}$ graphene in 5 mM NaCl.

Figure 5.6 Effect of pH on the neutral sorbate carbamazepine. Experimental conditions: 0.5 g l$^{-1}$ black carbon magnetite and initial sorbate concentrations of 70-80 mg l$^{-1}$ in a buffer solution of 1 mM NaHCO$_3$ and 20 mM NaCl.
**Figure 5.7** Carbamazepine sorption percentage by BC-Mag within consecutive six repeated steps of ethanol washing (bar graph) and the recovery of carbamazepine by ethanol as desorbent from every step (dots and line). Experimental conditions: carbamazepine initial concentration 10 mg l⁻¹, mass of BC-Mag 10 mg, solution volume 10 ml, buffer solution of 1 mM NaHCO₃ and 20 mM NaCl.
Chapter 6  Conclusions

6.1 Conclusions

This dissertation has addressed the usefulness of different types of commercial graphene powders and the efficacy of two new carbonaceous sorbents within water treatment and purification applications. The main conclusions and engineering implications are as follows:

- All studied graphene materials either purchased in the market or synthesized in the laboratory can process a wide range of physical chemical properties and sorption behavior for the removal of endocrine disrupting compounds and natural organic matters. All the graphene materials studied as well as black carbon magnetite exhibit very fast sorption rate and mostly described with pseudo-second order model, reflective of their planar surface with little mass transfer limitations.

- Specific surface area behaves as the most significant governing factor for the sorption of EDCs and NOM by commercial in aqueous solutions, which provides insights in selecting graphene materials in water treatment technologies. Not all the commercial graphene materials will have better performance than conventional carbonaceous materials, and our results showed that when the specific surface area of graphene is higher than 100 m² g⁻¹, graphene powers can outperform CNTs and traditional GAC. Therefore, it is suggested that any graphene materials to be used should be first tested for their specific surface area
and sorption behavior for the removal of targeted organics at specific water conditions.

- Water chemistry may greatly influence the surface charges of graphene as well as the charges on the organic molecules. By performing the sorption test with negative charged graphene, a concomitant 2-fold of decrease in sorption of an anionic compound (ibuprofen) and increase in sorption of a cationic compound (atenolol) were observed between pH of natural waters (6-9), suggesting a strong influence of electrostatic interactions on sorption extent. Graphene surface phenolic groups can promote the sorption extent by improve $\pi-\pi$ interaction between sorbent and sorbate. Graphene materials can remove several different EDCs to very similar extents, suggesting graphene could be used as an applicable carbonaceous material for a wide class of contaminants removal. Carbamazepine stays strongly on the surface of graphene with low potential of causing secondary pollution in water solutions, and it can also be nearly fully recovered by alcohol washing.

- NOM sorption extent can be influenced by graphene surface area, surface charge, and aromatic content. NOM sorption was improved with greater graphene aromatic content and higher NOM aromaticity, and the aromatic and high-molecular weight fractions of dissolved NOM were preferably retained by graphene surfaces. Lower solution pH, and consequently less negative graphene surface charge and NOM polarity, improved sorption presumably by lessening electrostatic repulsion. The consideration of surface functional groups will be helpful to achieve better NOM removal in graphene surface design. As SUVA is
an indication of aromaticity in NOM samples, NOM with low SUVA will need higher dose of graphene to fully remove.

- The functionalized ethylenediamine molecules provided a net positive surface charge in suspension. It was confirmed that the sorption of negative charge compound ibuprofen was greatly improved, whereas the positive charged compound atenolol was less competitive to be sorbed than ibuprofen. The presence of other organic and inorganic compounds can suppress the sorption of ibuprofen. Therefore, graphene oxide modified to hold positive charge may be a useful material for targeted removal of negatively charged micropollutants.

- Black carbon magnetite demonstrated a very fast sorption kinetic of carbamazepine within minutes to reach equilibrium, which is among the fastest sorption materials in our tested graphene sorbents. Sorption of carbamazepine wasn’t influenced by pH 2~10, but a drop of sorption extent was observed at pH 10.5 due to a fairly negative surface charge of less than -50 mV on BC-Mag. Sorbed carbamazepine could be efficiently recovered in ethanol with an average recovery percentage over 85%, and the used BC-Mag could be easily separated from liquid solution with the aid of magnet and reused at least 6 times with removal efficiency higher than 65%. With faster sorption rate and sorption capacity than conventional GAC, BC-Mag is one of the most practical carbonaceous materials processing magnetic properties with a great potential to be employed in modern water treatment technologies.
6.2 Recommendations for further work

In further work, it is recommended to study how NOM can influence EDCs sorption on commercial graphene and lab synthesized graphene. For ethylenediamine functionalized graphene, further work can focus on improving the specific surface area of ED-G to make it more powerful as the sorbent for various negative charged EDCs in water systems. More EDCs could be tested on black carbon magnetite to investigate the sorption rate and sorption extent. It will be also helpful to improve the synthesis method of BC-Mag to improve its magnetism, likely increasing the heating temperature in synthesis procedures.
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Chapter 2


doi:10.1002/etc.5620200610.


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Chapter 3


Chapter 4


Chapter 5


APPENDIX

APPENDIX A: SUPPLEMENTARY DATA OF CHAPTER 2

Sorption of Carbamazepine by Commercial Graphene Oxides: A Comparative Study with Granular Activated Carbon and Multiwalled Carbon Nanotubes

This supporting information document contains transmission electron microscopy images of graphene A; six X-ray photoelectron spectra and model parameters of graphenes C, M, and A; tables of information on EDC molecule structure or HPLC detection conditions; calculations of carbamazepine monolayer sorption capacities, and additional kinetic, isotherm, and pH-edge modeling figures.
Table S2.1. Molecular structure of EDCs in this study. $^a$

<table>
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<th>Compound</th>
<th>Molecular structure</th>
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$^a$The images were taken from [http://www.chemspider.com](http://www.chemspider.com)
Table S2.2. HPLC method conditions for detecting EDCs.

<table>
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<th>HPLC Eluent Composition</th>
<th>HPLC Method Reference</th>
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<td>[2]</td>
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<td>BPA</td>
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<td>60% H₂O, 40% CH₂CN</td>
<td>[3]</td>
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<td>Ibuprofen</td>
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<td>20% H₂O (pH 3, H₃PO₄), 80% CH₂CN</td>
<td>[4]</td>
</tr>
<tr>
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<td>220</td>
<td>60% H₂O, 40% CH₂CN</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70% H₂O (pH 3, H₃PO₄)</td>
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<tr>
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<td>Na₁-heptanesulfonate, Na₂HPO₄, 30% CH₃OH</td>
<td>The United States Pharmacopeial Convention.</td>
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<td>85% H₂O, 15% CH₂CN</td>
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$^a$Binding energy = peak location on binding energy axis. Rel. area = percent relative area for each component. FWHM = full width at half maximum.
**Table S2.4** The monolayer sorption capacity $Q_m$ showing surface site availability.

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<th>Sorbent</th>
<th>SSA (BET) (m²/g)</th>
<th>$Q_m$ (mg CBZ/g sorbent)</th>
<th>SSA (reported) (m²/g)</th>
<th>$Q_m$ (mg CBZ/g sorbent)</th>
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</thead>
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<td>720</td>
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<td>M</td>
<td>74</td>
<td>19</td>
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<tr>
<td>A</td>
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<td>4</td>
<td>100</td>
<td>25</td>
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<td>105</td>
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<td>GAC</td>
<td>1181</td>
<td>297</td>
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</table>

$Q_m = A_{sorbent} \times MW \times 10^{23}/(0.5 \times A_{as} \times N)$, where $A_{sorbent}$ is sorbent surface area (m²/g); $A_{as}$ is the solvent accessible surface area of carbamazepine (Å²); N is the Avogadro constant (6.02 × 10²³/mol); MW is the molecular weight (g/mol). The factor 0.5 refers to the assumption that approximately half of the value of $A_{as}$ interacts with the graphene oxide surface (that is, one side of a carbamazepine molecule when laid flat).
Figure S2.1 Effect of NaCl concentration on the sorption of 30 mg l\(^{-1}\) carbamazepine onto 0.1 g l\(^{-1}\) graphene C in 1 mM NaHCO\(_3\) buffer solution at pH 7.2. No change in sorption extent was observed within this NaCl concentration range.
Figure S2.2 Speciation diagrams of EDCs used in this study over the pH range of 2 to 12. Y-axis illustrates fractions of each species (0 to 1.0). Line color corresponds to species charge which is also indicated numerically next to each line. Red lines indicate a charge of +1, blue lines indicate neutral compounds with no charge (0), and green lines indicate a charge of -1.
Figure S2.3 Transmission electron microscopy image of a sheet of graphene A showing particle size (A) and a translucent nature with folded features (B, C). The sheet is resting on a holey carbon grid which appears visible through the graphene sheet as darker shades. Scale bar is 2 microns, 500 nm, and 100 nm in A, B, and C respectively.
Figure S2.4  C1s and O1s X-ray photoelectron spectra of graphenes C (A, C), M (B, E), and A (C, F). Model fits are listed in Table S1.

The model fits for the C1s and O1s spectra appear in Table S1. Spectra were modeled in CasaXPS software with Gaussian-Lorentzian curves with a Shirley background correction. Model peak locations closely resemble those reported for graphene or graphene oxide in the literature [6-9].
Figure S2.5 Alternative kinetic modeling for data in Figure 1. (a) Pseudo-first-order kinetics of carbamazpine sorption on graphene C (red diamonds), M (green circles), A (blue triangles). (b) Pseudo-first-order kinetics of carbamazpine sorption on activated carbon (black squares) and carbon nanotubes (pink inverted triangles). The equation for the rate law is \( dq_t / dt = k_1 (q_e - q_t) \). If the pseudo-first order rate law applies to the measured data, a linear relationship between \( \log(q_e - q_t) \) and \( t \) should be apparent. \( R^2 \) values for correlations in (a) and (b) were all less than 0.7. (c) Intraparticle diffusion model fitting of only the first 20 minutes of carbamazpine sorption on
activated carbon (solid line) and for the entire 24 hours (dashed line). A linear relationship between \( q_t \) and \( t^{0.5} \) is expected if the intraparticle diffusion model applies.

**Figure S2.6** Alternative isotherm models for data in Figure 2. (a) Langmuir model simulations for sorption isotherms of carbamazepine on graphene C (red diamonds), M (green circles), A (blue triangles), MWCNT-COOH (pink inverted triangles), and GAC (black squares). The equation for the model is \( q = Q C_w / (K + C_w) \), where \( Q \) is the sorption capacity and \( K \) is the Langmuir affinity constant. \( R^2 \) values are as follows: C 0.42, M 0.98, A 0.78, MWCNT-COOH 0.92, GAC 0.91. (b) Polanyi-Mane model simulations for sorption isotherms of carbamazepine on graphene C (red diamonds), M (green circles), A (blue triangles), MWCNT-COOH (pink inverted triangles), and GAC (black squares). The equation for the model is \( q = Q^0 \exp(a [RT \ln(S/C_w)])^b \), where \( Q^0 \) is the sorption capacity, \( R \) is the universal gas constant (8.314 x10\(^{-3}\) kJ/mol), \( T \) is temperature (298 K), \( S \) is carbamazepine solubility (170 mg/l), and \( a \) and \( b \) are
fitting constants. $R^2$ values are as follows: C 0.96, M 0.94, A 0.97, MWCNT-COOH 0.96, GAC 0.95.

**Figure S2.7** Effect of pH on the positive charged dye (crystal violet, CV) (pKa = 0.8) and the negative charged dye (mordant blue 3, MB3) (pKa2 = 2.32, pKa3 = 5.45, pKa4 = 12.1). Experimental conditions: 0.5 g l$^{-1}$ graphene C, initial dyes concentration of 130 mg l$^{-1}$ CV and 140 mg l$^{-1}$ MB3 within a buffer solution of 1 mM NaHCO$_3$ and 20 mM NaCl. Dye compounds were analyzed with a UV-Vis spectrophotometer (Shimadzu UV mini-1240) at wavelength of 590 nm for crystal violet and 440 nm for mordant blue 3 and calibrated to measurements of standard solutions of known concentrations.

The relationship between sorption extent and sorbate-sorbent charges was also studied with two model dye compounds. Crystal violet, with three benzene rings joined by a central carbon atom and possessing two electron-donating amines and one electron-withdrawing cationic amine, was chosen because it has a constant positive charge over the entire pH range, and its increased sorption at higher pH is therefore likely due solely to enhanced attractive forces to the increasingly negative graphene surfaces. Mordant blue 3, in contrast, sorbs to a three-fold less extent as a second carboxylic acid group deprotonates and yields a -3 charge at higher pH. Similar patterns of Mordant blue 3 removal by sorption with activated carbon and MWCNT over varied pH values has been reported [10].

Images were taken from http://www.chemspider.com
Literature Cited in Appendix A

APPENDIX B: SUPPLEMENTARY DATA OF CHAPTER 3

Factors influencing natural organic matter sorption onto commercial graphene oxides

This appendix contains supplementary data in the form of 3 tables and 4 figures. The tables include physical data for the sorbents used, x-ray photoelectron spectroscopy (XPS) model parameters for sorbents analyzed, and chemical information reported by the IHSS. The figures include XPS spectra, additional kinetic modeling for NOM sorption to sorbents, additional SUVA$_{254}$ measurements, and FTIR spectra.
Table S3.1 Specific surface areas, size dimensions, and X-ray photoelectron spectroscopy elemental compositions of sorbents. Data for graphenes C and M are taken from Cai and Larese-Casanova (2014). [1] XPS data were obtain in survey scans.

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<th>Name</th>
<th>SSA (reported) m²/g</th>
<th>SSA (BET) m²/g</th>
<th>Particle size (reported)</th>
<th>XPS Percent relative area</th>
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<td>1181</td>
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Table S3.2 Model fits for X-ray photoelectron spectra of graphene, CNT, and GAC powders in Fig. S1. Data for graphenes C and M can be found in Cai and Larese-Casanova (2014).

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<th>FWHM</th>
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**Table S3.3** Distribution of carbon-bearing functional groups within the NOM powders investigated in this study. Data are excerpted from International Humic Substances Society (IHSS) webpage (http://www.humicsubstances.org/thornnmr.html). Values are percentages of each functional group as determined by nuclear magnetic resonance spectroscopy.

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Figure S3.1 C1s and O1s X-ray photoelectron spectra of graphenes A-heated (A, F), C500 (B, G), C300 (C, H), pristine CNT (D, I) and activated carbon (E, J). Model fits are listed in Table S2. XPS spectra for graphenes C and M can be found in Cai and Lares-Casanova (2014).
Figure S3.2 Alternative kinetic modeling for data in Fig. 1 for SRNOM sorption (a) Pseudo-first-order kinetics of SRNOM sorption on different graphene sorbents (C 0.25 g l⁻¹, red open diamonds; M 0.25 g l⁻¹, green open circles; A-heated 0.25 g l⁻¹, blue filled triangles), MWCNTs (0.25 g l⁻¹, pink inverted triangles), and GAC (0.25 g l⁻¹, black open squares). The equation for the rate law is \( \frac{dq}{dt} = k_1 (q_e - q_t) \). If the pseudo-first order rate law applies to the measured data, a linear relationship between \( \log(q_e - q_t) \) and \( t \) should be apparent. \( R^2 \) values for correlations in (a) were all less than 0.8 except for GAC which was 0.99. (b) Intraparticle diffusion model fitting of SRNOM sorption on GAC. A linear relationship between \( q_t \) and \( t^{0.5} \) is expected if the intraparticle diffusion model applies. (c) This plot is sorption extent \( q_t \) plotted over time for
GAC which shows a somewhat linear uptake of SRNOM over the course of 24 hours, without any indication of reaching sorption equilibrium by that time.

Figure S3.3 SUVA at 254 nm for sorption of SRNOM by graphene C (red open diamonds), C500 (red dotted circles), C300 (red triangles), M (green open circles), A-heated (blue filled triangles), pristine MWCNTs (pink inverted diamonds) and GAC (black open squares) in isotherm study.
Figure S3.4 ATR-FTIR spectra of three graphene powders before and after sorption with SRNOM, and of dried Suwanee River NOM. Solid lines are spectra of dried graphene powders (A-heated, C, and M), and dashed lines are spectra of graphene powders after SRNOM has been sorbed at pH 3 followed by freeze drying. The graphene powders possess no recognizable functional groups and appears similar to spectra of clean graphene free of functional groups [2]. Spectra of SRNOM-sorbed graphene closely resemble those of bare graphene powders. The amount of sorbed SRNOM on these graphenes (10-30 mg TOC/g graphene) appears to be too low for SRNOM functional groups to be observed. Experimental conditions: initial SRNOM UV absorbance 0.8, TOC concentration ~40 mg l⁻¹, pH 3.0, 20 mM NaCl, 1 mM NaHCO₃, reaction time 24 hours. Graphene with sorbed SRNOM were freeze-dried to remove water molecules prior to analysis. The spectrum of SRNOM possesses peaks resembling those reported for Suwanee River humic acid and fulvic acid (International Humic Substances Society (IHSS) webpage http://www.humicsubstances.org/thornnmr.html) and previously identified by others. [3] Main peaks resemble the following groups: 1074 C-O stretching, 14000 symmetric stretch of carboxylic groups, 1620 carboxylic asymmetric stretch or aromatic C=C stretch, 1720 C=O stretch in carboxylic groups, 2940 C-H stretching in aliphatic compounds, 3400 –O-H stretch.
**Figure S3.5** Kinetic profile of SUVA for SRNOM sorption on different graphene sorbents (C 0.25 g l$^{-1}$, M 0.25 g l$^{-1}$, green open circles; A-heated 0.25 g l$^{-1}$, blue filled triangles), MWCNTs (0.25 g l$^{-1}$, pink open triangles), and GAC (0.25 g l$^{-1}$, black open squares). Experimental conditions: initial SRNOM UV absorbance 0.2, TOC concentration range 6.2~13.3 mg l$^{-1}$, pH 7.2, 20 mM NaCl, 1 mM NaHCO$_3$, reaction time 24 hours.
Literature Cited in Appendix B

