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# Sorption of carbamazepine by commercial graphene oxides: A comparative study with granular activated carbon and multiwalled carbon nanotubes



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## 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 was rapid and reversible with alcohol washing, consistent with  $\pi$ - $\pi$  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 m<sup>2</sup>/g) out-performed GAC and MWCNTs. Increasing pH caused more negative surface charge, a twofold decrease in sorption of anionic ibuprofen, a onefold increase in sorption of cationic atenolol, and no change for neutral carbamazepine, highlighting the role of electrostatic interactions.

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## 1. 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

**Abbreviations:** BET, Brunauer–Emmett–Teller; CNT, carbon nanotube; EDA, electron donor–acceptor; EDC, endocrine disrupting compound; GAC, granular activated carbon; MWCNT, multi-walled carbon nanotubes; MWCNT-COOH, carboxylated functionalized multiwalled carbon nanotubes; XPS, X-ray photoelectron spectroscopy.

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activity because their observed amounts (often 1–1000 ng l<sup>-1</sup>) 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 is 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 ( $\sim 200 \text{ mg l}^{-1}$ ) 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  $2630 \text{ m}^2 \text{ g}^{-1}$  [34], but in practice often  $<1000 \text{ m}^2 \text{ g}^{-1}$ ) compared to CNT may promote graphene-based materials as a preferred carbonaceous sorbent for interfacial organic contaminant reactions.

## 2. Materials and methods

### 2.1. 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, Angstrom 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, Duchar) was briefly washed with deionized water to remove soluble matter and dried at  $100^\circ\text{C}$ .

Specific surface area (SSA) was measured by 5-point Brunauer–Emmett–Teller (BET) analysis following degassing at  $80^\circ\text{C}$  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%  $\text{N}_2$ , 2%  $\text{H}_2$ ). 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.

### 2.2. 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  $\text{NaHCO}_3$  in deionized water ( $>18 \text{ M}\Omega\text{-cm}$ ) 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 (Fig. S1 in the Supplementary Materials). EDC stock solutions ( $4000 \text{ mg l}^{-1}$ ) were

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