



# Application of positively-charged ethylenediamine-functionalized graphene for the sorption of anionic organic contaminants from water



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## ABSTRACT

Graphene materials represent a new carbonaceous sorbent for the removal of organic micropollutants from water, and most applications of graphene utilize an oxidized, negatively-charged surface to improve dispersibility. However, classes of anionic micropollutants may undergo less sorption than cationic or neutral compounds on graphene oxide due to electrostatic repulsion forces. This work seeks to improve the sorptive capability of graphene for anionic micropollutants through amending surfaces with positive charges. Graphene oxide was functionalized with ethylenediamine (ED-G) through an acyl chlorination and amidation process that allows a net positive surface charge at pH < 8.1. ED-G held greater sorption capacity for anionic ibuprofen compared to cationic atenolol and neutral carbamazepine for nearly all water conditions within batch reactors. Ibuprofen sorption greatly increased, and atenolol sorption decreased, at more acidic solution pH. Competitive sorption experiments showed that ibuprofen is consistently preferred on ED-G over atenolol over a wide range of concentrations, and the presence of other anionic compounds can suppress the sorption of ibuprofen. These trends in sorption extent, sorbate charge, and sorbent charge indicate electrostatic interactions largely govern the binding of sorbate molecules. Consequently, a positively-charged graphene material could enhance the removal of anionic micropollutants within water treatment systems compared to graphene oxide.

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## 1. Introduction

Graphene powders are part of the growing list of carbon nanomaterials that are being considered as a new sorbent in water treatment technologies due to their remarkable chemical, mechanical, and electronic properties that allow a variety of interfacial reactions beneficial to water purification [1–3]. Idealized graphene is a two-dimensional sheet of pure carbon in benzene-ring structures of hybridized  $\text{Csp}^2$  electronic configuration, but in practice graphene particles usually contain numerous oxygen impurities imparted by synthesis and becomes graphene oxide with one to multiple layers of individual graphene sheets. A characteristic of graphene beneficial for water purification is graphene's ability to effectively adsorb contaminants of various

organic structures and properties due to abundance of aromatic  $\text{Csp}^2$  and hydrophobic surface regions available for non-covalent interactions with organic sorbates. Rapid and extensive sorption onto graphene has been demonstrated for aromatic and phenolic compounds [4–11], antibiotics and pharmaceuticals [12–16], halogenated aliphatics [17], and dye compounds [4,18–20]. Capitalizing on their broad affinity for diverse organic compounds, graphene and graphene oxides have been incorporated into membranes and composite materials in order to improve adsorption capacity or antifouling ability during water treatment [21–26].

Graphene's structural and chemical properties can provide advantages over other carbon nanomaterials for the sorption of organic water contaminants. For one, graphene sheets are flat, open faces that offer little diffusion resistance suited for fast adsorption kinetics, in contrast to carbon nanotubes and activated carbon which might hold diffusion restrictions in pores on surfaces or at tube ends. Graphene particles may be formulated into nanosheets with very high specific surface areas (commercially,  $<1000 \text{ m}^2 \text{ g}^{-1}$  [14]) that provide an abundance of exposed surface sites. The occurrence of polar or charged surface oxides such as hydroxyl or carboxyl groups created during synthesis can also provide improved wettability and colloidal stability, and

**Abbreviations:** ED-G, ethylenediamine functionalized graphene; BET, Brunauer-Emmett-Teller; SSA, specific surface area; XPS, X-ray photoelectron spectroscopy; FWHM, full width at half maximum; IBU, ibuprofen; AT, Atenolol; CBZ, carbamazepine; GO, graphene oxide; NOM, natural organic matter.

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consequently surface site exposure, compared to carbon materials with pristine  $\text{Csp}^2$  configuration [27].

Functionalizing graphene surfaces can improve sorption of water contaminants compared to pristine graphene. Surface oxygen impurities can provide additional sorption sites for organic contaminants beyond the  $\pi-\pi$  binding interactions at  $\text{Csp}^2$  surfaces. Carboxylic acid groups can deprotonate in aqueous suspensions at circumneutral pH and provide negative surface charges which enhance the removal of cationic organic contaminants through electrostatic interactions [14,16,18–20]. Carboxyl and hydroxyl groups on graphene oxide can also provide sites for H-bonding for phenolic compounds [6] or H- $\pi$  bonds for polycyclic aromatic hydrocarbons [8]. Sorption specificity can be improved by functionalizing graphene with reactive moieties specific to target sorbates. Grafting thiol groups allowed for recovery of Hg(II) ions from water [28], and functionalizing graphene with chitosan provided cationic amine sites for arsenic sorption [29]. Functionalization has also been employed for improving dispersibility in aqueous suspension by increasing abundance of negative surface charges, such as by attaching sulfonate groups [5] or tannic acid [20], which prevents re-aggregation by adhesion at nonpolar regions. However, the anionic surfaces of graphene oxide tend to diminish the sorption of anionic organic contaminants due to electrostatic repulsion [7,9,12,14–16]. Graphene oxide may generally favor sorption of neutral and cationic contaminants while neglecting anionic ones. Therefore, in order to improve removal efficacy for a wide range of anionic organic contaminants, it may be beneficial to introduce positively-charged functional groups onto graphene via chemical functionalization to exploit electrostatic attraction of compounds within this class.

Organic contaminants with anionic character belong to a small but important subset of contaminants of emerging concern (CEC) identified in drinking water resources, such as the pharmaceuticals ibuprofen, gemfibrozil, diclofenac, and fenoprofen [30–32]. Pharmaceuticals, personal care products, hormonal compounds, and many other synthetic organic contaminant classes are an environmental concern due to their documented adverse health effects to aquatic organisms, especially to their endocrine and neurological systems [33–35]. Despite occurring at very low concentrations (typically  $1\text{--}1000\text{ ng l}^{-1}$ ) [36], CECs are difficult to treat, often having well less than complete removal efficiencies within conventional water and wastewater treatment operations [30,37]. These CECs typically contain aromatic character and functional moieties that make them susceptible to interactions with carbonaceous surfaces and applicable to removal by sorption processes. Consequently there has been considerable attention to developing sorption technologies that employ carbonaceous nanomaterials such as carbon nanotubes and graphene for targeted removal of CECs [3,38,39].

The goal of the present study is to promote the sorption of anionic CECs to graphene surfaces by enhancing the electrostatic attraction mechanism through surface functionalization. We synthesized ethylenediamine-functionalized graphene powders (ED-G) through the acyl-chlorination and amidation processes to form a graphene with net positive charge at circumneutral pH, and tested the material in laboratory-prepared water samples for the influence of electrostatic interactions on the removal efficacy of anionic and cationic CECs. Ethylenediamine ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ) was chosen because it is the shortest diamine molecule with  $\text{pK}_{\text{a}1}=8.0$  and therefore positively charged at circumneutral pH. One terminal amine group is fixed to the graphene surface through amide bond formation with a carboxyl group, and the other terminal amine provides positive surface charge (as  $-\text{NH}_3^+$ ) when  $\text{pH} < \text{pK}_{\text{a}1}$ . Methylenediamine has one less C in its C chain but has  $\text{pK}_{\text{a}1}=6.2$  and would mostly be neutral, and butylenediamine with  $\text{pK}_{\text{a}1}=9.9$  would provide

positive charge over a wider pH range but may situate it too far from the graphene surface to allow sorbates to interact with the amine group and the surface simultaneously. Moreover, ethylenediamine has already demonstrated positive surface charge when functionalized to graphene [40–43]. These reports illustrate ethylenediamine-graphene usefulness to construct thin films, capsules, and hydrogels, often by binding with anionic regions of graphene or other compounds. Ethylenediamine has also been functionalized to graphene oxide [44], carbon nanotubes [45], and mesoporous carbon [46] for enhanced removal of metal cations or tetrabromobisphenol A from water. Similarly, carbon nanotubes functionalized with ethylenediamine have been shown to retain arsenate molecules from water by binding with  $-\text{NH}_3^+$  groups [47] and to sorb  $\text{Hg}^{2+}$  cations through bidentate coordination bonds with the amine and amide groups [48]. However, ethylenediamine-functionalized graphene for use as a sorbent for anionic CECs in water treatment applications still requires evaluation.

A positively-charged, amine-functionalized graphene surface should significantly contribute to the non-covalent bonding mechanisms of anionic CECs and lead to their more selective removal from water. To explore this hypothesis, ethylenediamine-functionalized graphene was tested for sorption extent for three CECs of different charges at circumneutral pH: anionic ibuprofen, cationic atenolol, and neutral carbamazepine. In addition to their varying molecular charges, these compounds were chosen because of their past detection in natural waters [31], their frequent study for removal by sorption-based treatment technologies [13,14,49–53], and their demonstrated toxicity to aquatic and marine organisms [54–56]. A graphene material with positive amine groups, negative O groups, and an abundance of aromatic character may be suitable to sorb a wide variety of organic contaminant classes through multiple and concurrent reaction mechanisms.

## 2. Experimental methods

### 2.1. Material synthesis

Ethylenediamine-functionalized graphene nanosheets were prepared by acyl-chlorination and amidation reactions performed in a manner similar to other reports [57,58]. Briefly, graphite was first oxidized to incorporate carboxylic groups, and reaction with thionyl chloride ( $\text{SOCl}_2$ ) replaced  $-\text{OH}$  groups with  $-\text{Cl}$ , which were then replaced by ethylenediamine (Fig. 1). Graphite powder was oxidized by processing 6 g of graphite (Fisher) using a modified Hummers method [59], washed repeatedly with deionized water, and then dried in a fume hood without any exfoliation. Dried chunks of the formed graphite oxide were ground by marble mortar and pestle, and sieved ( $150\text{ }\mu\text{m}$ ) to fine powder. 40 ml of thionyl chloride ( $\text{SOCl}_2$ , 99+%, Alfa Aesar) was added to dry graphite oxide powder in a 100 ml pyrex glass bottle with a screw cap and heated at  $70\text{--}80^\circ\text{C}$  under magnetic stirring for 24 h in order to complete the Cl replacement reaction. Most of the excess  $\text{SOCl}_2$  was then removed by evaporation under heat until dryness, and the remaining  $\text{SOCl}_2$  was washed away with methylene chloride ( $>99\%$ , anhydrous, Acros Organics) by vacuum filtration using  $0.22\text{ }\mu\text{m}$  PVDF membrane filter papers in a Buchner funnel. After drying by low heat, acyl-chlorinated graphite powder was suspended in 40 ml ethylenediamine ( $>99\%$ , Acros Organics) in a glass bottle while stirring at  $\sim 100^\circ\text{C}$  for 48 h. The ethylenediamine functionalized graphite was then washed with methanol and deionized water by vacuum filtration to remove excess reactant. The solids were then suspended in 300 ml deionized water and exfoliated by sonication with an ultrasonic cleaner (FS-30, Fisher Scientific) for 3 h and ultrasonic probe for 15 min. Dry

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