



Factors influencing natural organic matter sorption onto commercial graphene oxides



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HIGHLIGHTS

- Graphene powders rapidly sorb natural organic matter from water.
- Sorption capacity is influenced by graphene surface area and surface chemistry.
- Graphene prefers aromatic, high molecular weight fractions of organic matter.
- High surface area graphene may out-perform activated carbon or carbon nanotubes.

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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.

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1. 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

Abbreviations: BET, Brunauer–Emmett–Teller; ESHA, Elliott Soil humic acid standard; FA, fulvic acid; GAC, granular activated carbon; HA, humic acid; IHSS, international humic substances society; LeoHA, Leonardite humic acid standard; MWCNT, multiwalled carbon nanotube; NordFA, Nordic lake fulvic acid reference; NOM, natural organic matter; NordNOM, Nordic lake natural organic matter; PPHA, Pahokee Peat humic acid standard; RO, reverse osmosis; SRFA, Suwannee River fulvic acid standard II; SRHA, Suwannee River humic acid standard II; SRNOM, Suwannee River natural organic matter; SUVA₂₅₄, specific UV absorbance at 254 nm; XPS, X-ray photoelectron spectroscopy.

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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 $KMnO_4$ 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 π – π 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 $\sim 2\%$ 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 π – π 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 influenced 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.

2. Materials and methods

2.1. 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, Angstrom Materials, Inc.). After showing no NOM sorption in preliminary experiments, graphene A was thermally

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