



Interaction mechanisms of antibiotic sulfamethoxazole with various graphene-based materials and multiwall carbon nanotubes and the effect of humic acid in water



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ABSTRACT

We studied the interaction mechanisms between carbonaceous nanomaterials (CNMs) and sulfamethoxazole (SMX) to elucidate their adsorption behaviors. Three graphene-based materials, reduced graphene oxide (rGO), graphene oxide (GO), and graphene nanoplatelet pastes (GNP), and five multiwalled carbon nanotubes (MWCNTs), MWCNT10, MWCNT15, MWCNT15-OH, MWCNT15-COOH, and N-doped MWCNTs, were used as sorbents. Oxygen-containing functional groups and graphene wrinkling suppressed SMX adsorption on GO and GNPs due to fewer Csp² ring sites for π - π stacking and fewer accessible flat surface adsorption sites, respectively. Ring current-induced ¹H NMR upfield chemical shifts increased as the π -donor concentration increased, as well as π -donor strength of polycyclic aromatic hydrocarbons (PAHs) (pyrene > phenanthrene > naphthalene) as model graphene compounds, suggesting that π - π interaction strength of SMX with PAHs associated with π -donor strength. Moreover, ¹H NMR results further verified that carboxylic and hydroxyl groups in PAHs (9-phenanthrol and 3-phenanthrenecarboxylic acid) weakened the complexation between SMX and the graphitic surface. Additionally, the morphologies of rGO and MWCNT10 were observed using AFM, and transformed from being linear to scattered as the loading dose of the humic acid increased. Our results are useful to understand the distinct interaction mechanisms and subsequent adsorption behaviors resulting from various carbon nanomaterials with SMX in water.

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1. Introduction

The rapid advancement of nanoscience and nanotechnology, as well as the application extension of carbonaceous nanomaterials

(CNMs), particularly graphene, have attracted increasing research attention of application in various fields [1,2]. The production of carbon nanotubes (CNTs) reached 4600 t per annum (tpa) in 2011, and the estimated production of graphene will reach 1200 tpa by 2019 [3]. Among the different types of CNMs, graphene and CNTs are developed most widely because of their superior physicochemical properties [4]. The presence of sp² hybridized nanocarbons in these materials contribute to their outstanding features, which trigger the interest of both the scientific and technological communities [5]. Given their hydrophobicity and large surface area, graphene and CNTs are promising sorbents for removing various organic chemicals, such as aromatic amines, PAHs, and pesticides

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[6–10].

In contrast to CNTs, which were first reported in 1991 [11], graphene was only discovered in 2009 [12]. Hence, intensive studies are still needed to understand the interaction mechanisms between graphene and organic compounds. Although CNTs and graphene are both carbon-based nanomaterials, they are highly different nanomaterial entities, particularly in terms of shape (tubular vs. planar) and dimensions (1D vs. 2D). Their chemical properties (aqueous dispersibility and aggregation; e.g., stacking for graphene and bundling and tangling for CNTs) differ as well [4]. In addition, graphene oxides (GO) and reduced graphene oxides (rGO), which are two common members of the graphene family [13], typically possess a distinct range of functional groups, such as epoxy (C–O–C), hydroxyl (OH), and carboxylic (COOH) groups, on their basal planes and edges [9]. These oxygen-containing functional groups also exist in CNTs [14]. These self-physicochemical characteristics can affect the adsorption behavior of CNMs for organic chemicals, which in turn may alter their transport and fate in the environment. However, limited systematic reports have been conducted on adsorption differences induced by the dissimilar characteristics of graphene and CNTs. CNMs can be released into the environment from their products [15], and they have widely been detected from surface water, wastewater, sediments, and soil [16]. Once entering into the environment, which based on their current application is yet highly uncertain, CNMs are most likely to undergo various processes of surface modifications resulting from UV irradiation, microbial activity or interaction with natural organic matter. Moreover, industrial CNMs which widely applied in membranes and filtration system for water purification, thermal management, photodetectors, etc., are more typical than small amount of synthesized CNMs in research laboratories. Therefore, a systematic investigation must be conducted to reveal the differences in the adsorption behaviors of organic chemicals to various industrial CNMs.

Sulfamethoxazole (SMX), which is a commonly administered sulfonamide antibiotics, is widely used for human medicine and livestock production [17]. Often poorly metabolized and absorbed by humans and animals, SMX tends to enter into the aquatic environment [18–20]. Consequently, the environmental behavior of SMX has become a worldwide concern because of the potential proliferation of resistant pathogens [21]. Few works have been conducted to investigate the adsorption behaviors of SMX as an environmental contaminant to biochars [22], silica zeolites [23], carbon nanotubes [24,25], sediment [26], and graphene oxide and graphite [27]. In these studies, π - π electron donor–acceptor (EDA) interactions were identified as the main mechanism controlling adsorption. However, these reports merely mentioned π - π EDA interactions lack of spectroscopic evidence for π - π interactions. The present work will address this problem with direct measurements by proton nuclear magnetic resonance (^1H NMR) [28]. In addition, oxygen on the CNMs could localize the π -electrons. Hence, whether functional groups (OH or COOH) on the surface of CNMs affect π - π interactions, and to what extent, still remain unclear. Therefore, π - π EDA interaction, and the effect of OH or COOH on this interaction, must be elucidated to predict the potential environmental behavior of organic chemicals and various CNMs.

Dissolved organic matter (DOM) is an important aquatic component that significantly influences the adsorption of aromatic compounds [29], perfluoroalkyl acids [30], and carbamazepine [31] by acting as a competitor or modifying the surface properties of sorbents. Wang et al. reported that the adsorption of DOM masked numerous adsorption sites on MWCNTs, thereby reducing their adsorption for phenanthrene and 1-naphthol [29]. Similarly, SMX adsorption to CNTs was significantly reduced by the aggregation induced by DOM, but was increased as they were suspended as a

result of stable dispersion [25]. These varying results indicate that tripartite interaction systems are complex: that organic compounds bind with DOM adsorbed on adsorbates; and that the morphology of CNMs alter with different coating degrees of DOM, which associate with the degree of suspended CNMs due to the varying strength of electric repulsion from polar functional groups on DOM. The literature, however, does not provide ample information as regards morphology change of CNMs with different coating degrees of DOM. Moreover, few studies have reported on the effect of DOM on the adsorption of antibiotics on graphenes.

The objectives of this study are as follows: (1) to investigate the adsorption distinction of SMX on GO, rGO, GNPs, and various MWCNTs with the use of batch techniques; (2) to demonstrate the interaction mechanisms by analyzing the characteristics of CNMs with the use of SEM/EDX, XPS, FTIR, ^1H NMR methods; and (3) to evaluate the effect of DOM on the adsorption of SMX to CNMs with the aid of AFM imaging.

2. Experimental section

2.1. Chemicals and sorbents

SMX, naphthalene (NAPH), phenanthrene (PHEN), pyrene (PYR), 9-phenanthrol, 3-phenanthrenecarboxylic acid, and HA was purchased from Sigma-Aldrich (St. Louis, MO, USA). Eight types of CNMs, namely, three graphene-based materials and five multi-walled CNTs (MWCNTs), which have distinct physical structures and chemical compositions, were used as sorbents. The three graphene-based materials were reduced graphene oxide (rGO), graphene oxide (GO), and graphene nanoplatelet pastes (GNP). The MWCNTs included MWCNT10 with an outer diameter of <10 nm, three multiwall CNT with an outer diameter in the range of 8–15 nm (MWCNT15, MWCNT15-OH, MWCNT15-COOH), and one N-doped MWCNTs with an outer diameter in the range of 30–50 nm. MWCNT10 was purchased from Shenzhen Nanotech Port Co., China. The other CNMs were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences. The physicochemical properties of the CNMs and SMX are summarized in Table S-1 and S-2 in the Supplementary Information (SI).

2.2. Characterization of carbonaceous nanomaterials

The surface morphology of CNMs was determined by using a Nova NanoSEM 450 (FEI Ltd., Holland), and the content of C and O in CNMs were semi-quantified with an energy dispersive X-ray (EDX) spectrum. The abundance of surface functional groups on CNMs was obtained by using an AXIS Ultra DLD X-Ray photoelectron spectrometer (Kratos Analytical Ltd., UK). The surface area and porosity of CNMs were measured by using adsorption-desorption isotherms of N_2 at 77 K with a V-Sorb 2800P surface area and pore distribution analyzer (Gold APP Instruments Co., China). The surface characteristics of rGO with HA and SMX were investigated with a SEM/EDX after a part of the suspension containing rGO was air-dried. Four samples from the interaction systems with rGO and MWCNT10 containing 0.86 and 8.6 mg C/L HA were scanned with an atomic force microscope (AFM) (5500, Agilent, USA). rGO and MWCNT10 without HA and SMX in suspension were set as control samples.

2.3. Adsorption experiments

The batch equilibrium adsorption experiments of SMX to CNMs were conducted in aqueous solution, and performed in 15 mL glass vials with Teflon-lined screw caps at 25 °C. SMX was dissolved in methanol to prepare the stock solution. The methanol content in

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