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Electronic-property dependent interactions between tetracycline and graphene nanomaterials in aqueous solution

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ABSTRACT

Understanding the interactions between graphene nanomaterials (GNMs) and antibiotics in aqueous solution is critical to both the engineering applications of GNMs and the assessment of their potential impact on the fate and transport of antibiotics in the aquatic environment. In this study, adsorption of one common antibiotic, tetracycline, by graphene oxide (GO) and reduced graphene oxide (RGO) was examined with multi-walled carbon nanotubes (MWCNTs) and graphite as comparison. The results showed that the tetracycline adsorption capacity by the four selected carbonaceous materials on the unit mass basis followed an order of GO > RGO > MWCNTs > graphite. Upon normalization by surface area, graphite, RGO and MWCNTs had almost the same high tetracycline adsorption affinity while GO exhibited the lowest. We proposed π-electron-property dependent interaction mechanisms to explain the observed different adsorption behaviors. Density functional theory (DFT) calculations suggested that the oxygen-containing functional groups on GO surface reduced its π-electron-donating ability, and thus decreased the π-based interactions between tetracycline and GO surface. Comparison of adsorption efficiency at different pH indicated that electrostatic interaction also played an important role in tetracycline-GO interactions. Site energy analysis confirmed a highly heterogeneous distribution of the binding sites and strong tetracycline binding affinity of GO surface.

Introduction

Tetracycline, being a broad-spectrum antibiotic, is heavily used in livestock production for disease treatment and growth promotion. In the farming industry, tetracycline is poorly metabolized and absorbed by the treated animals, thus large fractions are excreted *via* urine and feces (Sarmah et al., 2006; Tolls, 2001). Conventional water and wastewater treatment technologies are not effective toward removal of a number of antibiotics; therefore, tetracycline has been frequently detected in soils, surface waters and even drinking waters (Karthikeyan and Meyer, 2006; Ling et al., 2013; Luo et al., 2011;

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Watkinson et al., 2009; Wu et al., 2013). Recently, the occurrence of tetracycline in aquatic environment has attracted great attention due to its variety of potential toxicity to aquatic organisms and it can also promote the development of antibiotic resistant genes among bacterial populations (Kim et al., 2014; Zhang and Zhang, 2011).

Graphene nanomaterials (GNMs), two-dimensional sheets composed of a single layer of sp^2 carbon atoms, have attracted increasing research interest due to their outstanding physical and chemical properties (Novoselov et al., 2004). Graphene oxide (GO) and reduced graphene oxide (RGO) are the two most important types of GNMs, which are different in structure, morphology and chemical composition. Due to rapid growth in production and industrial applications of GNMs (Obraztsov, 2009; Wassei and Kaner, 2013), significant concerns have been raised because of their the potential environmental impact (Fan et al., 2015; Lee et al., 2011; Liu et al., 2011, 2015, 2016a, 2016b; Zou et al., 2016). Once released into the aquatic environment, GNMs may play an important role in the fate, bioavailability, exposure, and reactivity of organic contaminants because of the possible strong interaction between them (Liu et al., 2014; Liu et al., 2016a). Therefore, understanding the mechanisms which control the adsorption of organic contaminants to GNMs is essential for both environmental engineering application and potential risk assessment of GNMs.

To date, there are a few studies about the interaction between GNMs and tetracycline. Gao et al. and Ehsan et al. investigated the adsorption properties of tetracycline onto GO and reported that GO is a potential effective adsorbent for tetracycline removal (Gao et al., 2011; Ghadim et al., 2013). Both of the two studies just focused on the basic adsorption performance of tetracycline by GO, but the interaction mechanism was not well understood. As another most important carbonaceous nanomaterial, carbon nanotubes (CNTs) also exhibited high adsorption affinity for tetracycline, which attributed to the strong π-based interactions between π electrons on both CNTs and tetracycline molecules. Similar with CNTs, GNMs were also composed of monolayer of carbon atoms arranged in a honeycomb network. Therefore, whether π-based interactions were the main interaction mechanisms between GNMs and tetracycline needs in-depth investigation. As mentioned before, GO and RGO were different in their surface physical–chemical properties. Especially, GO possesses large amount of oxygen-containing functional groups, which are expected to affect tetracycline adsorption significantly. Above all, in order to better understand the various interaction mechanisms, it is necessary to compare and investigate the tetracycline interaction with GO and RGO.

Therefore, the main objectives of this work were to investigate the interaction between tetracycline and two types of GNMs (GO and RGO). Multi-walled CNTs (MWCNTs) and graphite were used for comparison to better evaluate their adsorption behavior. The electronic potential distribution and molecular orbital information of GO and RGO were calculated by density functional theory (DFT) to explain the π-based interactions. Site energy distribution was also calculated to better understand the mechanisms of interaction by providing information about the inherent energetic changes involved in the interaction process.

1. Materials and methods

1.1. Chemicals and materials

Tetracycline (≥98%) was purchased from Sigma (St. Louis, MO, USA). The physicochemical properties and chemical structure of tetracycline are presented in Appendix A Table S1. Expandable graphite and MWCNTs (outer diameter: 10–30 nm) were purchased from Shenzhen Nanotech Port Co. Ltd. RGO was produced by reducing GO which was prepared by improved Hummers' method. Detailed procedures for preparation of GO and RGO are described in Appendix A. All the other chemicals and reagents used in this study were of analytical grade. Deionized water was used for adsorption experiments.

1.2. Characterization

The microstructure of adsorbents was investigated by a transition electron microscope (TEM, JEM-100CXII). Atomic force microscopy (AFM) was conducted with Bruker Dimension Icon (Veeco Instruments Inc.) in the tapping mode. The scanning area was 5 × 5 μm^2. Surface functional groups were characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, NEXUS 670, Thermo Nicolet Ind.). The spectra were taken in the region between 650 and 4000 cm^{-1}. Elemental composition analysis was carried out using X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). Raman spectra were obtained by a Jobin-Yvon HR800 confocal Raman system with 457.9 nm wavelength incident laser light. Nitrogen adsorption–desorption isotherms were conducted at 77 K with a Quadrasorb SI-MP system (Quantachrome) and all samples were degassed at 373 K for 8 hr in a vacuum before measurements. The Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area (S_{BET}) and the cross sectional area of a nitrogen molecule was assumed to be 0.162 nm^2. The specific surface area of the adsorbents was also calculated by a methylene blue (MB) adsorption method in water, where MB was employed as a molecular probe to measure the adsorption amount (McAllister et al., 2007). The details of the MB adsorption experiment and the calculation process is described in SI. Zeta potentials of the adsorbents (solid: 40 mg/L) at different pH were measured by a Malvern zeta potential analyzer (Zetasizer 2000). Six runs and fifteen cycles were set for each measurement. Each sample was measured at least three times.

1.3. Batch experiments

Batch adsorption experiments were carried out in 40-mL glass vials equipped with Teflon-lined screw caps at 293 ± 1 K. The test tetracycline solution contained 20 mmol/L NaCl to maintain constant ionic strength and pH of the solution was adjusted to neutral by adding 0.1 mol/L HCl and 0.1 mol/L NaOH. The initial concentrations of tetracycline ranged from 0.01 to 0.27 mmol/L. Different amounts of adsorbents were employed (5.0 mg for GO, 10.0 mg for RGO and MWCNTs and 20.0 mg for graphite) to make sure that the removal efficiency was in the range of 20%–80%. Adsorbents and 30 mL of tetracycline solution were added into the vials, and then

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