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Adsorption characteristics of diclofenac and sulfamethoxazole to graphene oxide in aqueous solution

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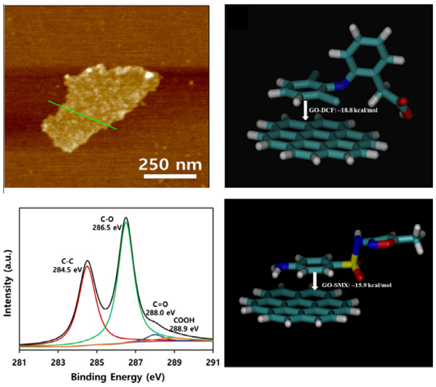
HIGHLIGHTS

- GO adsorptive properties were characterized by AFM, XRD, XPS, ZP, and DLS.
- The sonication of GO significantly improved the removal of target compounds.
- The main binding mechanisms were hydrophobic and π–π EDA interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorptive properties of graphene oxide (GO) were characterized, and the binding energies of diclofenac (DCF) and sulfamethoxazole (SMX) on GO adsorption were predicted using molecular modeling. The adsorption behaviors of DCF and SMX were investigated in terms of GO dosage, contact time, and pH. Additionally, the effects of sonication on GO adsorption were examined. GO adsorption involves "oxygen-containing functional groups" (OCFGs) such as —COOH, which exhibit negative charges over a wide range of pH values (pH 3–11). DCF ($-18.8\ \text{kcal mol}^{-1}$) had a more favorable binding energy on the GO surface than SMX ($-15.9\ \text{kcal mol}^{-1}$). Both DCF and SMX were removed from solution (adsorbed to GO), up to 35% and 12%, respectively, within 6 h, and an increase in GO dosage enhanced the removal of DCF. Electrostatic repulsion occurred between dissociated DCF/SMX and the more negatively charged GO at basic pH (>p*K*a). The sonication of GO significantly improved the removal of DCF (75%) and SMX (30%) due to dispersion of exfoliated GO particles and the reduction of OCFGs on the GO surface. Both DCF and SMX in the adsorption isotherm were explained well by the Freundlich model. The results of this study can be used to maximize the adsorption capacities of micropollutants using GO in water treatment processes.

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1. Introduction

Over recent decades, emerging micropollutants such as pharmaceuticals have become a concern in water and wastewater treatment plants. Although they occur at trace levels (sub $\mu g\ L^{-1}$) in drinking water sources and wastewater effluents, their bioaccumulation in aquatic creatures causes continuous human exposure through the food chain (Sharma et al., 2003; Daneshvar et al., 2010). Among numerous pharmaceuticals commonly detected in drinking water sources and wastewater effluents, diclofenac (DCF) and sulfamethoxazole (SMX) are representative micropollutants that are readily released into the water environment, and are detected frequently in drinking water (Feito et al., 2010; Santos et al., 2010; Yiruhan et al., 2010; Li et al., 2010a; Huerta-Fontela et al., 2011). DCF is a nonsteroidal anti-inflammatory drug used for fever and pain relief, and SMX is an antimicrobial drug, commonly used in humans and animals. Previous studies have reported that DCF and SMX may potentially cause adverse effects such as thyroid tumors and hemodynamic changes with chronic human exposure (Collier, 2007; Schriks et al., 2010). Since 'conventional' water and wastewater treatment plants are not optimized for the removal of such trace compounds, DCF and SMX have been reported in drinking water (Collier, 2007). Thus, it is important to develop effective technologies to remove these compounds from drinking water.

Adsorption is known as an effective treatment technique for the removal of organic micropollutants such as pharmaceuticals and pesticides (Adams et al., 2002; Westerhoff et al., 2005; Snyder et al., 2007). Conventional and emerging adsorbents (e.g., activated carbon and carbon nanotubes, CNTs) have thus been studied widely regarding the removal of micropollutants (Yu et al., 2008; Joseph et al., 2011; Sotelo et al., 2011). However, these adsorbents have unique physical and chemical properties (e.g., hydrophobicity, chemical functional groups, pore size, external surface area, and point of zero charge), which may not be suitable for certain compounds to attach to the surface of the adsorbents. For example, it has been reported that activated carbon can exclude the adsorption of larger molecules (>3000 Da) due to its small pore (<2 nm) (Kilduff et al., 1996). Ji et al. (2013) examined aggregation between CNT particles during adsorption, which can reduce the surface area available to organic pollutants. Thus, the limitations of adsorbents in adsorption must be specifically determined for each compound of interest, and easy modifiable materials are needed to apply adsorption treatments broadly.

Graphene oxide (GO), exfoliated from graphite, has recently been considered an emerging adsorbent, since it has abundant carbonaceous materials and various functional groups such as carboxylic (—COOH), hydroxyl (—OH), and epoxy (—C—O—C—) groups on its surface (Ji et al., 2013; Wang et al., 2014). The electrical and chemical properties of GO have been considered potentially useful in the various applications including sensors, transistors, computer memories, solar energy, and hydrogen storage (Ataca et al., 2008; Elias et al., 2009; Schwierz, 2010; Li et al., 2010b; Liu et al., 2012).

In a previous graphene adsorption study, Mishra and Ramaprabhu (2011) removed trivalent and pentavalent arsenic (65-66%) at an initial concentration of $300\ mg\ L^{-1}$ using functionalized graphene sheets. Wang et al. (2014) suggested an affinity between polycyclic aromatic hydrocarbons and sonicated graphene. Their results indicated indirectly that the modification (e.g., functionalization and sonication) of GO could potentially enhance the removal of various micropollutants. However, the fundamental characteristics of GO and its modification have not yet been determined in terms of adsorption.

The objectives of this study were to determine the adsorptive properties of GO in micropollutant removal and to evaluate the suitability of modified GO with sonication. To that end, we selected DCF and SMX as representative micropollutants and investigated their removal mechanism(s) with GO adsorption. The adsorptive binding energies of the compounds were calculated using molecular modeling to examine the affinity between the compounds and the GO surface. We also assessed the effects of pH and sonication on GO adsorption. To estimate the improvement in GO adsorption with sonication, we determined the adsorption isotherm of both pristine GO and sonicated GO using the Freundlich and Langmuir models.

2. Materials and methods

2.1. Adsorbents and adsorbates

Commercially available single-layer GO (purity > 99%) was purchased from Cheap Tubes, Inc. (Brattleboro, VT, USA). As described by the manufacturer, the *X* and *Y* dimensions for standard GO particles are in the range of 300–800 nm with a thickness of 0.7–1.2 nm. Pristine GO was produced by oxidation from graphite using a modified Hummer method (Chen et al., 2009). To modify the adsorbent, sonication for GO was carried out at 12 and 24 W for 10 min with a Misonix S4000 sonicator (Farmingdale, NY, USA). All GO stock solutions were prepared at $1\ g\ L^{-1}$ of deionized (DI) water. These solutions were stirred at room temperature for 24 h prior to use, because hydration is needed to activate the surface of GO. DCF (purity > 99%) and SMX (purity > 99%) were obtained from Sigma–Aldrich (St. Louis, MO, USA). As necessary, stock solutions were diluted for the experiments. The physicochemical properties of DCF and SMX are described in Table S1.

2.2. Adsorption experiments

Kinetic batch tests were performed with $100\ mg\ L^{-1}$ of the GO stock solution diluted to 10–100 $mg\ L^{-1}$. The testing jar of GO solution was stirred at 600 rpm during the experiments, and surrounded by aluminum foil to prevent photo-degradation of the target compounds. The initial concentrations of DCF and SMX were maintained at 10 μM by spiking of the GO stock solution, and confirmed by measuring control samples when the test started. Then, aliquots of the tested solution were withdrawn from the testing jar at time points of 0, 0.5, 1, 2, 4, 6, and 24 h. The tested samples were filtered through a 0.22-μm Durapore membrane filter (Millipore, Cork, Ireland), and analyzed by high-performance liquid chromatography (HPLC). The detailed HPLC measurement conditions are described in more detail (see Section 2.3). Adsorption on the sonicated GO was completed by the same process. The pH conditions in the solutions were adjusted with 1 N NaOH or HCl, and monitored with a pH meter during the experiments.

In this study, the adsorption isotherms for DCF and SMX were completed individually in amber vials, and the total volumes of each test solutions were 40 mL including $100\ mg\ L^{-1}$ of GO. There was no head space in the test vials. They were adjusted to neutral pH (pH 7), and the vials were stirred at 60 rpm for 2 d. The initial concentrations of DCF and SMX ranged from 10 to 300 μM. During the test, room temperature was maintained at 20 °C. The isotherm results for the compounds were fitted to the Freundlich (Eq. (1)), and Langmuir models (Eq. (2)). The relevant equations of the adsorption models are as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{1}$$

$$q_e = (q_{max} K_L C_e)/(1 + K_L C_e) \tag{2}$$

where q_e is the equilibrium adsorption capacity ($mg\ g^{-1}$), K_F is the Freundlich adsorption coefficient ($(mg\ g^{-1})\ (mg\ L^{-1})^{-(1/n)}$), C_e is