



# Comparing the effects of different oxygen-containing functional groups on sulfonamides adsorption by carbon nanotubes: Experiments and theoretical calculation



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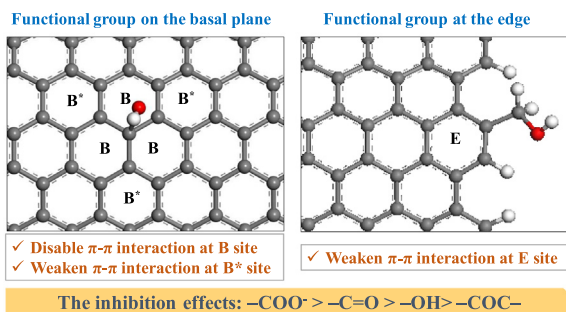
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## HIGHLIGHTS

- Effect of oxygen-containing functional groups on SAs adsorption by CNTs.
- Functional groups inhibited SAs adsorption in the order of  $-\text{COO}^- > -\text{C}=\text{O} > -\text{OH} > -\text{COC}-$ .
- Functional groups disabled or/and weakened the  $\pi$ - $\pi$  interactions.
- The extension degree of V-shaped SAs resulted in different adsorption by CNTs.
- The type of heteroatoms in heterocyclic groups of SAs affected adsorption.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Combined with batch adsorption experiments of sulfadimethoxine (SDM), sulfamethizole (SMZ), sulfamethazine (SMT), sulfamethoxazole (SMX) by carbon nanotubes (CNTs) with different oxidation degree, this study investigated the effect of different oxygen-containing functional groups ( $-\text{COC}-$ ,  $-\text{OH}$ ,  $-\text{C}=\text{O}$ ,  $-\text{COO}^-$ ) on sulfonamides (SAs) adsorption by CNTs using density functional theory (DFT) calculation. The experimental results showed that the SAs adsorption decreased with increasing oxidation degree of CNTs, and followed the order of  $\text{SDM} > \text{SMZ} > \text{SMT} > \text{SMX}$ . The  $\pi$ - $\pi$  interactions of the benzene and heterocyclic rings in SAs with the benzene-type rings of CNTs were the predominant adsorption mechanisms. DFT calculation showed that the oxygen-containing functional groups inhibited SAs adsorption, and the inhibitory effects declined in the order of  $-\text{COO}^- > -\text{C}=\text{O} > -\text{OH} > -\text{COC}-$ . The  $-\text{COO}^-$  and  $-\text{C}=\text{O}$  groups could damage the ring structure of CNTs while  $-\text{OH}$  and  $-\text{COC}-$  only damaged the conjugated structure of benzene-type rings of CNTs if they were located on the basal plane of CNTs. This disabled the  $\pi$ - $\pi$  interactions of the damaged benzene-type ring and weakened the  $\pi$ - $\pi$  interactions of the adjacent rings with SAs. However, the functional groups could only weaken the  $\pi$ - $\pi$  interactions between CNTs and SAs if they were located on the edge of CNTs. The extension degree of V-shaped SAs and the type of heteroatoms in heterocyclic groups of SAs led to their different adsorption by CNTs. The results highlight the type of oxygen-containing functional groups is great importance in their effects on pollutants adsorption by CNTs.

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## 1. Introduction

Carbon nanotubes (CNTs) have been widely used in environmental, manufacturing and biomedical areas for their unique properties in mechanical strength, electrical and thermal conductivity [1]. The great specific surface area, high hydrophobicity, and diverse functional groups of CNTs have led to their increasing application in pollutants removal [2]. CNTs can effectively adsorb various biological [3], inorganic [4,5], and organic [6–8] contaminants, especially for hydrophobic organic chemicals [1,2]. Different adsorption mechanisms, including hydrophobic interaction,  $\pi$ - $\pi$  interaction, hydrogen bond, and electrostatic interaction, have been proposed for the adsorption of organic chemicals by CNTs [8]. The relative importance of various mechanisms controlling the adsorption by CNTs is highly dependent on the properties of organic chemicals (such as polar or nonpolar) and the surface characteristics of CNTs [9].

CNTs may be intentionally oxidized to improve their dispersibility in aqueous solution. Consequently, the CNTs surfaces often contain various oxygen-containing functional groups. It has been reported that the oxygen content on the surfaces of CNTs could largely affect the adsorption capacities of pollutants [10–12]. The overall adsorption of organic pollutants may decrease [10–12] or increase [13] with increasing oxygen contents of CNTs. The introduction of oxygen-containing functional groups resulted in more hydrophilic and negatively charged CNTs surface. This induces less adsorption of hydrophobic organic chemicals [12] and some ionic chemicals due to repulsion of negative charges [10]. Besides, the introduction of functional groups may increase steric hindrance and reduce adsorption sites, which prevents the adsorption of organics [14–16]. In contrast, the functional groups can result in high dispersion of CNTs, which make CNTs better interaction with relatively polar and low molecular weight organics [17,18]. Considering the complex effects of surface functional groups, it is imperative to investigate the exact role of different oxygen-containing functional groups on the adsorption of organic chemicals by CNTs, which is important to reveal the adsorption mechanisms of pollutants by CNTs with different oxidation degree.

Density functional theory (DFT) is a powerful tool that describes the adsorption reactions and understands adsorption mechanisms [19,20]. It has been widely used to in metal adsorption by graphene oxide (GO) [21,22], CNTs [20], graphitic carbon nitride [23] and hematite nanocrystals [24], gases adsorption by CNTs [25,26], and organic chemicals adsorption by graphitic carbon nitride [23], boron nitride sheets [27], metal-organic frameworks [28], reduced GO (rGO) [29,30], and goethite [31]. Through DFT calculation, Jin et al. [29] found that the binding energy between 4-*n*-nonylphenol (4-*n*-NP) and GO increased because of the overlapping the phenol ring of 4-*n*-NP with —OH groups on the surface of GO. On the basis of DFT calculation, Wang et al. [20] found that the oxygen-containing functional groups increased the binding affinity of Eu(III) and  $^{243}\text{Am(III)}$  with CNTs in the order of —OH < —COOH < —COO<sup>-</sup>. There could be several oxygen-containing functional groups on the surface of CNTs, including —OH, —C=O, —COOH, and —COC— [32]. However, how the different oxygen-containing functional groups of CNTs affect the adsorption of organic chemicals are poorly understood.

Sulfonamide antibiotics (SAs), a series of sulfanilamides containing a —SO<sub>2</sub>NH<sub>2</sub>— group, synthesized in large quantities and widely used to prevent diseases in human therapy and livestock production [33,34]. SAs are not completely metabolized [35], hard to degrade, and easy to be transported [36]. Therefore, SAs and their metabolic products are frequently detected in wastewater [34,37], surface water [38,39] and ground water [40]. Increasing

exposure to SAs through water supply and food chain can cause toxic and allergic reaction [12,33]. Moreover, SAs could accelerate the proliferation of bacteria and select their resistance gene [41], thus induce the prevalence and dissemination of SAs-resistance genes and resistant bacteria [42]. Therefore, it is necessary to develop the effective removal technologies for SAs. As adsorbents, CNTs showed great potentials for removal of SAs. Several studies have investigated the adsorption of SAs by CNTs and oxidized CNTs [12,33,43–46]. However, the influence of different oxygen-containing functional groups on the SAs adsorption by CNTs has not been well investigated.

In this study, four SAs, including sulfadimethoxine (SDM), sulfamethizole (SMZ), sulfamethazine (SMT), and sulfamethoxazole (SMX), were selected. To explore how the oxygen-containing functional groups affect the SAs adsorption by CNTs, four types of CNTs with different oxidation degree were prepared. The adsorption behavior of SAs by four types of CNTs were investigated using batch experiments. The influencing mechanisms of different oxygen-containing functional groups on SAs adsorption by CNTs were revealed by DFT calculation. In combination with the functional groups analysis through X-ray photoelectron spectroscopy (XPS), the variation of SAs adsorption amounts with rising oxidation degree of CNTs was explained by DFT calculation.

## 2. Experimental

### 2.1. Reagents and materials

SDM (99%), SMZ (99%), SMT (99%), and SMX (99%) were purchased from Sigma-Aldrich (USA). The chemical structures and associated protonation/deprotonation species of the four SAs were presented in Fig. 1. SAs are typical amphoteric compounds and can show two-step dissociation pathway.  $K_{a1}$  and  $K_{a2}$  are the dissociation constants of aromatic amine ( $\text{H}_3\text{N}^{(+)}\text{-C}_6\text{H}_4\text{-SO}_2\text{-NHR}$ ) and sulfonic ( $\text{H}_2\text{N-C}_6\text{H}_4\text{-SO}_2\text{-N}^{(-)}\text{-R}$ ) groups, respectively. The properties of SAs were listed in Table 1. HPLC grade methanol and formic acid were obtained from Fisher Scientific (USA). Milli-Q water (18 M $\Omega$ -cm) was used for HPLC-MS analysis. The stock solutions of SAs were prepared by dissolving solids in methanol, and stored in 4 °C. All the other chemicals used in the experiments were of analytical grade.

### 2.2. Sample preparation

The pristine capped CNTs (MP) was supplied by Chengdu Organic Chemistry Co., Chinese Academy of Sciences (outer diameter 8–15 nm, length ~50  $\mu\text{m}$ , purity >95 wt%). The oxidized CNTs were synthesized according to the method published by Yu et al. [12]. Generally, M10, M30 and M50 represent the MP was oxidized by the solutions which contain 10%, 30% and 50% (w/w) HNO<sub>3</sub>, respectively. Before the oxidization process, the MP were sonicated in Milli-Q water for 1 h until the aggregated CNTs completely dispersed. After sonication, the MP was mixed in HNO<sub>3</sub> for 1.5 h with strong stirring at 120 °C. In all experiments, keep the solid/liquid ratio at 1.0 mg/mL. After the oxidization process, the mixture was subject to repeated centrifugation, decantation and dilution with Milli-Q water to remove the residual oxidants, carbonaceous byproducts, and metallic impurities until the supernatant pH was steady at about 5.0–6.0. The oxidized CNTs were then dried overnight in an oven at about 105 °C and stored in a desiccator. They were labeled as M10, M30, and M50 respectively according to the HNO<sub>3</sub> concentrations used in the treatment.

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