



## Adsorption of ofloxacin and norfloxacin on carbon nanotubes: Hydrophobicity- and structure-controlled process

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### HIGHLIGHTS

- ▶ A significant relationship between  $K_d$  and SSA for both OFL and NOR on CNTs.
- ▶ No relationship was observed between  $K_d$ s and oxygen content of CNTs.
- ▶ Normalizing  $K_d$ s by solubilities enlarged OFL and NOR sorption difference.
- ▶ OFL and NOR sorption was controlled by their structural- and hydrophobic-properties.

### ARTICLE INFO

#### Article history:

Received 21 March 2012  
 Received in revised form 26 June 2012  
 Accepted 27 June 2012  
 Available online 4 July 2012

#### Keywords:

Emerging contaminants  
 Environmental fate  
 Nanoparticles  
 Sorption mechanisms

### ABSTRACT

Adsorption of antibiotics on solid particles is a key process controlling their fate in the subsurface. This study compared the adsorption of ofloxacin and norfloxacin (NOR) on carbon nanotubes (CNTs) to evaluate the role of structural and hydrophobic properties in regulating their adsorption. A significant relationship was observed between single-point adsorption coefficients ( $K_d$ ) and specific surface area (highly hydrophobic), but not between  $K_d$ s and oxygen content. This result suggested that site-specific adsorption was not important but hydrophobic effect may have an important contribution to OFL and NOR adsorption on CNTs. However, normalizing the adsorption coefficients by OFL and NOR solubilities enlarged their adsorption difference indicating that hydrophobicity was not the only factor controlling the difference between OFL and NOR adsorption on CNTs. Their chemical structures show that both chemicals could interact with CNTs through an electron-donor-acceptor mechanism. This mechanism was correlated with the different adsorption of OFL and NOR on functionalized CNTs (namely hydroxylized, carboxylized, and graphitized CNTs). This study revealed that OFL and NOR adsorption was controlled by their both structural- and hydrophobic-properties.

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### 1. Introduction

Antibiotics have been used for therapy of infectious diseases in human and livestock for almost one hundred years. However, wide and persistent application of antibiotics has recently created great public concerns. Generally speaking, antibiotics used in human beings and livestock are poorly absorbed with 50–90% of the applied antibiotics excreted as metabolites or parent chemicals [1]. Antibiotics in field-applied manures could be leached during rain events and thus contaminate surface water and groundwater [2]. In addition, current water treatment technologies are not able to remove antibiotics effectively [3] and thus, antibiotics are discharged into the environment. In addition, the excessive use of antibiotics and their disposal after expiration increase their

presence in the environment. Bacteria have been observed to develop drug resistance genes during long-term contact with antibiotics or through gene transfer [4,5]. These processes have led to the wide failure of antibiotics in medication [6]. Therefore, the health risk of antibiotic efficacy originated from their environmental occurrence is of a major research interest. Among the antibiotics, fluoroquinolones are ubiquitously detected in wastewater, surface, soil and sediments [7]. Thus, their environmental fate deserves special attention.

Adsorption of antibiotics to solid particles is a key process controlling their leaching and transport in soil columns. Consequently, many studies have focused on the interaction mechanisms between antibiotics and soils and/or soil components. Analogous to studies on traditional hydrophobic contaminants, investigations have attempted to establish relationships between soil properties and adsorption coefficients. Strong positive correlation between adsorption parameters  $K_d$  and organic carbon content have been observed [8,9] indicating hydrophobic interactions may be an

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important contributing mechanism to the adsorption of antibiotics. However, other investigations have observed that the carbon normalized sorption coefficient,  $K_{OC}$  for a given chemical, varied greatly for soils from different locations [10,11]. These studies imply that hydrophobic interaction was not sufficient to explain antibiotics sorption in soils/sediments [12–14]. The variations in  $K_{OC}$  were explained by the heterogeneous nature of soil particulars and different polar and charged functional groups on the molecular structure in environmentally relevant pH range. Soil particles contain organic matter with differing chemical compositions and properties, and inorganic particles with exposed hydrophilic and hydrophobic surfaces. All these components may contribute significantly to the overall adsorption of antibiotics. Different species of antibiotics may be adsorbed on soil particles through different mechanisms. It was reported that combined mechanisms play roles in antibiotics adsorption on soils, including cation and anion exchange, cation bridging, surface complexation, hydrogen binding, and hydrophobic interactions [10,15]. Knowledge of the contributions of different mechanisms will greatly improve our understanding of the environmental behavior and risk of antibiotics.

Previous research indicates that hydrophobic interactions are important for the adsorption of antibiotics [16–18]. The goal of this study is to investigate the adsorption of zwitterion antibiotics in relation to their hydrophobicity. Two heavily used and widely detected antibiotics, norfloxacin (NOR) and ofloxacin (OFL) were selected as adsorbates. They have been detected in water, soils, and influent and effluent of municipal wastewater treatment plants [19,20]. Thus, they are a potential risk to human health and the environment [21]. These two chemicals have a same chemical structure with one more  $-C-O-$  and one more  $-CH_3$  functional groups on OFL. But their solubilities differ by one order of magnitude.

This study used carbon nanotubes (CNTs) as model adsorbents. These solids have explicit and well organized structures. Different CNTs, including CNTs with different diameters, functional groups, and types (single-walled and multi-walled) were used to investigate CNT properties affecting OFL and NOR adsorption. In addition, activated carbon (AC) was also included for comparison because of its similar carbon-based composition but differing structure relative to the CNTs. Other studies have mainly focused on the adsorption of fluoroquinolone antibiotics by natural adsorbents [22,23]. However, the complex compositions of natural adsorbents hindered the detailed discussion of sorption mechanisms. This study on one hand provides a simplified model sorption system to study fluoroquinolone sorption mechanisms, on the other hand, supplies fundamental information for CNT risk assessment.

## 2. Experimental

### 2.1. Materials and reagents

The carbon nanotubes used in the study were functionalized multi-walled CNTs (MWCNTs): hydroxylized (MH), carboxylized (MC), and graphitized (MG) MWCNTs [24]; MWCNTs with three different diameters: 15 nm (M15), 30 nm (M30), and 50 nm (M50); and three functionalized single-walled CNTs (SWCNTs): hydroxylized (SH), carboxylized (SC), and purified (SP) SWCNTs. AC from wood charcoal was obtained from Fisher Scientific. All CNTs and AC were characterized for their surface area (Autosorb-1C, Quantachrome), elemental composition (MicroCube, Elementar, Germany), and surface functional groups (X-ray photoelectron spectroscopy). The surface areas of all CNTs and AC were measured using  $N_2$  (Autosorb-1C, Quantachrome). Elemental compositions of C, H, N, S (using oxygen) and O (using helium) were measured at 1150 °C with an elemental analyzer (MicroCube, Elementar,

Germany). Surface functional groups were analyzed (X-ray photoelectron spectroscopy, PHI5500) using  $MgK\alpha$  radiation (1253.6 eV). Spectra correction was based on adventitious carbon, using a C1s binding energy of 284.8 eV. OFL and NOR were obtained from Bio Basic Inc. All the other chemicals were analytical grade or better.

### 2.2. Batch adsorption experiments

OFL (700 mg/L) and NOR (60 mg/L) were separately dissolved in background solution containing 0.02 M NaCl (background electrolyte) and 200 mg/L  $NaN_3$  (bio-inhibitor) as stock solutions [25,26]. The adsorption experiments were conducted in glass vials with Teflon-lined screw caps. According to preliminary studies, 1–3 mg of adsorbents were mixed with 5–40 mL adsorbate solutions. The aqueous:solid ratios of 15,000:1 to 15,000:3 at pH  $7.0 \pm 0.2$  were used in the sorption experiments to ensure 20–80% adsorption. The stock solutions were diluted by the background solution to 6–8 different concentrations, and the concentration range of OFL and NOR are 2–700 mg/L and 2–60 mg/L. Samples of OFL and NOR solution without solid particles were kept in the same condition as the suspensions and referred to as the initial concentration references. All the vials were stored in a dark area and shaken in an air-bath shaker at 25 °C for 7 d which was sufficient to reach apparent equilibrium according to our preliminary study up to 9 d [27]. During this process, OFL and NOR were relatively stable and no apparent degradation was observed (Fig. S3). After equilibrated for 7 d, all the vials were centrifuged at  $1000 \times g$  for 10 min and the supernatants were subjected to determination of solutes concentration.

### 2.3. Measurement of solubilities and $K_{OW}$ s of OFL and NOR

Water solubility ( $C_s$  values) and n-octanol – water partitioning coefficient ( $K_{OW}$  values) are two parameters widely used to describe chemical hydrophilicity and hydrophobicity. However, literature provided a wide range of  $C_s$  and  $K_{OW}$  values for OFL and NOR [28–31]. Thus, these parameters were measured to allow a better comparison between OFL and NOR adsorption properties. For the measurement of  $C_s$  values, 1 mg OFL and 0.1 mg NOR were separately put into 1.5 mL glass vials with Teflon-lined screw caps. One milliliter of background solution (0.02 M NaCl and 200 mg/L  $NaN_3$ ) was injected in the vials. The pH values of all the solutions were adjusted to  $7.0 \pm 0.2$ . All the vials were stored in a dark area and shaken in an air-bath shaker at 25 °C for 2 d. Subsequent amount of OFL or NOR were added in the vials until solid residuals were observed. These vials were shaken for another 5 d. All the vials were centrifuged at  $1000 \times g$  for 10 min and then filtered. The supernatants were subjected to determination of solutes concentration.

The  $K_{OW}$  values of OFL and NOR were measured based on their partitioning between n-octanol and water assuming no dissolution of n-octanol in water [32]. Five milliliters of 5 mg/L (or 20 mg/L) OFL or NOR were mixed with 10 mL n-octanol in 20 mL vials with Teflon-lined screw caps. The pH of the solution was about 7.0. These vials were shaken vigorously by hand and then oscillated at 25 °C for 24 h. The vials were then left to stand for stratification. The water phase were subjected to solute analysis and the solute partitioned in octanol was calculated by the difference of OFL or NOR concentrations in water before and after octanol extraction. Five replications were prepared for  $C_s$  and  $K_{OW}$  measurements.

### 2.4. FTIR characterization of OFL- or NOR-adsorbed adsorbents

A separate batch of solid particles was prepared for Fourier transform infrared (FTIR) spectroscopy measurements. OFL or NOR solution of 0.1  $C_s$  (340 mg/L or 32 mg/L) was mixed with 10 mg of different adsorbents and shaken in the dark for 5 d. The vials were

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