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Sorption of tylosin and sulfamethazine on solid humic acid

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ABSTRACT

Tylosin (TYL) and sulfamethazine (SMT) are ionizable and polar antimicrobial compounds, which have seeped into the environment in substantial amounts via fertilizing land with manure or sewage. Sorption of TYL and SMT onto humic acid (HA) may affect their environmental fate. In this study, the sorption of TYL and SMT on HA at different conditions (pH, ionic strength) was investigated. All sorption isotherms fitted well to the Henry and Freundlich models and they were highly nonlinear with values of n between 0.5 and 0.8, which suggested that the HA had high heterogeneity. The sorption of TYL and SMT on HA decreased with increasing pH (2.0–7.5), implying that the primary sorption mechanism could be due to cation exchange interactions between TYL^+/SMT^+ species and the functional groups of HA. Increasing ionic strength resulted in a considerable reduction in the K_d values of TYL and SMT, hinting that interactions between H bonds and π–π EDA might be an important factor in the sorption of TYL and SMT on HA. Results of Fourier transform infrared (FT-IR) and ^{13}C-nuclear magnetic resonance (NMR) analysis further demonstrated that carboxyl groups and O-alkyl structures in the HA could interact with TYL and SMT via ionic interactions and H bonds, respectively. Overall, this work gives new insights into the mechanisms of sorption of TYL and SMT on HA and hence aids us in assessing the environmental risk of TYL and SMT under diverse conditions.

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Introduction

In recent years, pharmaceutical antibiotics including tylosin (TYL) and sulfamethazine (SMT) have been produced in large quantities and extensively used in the farming industry as veterinary therapeutic agents and growth promoters, which will be inevitably released into the environment and then generate potential ecological risk (Zhou et al., 2014). Actually, releases of antibiotics into various media (*i.e.*, water, soil, and sediment) and the consequent risks to various ecological receptors have been reported (Leone et al. 2014; Mutavdžić Pavlović et al. 2014; Wu et al. 2014). Therefore, understanding the environmental behavior of antibiotics is important for evaluating environmental and health impact of antibiotics.

Numerous studies have been focused on the sorption behaviors of TYL and SMT in manure and soils (Aust et al. 2008; Guo et al. 2014; Jeong et al. 2012; Pei et al. 2014; Zhang et al. 2011b, 2013). It was found that TYL and SMT could interact with the surfaces and functional groups in manure and soils such as minerals and HAs (Kolz et al. 2005; Sassman et al. 2007; ter Laak et al. 2006). They revealed that the sorption of TYL and SMT on clays was primarily due to cation exchange effects, especially under acidic conditions (Zhang et al. 2013). Moreover, van der Waals forces could also play an important role on the distribution of TYL and SMT in the soil and water (Aust et al.

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2008; Halling-Sorensen et al. 2005; Pei et al. 2014; Sassman et al. 2007; ter Laak et al. 2006; Zhang et al. 2011b). Guo et al. (2013, 2014) reported that TYL and SMT sorption on goethite was positively correlated to the formation of surface complexes, π–π EDA interactions and hydrophobic interactions, which might contribute partially to the overall sorption. In fact, TYL and SMT, like most antibiotics, are ionic compounds. TYL is a weak base with a pK_a of 7.1 (Zhang et al. 2013). In acidic conditions, ionic bonds could form between protonated TYL and anionic components in soil and manure matrices. SMT is an amphoteric compound with pK_a values at 2.28 and 7.42 (Guo et al. 2013). The net charges of SMT at different pH levels would be more complicated and thus lead to heterogeneous sorption activities between SMT and solid phases. When TYL and SMT are released into the environment, they might be adsorbed by soils and sediments, which would be a major process affecting the transport and fate of antibiotics in the environment.

HAs are natural polymers with a broad molecular-weight distribution and high chemical heterogeneity. They consist mainly of a skeleton of cross-linked aromatic blocks that are full of carboxylic and phenolic groups (Minella et al. 2013). Sorption of antibiotics onto HA is a major process determining the fate and bioavailability of antibiotics in soils and sediments. Once antibiotics are released into the environment, they would interact with HA. As a consequence of the interaction, the environmental behavior would be altered (Leone et al. 2014). The pH of the environment could also affect existing TYL and SMT forms. Thus, sorption mechanisms might be different at different pH levels (Zhao et al. 2014b). On the other hand, many kinds of ions coexist with TYL and SMT in the environment; however, interactions of these ions with HA have not been well elucidated. In order to assess the environmental risks of TYL and SMT, the sorption mechanisms of TYL and SMT on HA were investigated.

The objective of this study is to assess the sorption behavior and mechanism of TYL and SMT on HA and to understand the effect of HA on their environmental fate. The influences of solution chemical factors (*i.e.*, pH and ionic strength) on the sorption of TYL and SMT on HA were also investigated.

1. Materials and methods

1.1. Materials and preparation

Tylosin tartrate (purity > 95%) and sulfamethazine (purity > 99%) were purchased from Sigma-Aldrich Corporation (St Louis, MO, USA). Acetonitrile and formic acid (HPLC grade, Merck Chemicals Co. AQ5) were used as received. Pure water was prepared by a Milli-Q® water purification system (Millipore Co., Guangzhou, China). All the other chemicals were analytical reagent grade and used without further purification.

Primary stock solutions of TYL and SMT at 1000 mg/L were prepared with pure water and stored at 4°C for a maximum of 1 month. The working solutions were prepared by diluting stock solution using 0.01 mol/L KNO_3 solution.

HA (solid granules with particle size 0.5–2 μm) used in this study was obtained from JuFeng Chemical Corporation, Shanghai, China. The elemental composition of HA is: 52.37% C, 3.57% H, 36.12% O, and 1.80% N.

1.2. Chemical analysis

The concentrations of TYL and SMT in aqueous solution were measured by reverse-phase high-performance liquid chromatography (AS-2455Plus, JASCO, Tokyo, Japan) with a C_{18} column (5 μm, 4.6 × 250 mm; Agilent) and diode array UV detector (Pgeneral, Beijing, China) (wavelength at 290 nm for TYL and 264 nm for SMT). The mobile phase by volume (at a flow rate of 0.5 mL/min) for TYL was a 35:65 mixture of acetonitrile and an aqueous solution containing 0.01 mol/L KH_2PO_4 (pH = 2.0) while for SMT it was a mixture of acetonitrile and formic acid solution (0.05%, *V*/*V*) at a volumetric ratio of 60:40 with a flow rate of 1 mL/min. The injection volume was 20 μL. External standards of TYL and SMT (0.1–100 mg/L) were employed to establish a linear calibration curve and the sample concentrations were calculated from its integrated peak areas. The solid phase concentrations were calculated based on the mass balance of the solute between the two phases.

1.3. Sorption and desorption procedure

The sorption experiments were conducted using a batch equilibrium technique at 25°C and pH 7.0. The initial TYL and SMT concentrations were set from 0.5 to 50 mg/L. The background solution contained 0.003 mol/L NaN_3 to minimize bioactivity and 0.01 mol/L KNO_3 to adjust ionic strength. A predetermined amount of HA was mixed with the initial aqueous solution in completely mixed batch reactor systems with Teflon gaskets and mixed on a shaker at 150 r/min to reach sorption equilibrium. The sorption equilibrium time for TYL and SMT was 24 hr. After the sorption experiments, the screw cap vials were centrifuged at 4000 r/min for 30 min, and 1 mL of supernatant was transferred into a pre-weighed 1.5 mL amber glass vial for chemical analyses. Each concentration level, including blanks, was run in triplicate. KOH or HNO_3 solutions were used for pH adjustment.

Desorption experiments were performed with a single cycle decant refill technique (Ramaswamy et al. 2012). In brief, after completion of the sorption test, each completely mixed batch reactor was weighed. Subsequently, the supernatant in each reactor was emptied with a pipette and then the reactor with the precipitates was weighed so that the amount of TYL/SMT-free background aqueous solution could be calculated and added. Afterwards, the reactor was reweighed, capped, and placed in the shaker for desorption experiments. After mixing under the same conditions, the tubes were centrifuged and set upright for 12. The supernatant was withdrawn from each reactor for quantification of TYL/SMT in the solution phase.

1.4. Sorption isotherm models

The equilibrium sorption data was fitted using Henry (Eq. (1)) and Freundlich (Eq. (2)) models (Ji et al. 2009):

$$q_e = k_d C_e \tag{1}$$

$$q_e = k_f {C_e}^n \tag{2}$$

where C_e (mg/L) and q_e (mg/kg) are the equilibrium concentration of TYL/SMT in the liquid phase and solid phase, respectively; k_d (L/kg) is the distribution coefficient of solute between

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