



Effects of copper and aluminum on the adsorption of sulfathiazole and tylosin on peat and soil



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ABSTRACT

Effects of copper (Cu) and aluminum (Al) on the adsorption of sulfathiazole (STZ) and tylosin (T) to peat and soil were investigated using a batch equilibration method. Results show that Cu suppressed STZ adsorption onto peat and soil at pH < 5.0 because of the electrostatic competition, while increased STZ adsorption at pH > 5.0 due to the formation of STZ–Cu complexes and/or Cu bridge. In contrast, Al only decreased STZ adsorption at pH < 6.0, and exerted slight effect on STZ adsorption at >6.0. As for T, both Cu and Al suppressed its adsorption over the entire pH range owing to three reasons: 1) electrostatic competition between Cu/Al and T⁺; 2) Cu/Al adsorption made the soil and peat surface less negatively charged, which was unfavorable for T⁺ adsorption; 3) the shrunken pore size of peat and soil retarded the diffusion of large-sized T into these pores.

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1. Introduction

Pharmaceutical antibiotics are widely used to treat diseases of human and animals or incorporated into animal feeds to improve growth rate and feed efficiency. However, these antibiotics are often poorly metabolized and absorbed by humans and animals, with most leaving the treated agents unmodified and consequently entering the environment (Sarmah et al., 2006). Removal of antibiotics by conventional water treatment technologies is incomplete (Zoritaa et al., 2009). A considerable portion of antibiotics can reach the soil environment through application of fertilizers, sewage sludge, wastewater irrigation, or the discarding of out-of-date pharmaceutical prescriptions (Golet et al., 2002). Exposures to residues of antibiotics and their transformed products might cause a variety of adverse consequences, including acute and chronic toxicity, and microorganism antibiotic resistance, etc (Schmitt et al., 2006). Adsorption of antibiotics to soils and sediments is an important process and influences their fate and transport in the environment. Currently, more concern is being paid to illustrate the environmental behavior and risks of antibiotics. Previous studies

examined pH-dependent adsorption of antibiotics onto clays (Heberer, 2002), aluminum oxides (Zoritaa et al., 2009; Golet et al., 2002; Gu and Karthikeyan, 2005), amorphous iron oxides (Zoritaa et al., 2009), goethite (Golet et al., 2002), soil and soil minerals (Kolpin et al., 2002; Nowara et al., 1997), and carbon nanotubes (Wang et al., 2010). In addition to hydrophobic partitioning, antibiotics may be adsorbed via cation exchange and cation bridging (Trivedi and Vasudevan, 2007), surface complexation (Zoritaa et al., 2009; Golet et al., 2002), salting out effects (Zhou, 2006), and hydrogen bonding (Tolls, 2001).

The coexistence of heavy metals and antibiotics is common in the environment (Wang et al., 2008). Many antibiotics with various acidic or basic functional groups can complex with heavy metal ions in solution, which alter their individual speciation and consequent environmental behaviors (Pan et al., 2012). Compared to single solute system, studies on the mutual adsorption of antibiotics and metal ions on solid particles could significantly further improve our understanding of antibiotic risks (Pan et al., 2012). However, it should be noted that previous studies generally chose antibiotics with complexation ability as adsorbates, and mainly focused on the role of complexation reaction in the adsorption (Wang et al., 2008). In fact, there are many antibiotics with no complex ability or with complex ability only under certain pH condition (Tolls, 2001). How heavy metals affect these antibiotics

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adsorption on soil was unknown. In addition, it was reported that the presence of heavy metals could result in changes in soil properties and structure (Pei et al., 2011; Wang et al., 2007; Yuan and Xing, 2001). For example, it was found that heavy metals could decrease the negatively charged density on soil surfaces (Hou et al., 2007), and make humic acids and biopolymers more condensed and rigid (Wang et al., 2007). Heavy metals also promote the aggregation and precipitation of soil colloid in solution (Ugochukwu et al., 2011). It is therefore to be expected that these changes of soil properties and structures will consequently influence the adsorption of antibiotics to certain extent (Luo et al., 2008). However, as far as we know the question on how the changed characteristics of soil by heavy metals on the adsorption of antibiotics have not been appropriately addressed, and the underlying mechanisms are unknown.

In this study, we chose sulfathiazole (STZ) and tylosin (T) as common representative of antibiotics. STZ has two pK_a (2.0 and 7.24), and can exist either as STZ^+ , STZ^0 or STZ^- forms in aqueous solution at different pH conditions due to protonation and deprotonation (Fig. S1). The result of copper-ion-selective electrode experiment suggested that STZ^- could form Cu–STZ complexes with Cu using its deprotonated imino group through electrostatic attraction, while STZ^+ and STZ^0 had very slight complex ability with Cu (Fig. S2). T has one pK_a (7.1), and can exist as T^+ at acidic pH, and as T^0 at basic pH (Fig. S1). Fig. S2 showed that both T^+ and T^0 could not complex with Cu. Cu was chosen due to wide use in animal feed as a growth promoter, while Al was one of the most frequent elements within the Earth's crust. In addition, different chemical species of Cu and Al at different pH help to explore the underlying adsorption mechanisms. The objectives of this study were (i) to reveal the effects of Cu and Al on the adsorption of STZ and T on peat and soil; and (ii) to elucidate the relevant mechanisms by exploring the interactions of metals and antibiotics in solution and in solution/adsorbent interface, which could be a useful approach to provide an insight into the mechanisms governing the adsorption in multi-solute systems.

2. Materials and methods

2.1. Materials

A black chernozem soil (a clay loam Mollisol) was collected from surface horizon (0–20 cm) in Heilongjiang Province, northeastern China. Soil was air-dried, ground, and homogenized to pass a 1.0 mm sieve. The peat sample was also collected from Heilongjiang Province and was dried at 105 °C, ground, and homogenized to pass through a 0.15 mm sieve. Nitrogen specific surface area (SSA) of peat and soil were measured using an accelerated surface area system by applying the Brunauer–Emmett–Teller (BET) equation to adsorption of N_2 at 77 K. Other characteristics of peat and soil were determined by the methods of Nelson and Sommers (1996) and Sumner and Miller (1996), and the properties are listed in Table S1.

Two antibiotics, STZ and T (purity of >98%), were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI, USA) and the structures and properties are shown in Table S2. $Cu(NO_3)_2$, $Al(NO_3)_3$, $NaNO_3$, NaOH, and HNO_3 were all reagent grade chemicals and methanol was HPLC grade.

2.2. Adsorption experiments

STZ and T were dissolved in 0.01 M $NaNO_3$ solution, to which NaN_3 (0.1 g L^{-1}) was added to suppress the growth of bacteria. All adsorption experiments were conducted in triplicates using a batch equilibration technique at 23 ± 1 °C. Adsorption of STZ and T (2.5, 5.0, 12.5, 17.5, 25.0, and 37.5 mg/L) were carried out by mixing a certain amount of peat and soil with 0.01 M $NaNO_3$ solution in presence of 0, 0.5 and 1.0 mM Cu or Al in 50 mL glass centrifuge tubes sealed with Teflon-lined screw caps. The pH of the adsorbent suspension was adjusted to 6.0 ± 0.1 by dropwise addition of 0.1 M HNO_3 or NaOH. In order to maintain the final pH within experimental error, the suspension pH was readjusted every 2 h during the first 8 h of equilibration, subsequently the final pH was maintained within ± 0.1 pH units. Under such conditions, STZ was present in solution as neutral and anionic forms, and T was in cationic form, respectively. Our previous experiments also indicated that coprecipitation of STZ or T with Cu/Al was unlikely at pH 6.0 (data not shown). The suspension was rotated continuously for 24 h for STZ and 72 h for T to ensure complete adsorption (apparent equilibrium was reached before this time). After

centrifugation at 1667 g for 20 min, the concentrations of STZ and T in the supernatant were determined by HPLC (Agilent 1200 HPLC). Controls were also prepared identically but contained no adsorbents, which were simultaneously run to assess loss of solutes. Results show that no significant loss of solutes was observed, indicating that microbial degradation, volatilization, or adsorption to the glass walls were negligible during the adsorption experiments.

At the end of adsorption experiments, aliquots of supernatant (10 mL) were withdrawn, the same volume of background desorption solution was added to replenish the adsorption suspension, after that the suspensions were shaken for 24 h for STZ and 72 h for T, then centrifuged, and the concentrations of STZ and T were analyzed. This procedure was repeated three cycles.

2.3. Effect of pH on the adsorption of STZ and T

The pH effect was conducted using a batch adsorption approach as mentioned above. Initial concentrations of both STZ and T were 12.5 mg/L, and concentration of Cu/Al was 1.0 mM, respectively. The pH was adjusted from 3.0 to 8.0 for peat and soil by addition of 0.1 M HNO_3 or NaOH. After equilibrium, the suspension was centrifuged at 1667 g for 20 min to separate the liquid and solid phases. The antibiotic and metal concentrations in the supernatant were determined by HPLC or ICP–AES (Plasma Quad3, Manchester, UK), respectively.

2.4. Zeta potential (ζ) measurement

The suspension for ζ -potential measurements was prepared by mixing a certain amount of peat and soil with 0.01 M $NaNO_3$ solution (20 mL) containing different concentrations of Cu or Al (0 and 1.0 mM). The suspension was rotated continuously for 24 h at room temperature (23 ± 1 °C). The solution pH was adjusted to 3.0–7.0 using 0.1 M HNO_3 or NaOH. The ζ -potentials were measured on the basis of microelectrophoresis measurements on a Zetasizer 2000 (Malvern Instruments, U.K.). The voltage applied to the capillary cell was set at 150 V and the Henry function $[f(Ka)]$ of 1.5 was used to directly calculate ζ -potentials. The electrophoretic capillary cell was rinsed three times with 50 mL of deionized water (18 M Ω) before each analysis. Five independent ζ -potential measurements were collected for each sample to ensure accurate and reproducible data.

2.5. Analysis

STZ and T in the supernatants were determined by an Agilent 1200 reversed-phase HPLC (Atlantis-dC18 ODS HPLC column, 4.6 i.d. \times 150 mm, 5 μ m) equipped with UV detector. The determination wavelengths were set at 265 nm and 290 nm for STZ and T, respectively. The mobile phases were methanol:water (30:70, v:v, pH 3.0, adjusted with acetic acid) for STZ, and methanol:water (55:45, v:v, pH 3.0, adjusted with acetic acid) for T at a flow rate of 1.0 mL min^{-1} . The concentrations of Cu and Al in the equilibrium solutions were determined by ICP–AES (Plasma Quad3, Manchester, UK). The adsorbed antibiotics and metals were calculated from the differences between the initial and final equilibrium concentrations.

2.6. Data analysis

Adsorption data were fitted to the Freundlich equation using software Origin 7.5, and nonlinear regression analyses were conducted by the least-squares method. Freundlich equation can be expressed as $Q = K_f C^n$, where Q (mg/g) is the amount of adsorbed organic compounds by soil and peat, C (mg/L) is the equilibrium concentration in solution, K_f is an empirical constant related to adsorption capacity ($mg^{(1-n)} g^{-1} L^n$), and n is the Freundlich exponent or a site energy heterogeneity factor, often used as an indicator of isotherm nonlinearity.

3. Results and discussion

3.1. Adsorption isotherms

Fig. 1 shows the adsorption isotherms of STZ and T at pH 6.0 on peat and soil in the absence and presence of Cu and Al (0.5 and 1.0 mM, respectively). The isotherms fitted Freundlich equation well, and are clearly nonlinear as characterized by low Freundlich parameter n (Table S3).

As shown in Fig. 1a and b, the adsorption of STZ on peat and soil increased with increasing Cu concentrations from 0 to 1.0 mM, suggesting that Cu facilitated the adsorption of STZ. For example, the adsorption distribution coefficients (K_d) (initial concentration of 12.5 mg/L) were used to compare the adsorption behavior of STZ (Table S3). Obviously, the K_d values increased from 0.1 to 0.27 L/g for peat and 0.007 to 0.016 L/g for soil when the Cu concentrations increased from 0 to 1.0 mM. In contrast, interestingly, the presence of Al had little effects on the adsorption of STZ on soil and even slightly decreased the adsorption of STZ on peat (Fig. 1a and b). The

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