Impact of concentration and species of sulfamethoxazole and ofloxacin on their adsorption kinetics on sediments

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HIGHLIGHTS

- The sorption kinetics of SMX is concentration and pH-independent.
- The sorption kinetics of OFL is dependent on the concentration and pH.
- The neutralization effect of adsorbed OFL^+ slows down subsequent OFL^+ sorption.
- The sorption rate of antibiotics is concentration-dependent of adsorbable species.

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ABSTRACT

Antibiotics are used widely in human and veterinary medicine and are ubiquitous in environmental matrices worldwide. The influence of the concentration of antibiotics on adsorption kinetics is still unclear. This study used sulfamethoxazole (SMX) and ofloxacin (OFL) as adsorbates to investigate the adsorption kinetics on sediment affected by varying concentrations of antibiotics adsorbable species. At the experimental pH values, the major adsorbed species of SMX and OFL on sediment were SMX^0 and OFL^+ by hydrophobic interaction and electrostatic attraction, respectively. The apparent adsorption rate of SMX was not affected by the initial concentration and the pH values because the hydrophobic interactions were concentration-independent and charge-independent. However, the apparent adsorption rate of OFL significantly slowed down as the initial concentration increased. The adsorbed OFL^+ effectively neutralized the negative charges of the sediment, leading to a reduced adsorption rate of subsequent OFL^+. The neutralization effect was greatly enhanced due to the increased OFL^+ with the increasing OFL concentration. Additionally, the apparent adsorption rate of OFL significantly increased at higher pH due to the reduced neutralization effect that resulted from the decreased OFL^+ and increased negative charges of the sediment surface. This study implied that the adsorption kinetics of antibiotics was greatly dominated by the concentration of adsorbable species rather than apparent overall concentration.

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1. Introduction

Antibiotics have been used extensively in human and veterinary medicine (Laxminarayan et al., 2013). Most antibiotics are incompletely metabolized; thus, their residues and degradation products are excreted and can enter water environments in various ways (Kümmerer, 2009). Exposure to the residues and metabolites of antibiotics may cause a variety of adverse effects in the environment, such as antibiotics resistance of microorganisms and chronic and acute toxicity for organisms (Boxall et al., 2003; Schmitt et al., 2006). Among the antibiotics used, sulfamethoxazole (SMX) and ofloxacin (OFL), representative of sulfonamides and fluoroquinolones, are hydrolytically stable, difficult to degrade in water and widely detected in wastewater, soil and sediments (Vazquez-Roig et al., 2010). Environmental risks associated with SMX and OFL, including antibiotic resistance of bacteria, have been reported (Zhang et al., 2014b). Understanding the environmental behavior of SMX and OFL in aquatic systems is vital to assess and control associated environmental risks.

It is generally regarded that the adsorption of organic

contaminants, including antibiotics, on soil and sediment controls their mobility, bioavailability, and risks (Aga et al., 2016). The adsorption kinetics of organic contaminants has been examined to reveal mechanisms of the adsorption process. Some consensuses and concepts have been achieved. For example, the adsorption process of organic contaminants on soil or sediment particles often exhibited fast and slow adsorption compartments (Xing and Pignatello, 1996; Liu et al., 2010; Zhang et al., 2014a, 2014b). The most commonly postulated mechanism of slow adsorption was the diffusion of organic contaminants into organic matter of soil or sediment (Brusseau et al., 1991; DiVincenzo and Sparks, 1997). The surface adsorption on specific sites was generally believed to control the fast adsorption (Wu and Zhao, 2011). However, we also found that some conflicting results still existed in the previous literature. Some scholars believed that the adsorption kinetics of organic contaminants was dependent on concentration. For example, in a theoretical analysis, the observed adsorption kinetics rate was a linear function of the initial solute concentration on various adsorbents (Azizian, 2004). It was also reported that the adsorption rate of tylosin and sulfamethazine decreased as the initial concentrations increased because of the rearrangement of adsorbed tylosin and sulfamethazine (Guo et al., 2013). However, other researchers proposed that the adsorption kinetics of organic contaminants was concentration independent. For example, the adsorption process of norfloxacin on soils was governed by the availability of adsorption sites instead of the norfloxacin concentration (Peruchi et al., 2015). A second-order kinetics rate was also observed with respect to the availability of adsorption sites on the surface of adsorbent rather than adsorbate concentration in bulk solution (Liu, 2008). Azizian et al., successfully estimated the concentration-independent rate constant of methyl violet on activated carbon by the extended geometric method (Azizian et al., 2007, 2009). Obviously, the effects of the concentration of solutes on the adsorption kinetics of organic contaminants are still unclear.

When compared to traditional hydrophobic organic chemicals, the adsorption of ionic antibiotics is relatively more complicated due to the different adsorption mechanisms of varying species, including electrostatic interaction, hydrogen bond, and electron donor-acceptor interaction (Li et al., 2013; Apul and Karanfil, 2015). Thus, it could be inferred that the adsorption kinetics of ionic antibiotics is likely controlled by the concentration of adsorbable species, rather than the apparent total concentration. However, in the aforementioned studies, most researchers only focused on the influence of apparent total concentration of organic contaminants on adsorption kinetics. The effects of varying concentrations of adsorbable species on adsorption kinetics were generally ignored. To our knowledge, there was no available study on the impact of varying concentrations of adsorbable species on the adsorption kinetics of antibiotics.

Therefore, the objective of this study was to illustrate the underlying mechanisms of the adsorption kinetics of SMX and OFL on sediment as affected by their varying concentrations and species. This study offers new insights in understanding the adsorption mechanisms and kinetics process of ionic antibiotics on sediment.

2. Materials and methods

2.1. Chemicals

The antibiotics, SMX and OFL (purity >98%), were purchased from Bio Basic Inc. (Canada). Selected physico-chemical properties of the two antibiotics were given in Table 1. The organic solvents used in this study were purchased from Merck Co. (Germany) with chromatographic purity. Other chemicals were higher than analytical grade.

2.2. Sediment

A lake sediment sample was collected from Dianchi Lake (N 24°48′19.22″, E 102°39′52.16″), Yunnan province, China. The collected sample was freeze-dried, ground, and sieved through a 2-mm sieve. Plant residues were manually picked out. The organic elemental compositions of the sediment were analyzed by an elemental analyzer (MicroCube, Elementar, Germany). The mineral compositions of the sediment were analyzed using X-ray diffraction (XRD) (D/Max2200, Rigaku, Japan). The surface charge of the sediment was measured at different pH values using a zeta potential analyzer (ZetaPALS, Brookhaven Instruments Corporation, USA) to determine the zero point of charge (pH_{zpc}). The surface charge of the sediment after SMX and OFL adsorption was also measured at the initial SMX and OFL concentration of 32 mg L^{-1}.

2.3. Adsorption experiment

SMX and OFL (100 mg L^{-1}) were dissolved in background solution containing 0.01 M CaCl$_2$ and 200 mg L^{-1} NaN$_3$ (bio-inhibitor) as a stock solution. The adsorption isotherms (a) and adsorption kinetics (b) of SMX and OFL on sediment were conducted in 40 mL amber vials equipped with Teflon-lined screw caps using a batch technique. According to a preliminary experiment, the aqueous:solid ratio was fixed at 8000:1 (w/w). The stock solutions of SMX and OFL were diluted with background solution to six different concentrations (1—64 mg L^{-1}). Samples of SMX and OFL solutions without solid particles were referred to as the initial concentration references. All of the vials were kept in dark and shaken in a temperature-controlled shaker at 25 °C for 7 d to reach adsorption equilibrium. After that, the vials were centrifuged at 2000 g for 15 min and the supernatants were subjected to quantification of SMX and OFL. The pH values of SMX and OFL solutions after equilibrium were 5.4 ± 0.1 and 6.1 ± 0.2, respectively. For the adsorption kinetics experiment (b), the concentrations of SMX and OFL in supernatants were quantified at given time intervals (0.5, 1, 3, 5, 8, 12, 24, 36, 72, 120 and 168 h). Other experimental procedures were the same as experiment (a). All experiments were done in duplicates.

2.4. Detection of SMX and OFL

The concentrations of SMX and OFL in the supernatants were quantified by high-performance liquid chromatography (HPLC, Agilent Technologies 1200, USA) equipped with a reversed-phase C8 column (5 μm, 4.6 × 150 mm) and an UV detector at 265 nm and 286 nm, respectively. For SMX, the mobile phase was 40:60 (v:v) of acetonitrile:deionized water with 0.1% acetic acid. The flow rate was 1 mL min^{-1} and the detection limit was 0.05 mg L^{-1}. For OFL, the mobile phase was 10:90 (v:v) of acetonitrile:deionized water with 0.8% acetic acid. The flow rate was 1 mL min^{-1} and the detection limit was 0.1 mg L^{-1}. The detected results of the reference samples indicated that there was no degradation of SMX and OFL in the equilibrium period. Thus, the loss of SMX and OFL in the aqueous solution was attributed to their adsorption on sediment.

2.5. Data analysis

The Freundlich equation was modified to describe the temporal adsorption isotherms (Weber and Huang, 1996).
Modified Freundlich equation (MFE):

$$Q_t = K_F(t)C_t^{N(t)} \tag{1}$$