



Enrofloxacin uptake and retention on different types of clays



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ABSTRACT

The adsorption and retention of enrofloxacin (EN) on different types of clays was studied in batch tests under different pH, contact time, and initial concentration conditions. XRD and FTIR analyses were utilized to characterize EN adsorption and to elucidate mechanisms of EN adsorption. The EN adsorption equilibrium followed the Langmuir isotherm and reached capacities of 667, 228 and 20 mmol/kg at pH 4–5 on the montmorillonite (SWy-2), illite (IMt-2), and kaolinite (KGa-1b), respectively. The pseudo-second-order model fitted the EN sorption kinetics well. Although EN had a much lower adsorption capacity on KGa-1b compared to that on the other two clays, the adsorption rate constant was the fastest at 0.73 kg/mmol-h. Cation exchange interaction was attributed to the major mechanism for EN adsorption on SWy-2 and IMt-2, and non-electrostatic interactions attributed to EN adsorption when solution pH was above 7. Intercalation of EN molecules into the interlayer space of SWy-2 was confirmed by the XRD patterns after EN adsorption. In contrast, the basal spacing and intensity remained the same after EN adsorption on IMt-2 and KGa-1b, indicating that the EN adsorption on the non-swelling clays were limited to the external surfaces.

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1. Introduction

Fluoroquinolones (FQs) are broad-spectrum antibacterial drugs for a variety of serious bacterial infections. This increasingly popular class of antibiotics is also widely used in human therapy and poultry husbandry (Wispeley and Schafer, 2010; Witte, 1998). Many antibiotics were metabolized incompletely after administration and excreted into wastewater. Residual antibiotics would enter surface water if not completely eliminated by sewage treatment (Sayah et al., 2005). Although compared to other persistent organic pollutants such as polyaromatic hydrocarbons, FQs seemed easy to be degraded (Pico and Andreu, 2007). Still, due to their low biodegradation rates, this type of antibiotics might be persist in the aquatic environment and be responsible for the increasing resistance of pathogenic bacteria (Al-Abmad et al., 1999). The high concentration of FQs in the environment could also be due to continuous discharge, resulting in pseudo-persistent occurrence of FQs. As such, FQs were often detected in municipal wastewater effluent and surface water (Hartmann et al., 1998; Babić et al., 2010).

Enrofloxacin (EN), the second generation of the FQs, was the first of the FQs approved for use in animals and the most commonly used FQs in agriculture (Martinez et al., 2006), because of its great efficiency in treatment of respiratory and enteric bacterial infections (Mitchell, 2006). EN has been detected in wastewater (Seifrtová et al., 2008), mineral water (Herrera-Herrera et al., 2008), untreated drinking water (Focazio et al., 2008), tap water (Yiruhan et al., 2010), and surface water (Tong et al., 2011). The emerging contaminants in the environment have caused increasing concern in recent years, for the potential risk to the biotic environment (Trivedi and Vasudevan, 2007). Therefore, it was urgent to find out an effective method to remove its residue from the aquatic environment on one hand, and to investigate its transport and retention in the environment on the other hand.

Clay minerals were often used as additives in pharmaceutical preparations for their large specific surface area (SSA), high cation exchange, small particle size, heat-retention, and non-toxic to human (Carretero and Pozo, 2009). However, many reports showed that clay minerals could adsorb a variety of drugs, thus affecting the drug efficiency. Three sulfonamide antimicrobials could adsorb on montmorillonite and kaolinite under different pH, ionic strengths and types of exchangeable cations (Gao and Pedersen, 2005). Adsorption of tetracycline (TC) on kaolinite and smectite was attributed to cation exchange as confirmed by the desorption of exchangeable cations (Li et al., 2010a,b). Interaction between

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diphenhydramine, an important antihistamine drug, and a montmorillonite showed that this swelling clay was a good candidate to remove cationic pharmaceuticals from water (Li et al., 2011). Therefore, clay minerals could be regarded as potential adsorbent to remove residual antibiotics from water. Meanwhile, as clays minerals are the most important soil components, it would be of great interests to study the interactions and retentions of antibiotics on clay minerals.

EN exhibited amphoteric properties owing to a carboxylic acid and a tertiary amine (Mitchell, 2006) and could adsorb strongly on montmorillonite. Electrostatic interaction between ionized carboxylated groups of EN and exchangeable cations bound to the negatively charged mineral surfaces was regarded as the mechanism of the adsorption, and the dissociated antibiotics was immobilized on the interlamellar space of the clay mineral by cation bridging (Nowara et al., 1997). A recent study confirmed that both outer-sphere cation exchange and inner-sphere surface complexation contributed to high EN sorption on smectite, and dissolved humic acid had little influence on the EN sorption (Yan et al., 2012).

In this study, the adsorption and retention of EN on different types of clay minerals was studied. The minerals chosen were 2:1 swelling montmorillonite, 2:1 nonswelling illite, and 1:1 kaolinite, as they are all important soil components under different climate conditions. Batch experiments were conducted to examine different factors, such as the initial EN concentration, solution pH, and equilibrium time, on the antibiotic adsorption to these clays. In addition, the mechanisms of EN adsorption on these different types of clay minerals were discussed. The results could be used to guide the selection of different types of clay minerals to remove antibiotics from water and to prevent antagonistic effects when clays minerals were used as fillers for the manufacture of pharmaceuticals.

2. Experiment

2.1. Materials

The enrofloxacin used was in an HCl form with a purity of 99.7% obtained from Wuhan Yuancheng Pharmaceutical Technology Co. Ltd., China. The reported pK_{a1} and pK_{a2} values were 5.94 and 8.70

(Lizondo et al., 1997), 6.09 and 7.91 (Jiménez-Lozano et al., 2002), 6.1 and 7.7 (Barbosa et al., 2001), and 6.26 and 7.81 (Escribano et al., 1997), respectively. The molecular structure and the speciation under different pH values using the pK_{a1} and pK_{a2} values of 6.1 and 7.7 (Barbosa et al., 2001) were illustrated in Fig. 1. To prepare the EN solution, the mixture was sonicated with an S-4000 Sonicator (Qsonica, LLC., Newtown, CT, USA) for 10 min at an output energy of 45 W to ensure complete dissolution as evidenced by no appearance of un-dissolved EN in solid form. The final solution pH was 4.8 for EN solution at a concentration of 1500 mg/L.

The standard clays montmorillonite (SWy-2), illite (IMt-2), and kaolinite (KGa-1b) obtained from the Clay Mineral Repository in Purdue University (West Lafayette, IN) were used as received. Their cation exchange capacity (CEC) and SSA values were listed in Table 1.

2.2. Adsorption experiments

In the adsorption experiments, 0.1 g of clay and 20 mL of EN solution were mixed in each 50-mL centrifuge tube. As different minerals had different CEC values and the uptake of EN by these clay minerals was attributed to cation exchange, different initial EN concentrations were used. Control experiments in the presence of EN but absence of clays were performed to monitor potential loss due to handling and degradation and no measurable results between the initial and final concentrations were observed.

The adsorption kinetics were measured at an initial EN concentration 4.17 mmol/L for SWy-2, 2.23 mmol/L for IMt-2, and 0.125 mmol/L for KGa-1b at different equilibrium times. In the study of adsorption isotherms equilibrated for 24 h, the initial EN concentration varied from 1.11 to 6.68 mmol/L for SWy-2, 0.287 to 5.56 mmol/L for IMt-2 and 0.0556 to 0.223 mmol/L for KGa-1b. In order to investigate the influence of pH value on the adsorption, 1 M HCl or 1 M NaOH was added after several hours of equilibration to reach a desired pH value from 3 to 11. All above experiments were carried out in duplicate.

All tubes were shielded from light and shaken on a horizontal shaker at room temperature. After equilibrium, all samples were centrifuged at 4500 rpm for 10 min. The supernatant was filtrated

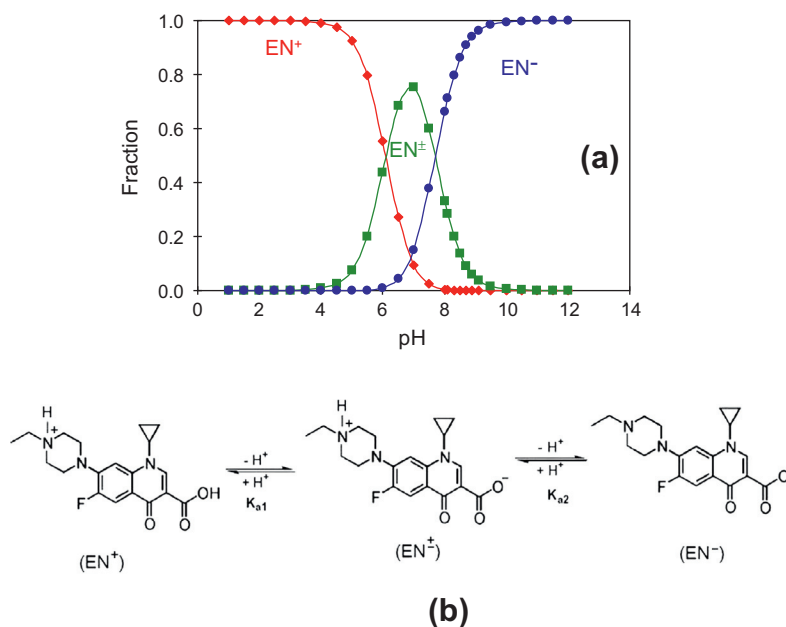


Fig. 1. Molecular structure (a) and speciation of EN under different pH conditions (b).

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