Adsorption of levofloxacin onto an iron-pillared montmorillonite (clay mineral): Kinetics, equilibrium and mechanism

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ABSTRACT

Antibiotics have been recognized as a class of emerging pollutant. In this study, Fe-pillared montmorillonite (Fe-P-Mt) was prepared and characterized by XRF, XRD, BET, and UV–vis-DRS analyses. Adsorption of levofloxacin (LVX), a fluoroquinolone antimicrobial agent, onto Fe-P-Mt was investigated as a function of contact time, LVX concentration, pH, temperature, and ionic strength by using a batch adsorption method. FT-IR spectroscopy was used to reveal the interaction of LVX and Fe-P-Mt at the molecular level. The obtained results showed that the adsorption of LVX on Fe-P-Mt followed the pseudo-second-order kinetics, and the adsorption isotherms conformed to the Langmuir model with a maxima adsorption capacity of 48.61 $mg \cdot g^{-1}$ at 25 °C. The solution pH exerted a strong influence on LVX adsorption. The maximum adsorption was found to occur around pH 7. The addition of NaCl had a minor effect on LVX adsorption, whereas the presence of NaH_2PO_4 depressed LVX adsorption due to its stronger affinity to Fe species. The thermodynamic parameters indicated that the adsorption process was endothermic and spontaneous. The mean free energies of adsorption calculated from a D–R model, on the other hand, suggested a chemisorption process. FT-IR spectroscopic analysis further revealed that LVX was adsorbed onto Fe-P-Mt via the coordination of ketone and carboxylate functional groups with an Fe atom to form a mononuclear bidentate complex. This study indicates that pillaring montmorillonite with iron species could significantly influence its adsorption behavior and mechanism toward fluoroquinolone antimicrobial agents.

1. Introduction

Fluoroquinolone (FQ) antibiotics are one of the most successful classes of drugs, and thus are widely used in human and veterinary medicines (Sukul and Spiteller, 2007). Ofloxacin, ciprofloxacin, enrofloxacin, and norfloxacin are the representatives of third generation quinolone derivatives, while levofloxacin is an active optical isomer of ofloxacin. In common with other antibiotics, a large portion of administrated FQs are excreted unmetabolized and released into the environment through application of manure and slurry to agricultural land, and receiving waters of wastewater treatment plants (Sarmah et al., 2006; Sukul and Spiteller, 2007; Teske and Arnold, 2008). As a result, low levels of various pharmaceuticals were frequently detected worldwide in diverse environmental compartments and even in drinking water (Thiele-Bruhn, 2003; Sarmah et al., 2006; Kemper, 2008). The continuous input and persistent presence of antibiotic residues in the environment may induce an irreversible adversity by directly threatening the function of the ecosystem, increasing the resistance of bacteria to drugs, and spreading the antibiotic resistance genes into the environment (Jiao et al., 2008; Kemper, 2008). Therefore, understanding the occurrence, transport, fate, and ecological toxicity of antibacterials in the soil–water environment has received growing concern over recent decades.

Adsorption and desorption are important factors governing the environmental fate of exogenous pollutants. Accordingly, much research has been done on the adsorption of FQ in soils, sediments, and soil minerals (Nowara et al., 1997; Hari et al., 2005; Carrasquillo et al., 2008; MacKay and Seremet, 2008; Vasudevan et al., 2009). The obtained results reveal that minerals play a critical role in the adsorption of antibiotics, in contrast to nonionic hydrophobic organic contaminants, in soils and sediments. So several studies focused on examining the adsorption properties and mechanisms of ciprofloxacin on pure clay minerals (montmorillonite and kaolinite) and metal oxides (aluminum and iron hydrous oxides) (Nowara et al., 1997; Goyne et al., 2005; Gu and Karthikeyan, 2005; Trivedi and Vasudevan, 2007; Wang et al., 2010, 2011; Wu et al., 2010, 2013; Li et al., 2011). The proposed adsorption mechanisms include cation exchange, cation bridge, electrostatic attraction, and hydrogen bonding with montmorillonites (Wang et al., 2011), and surface complexation with metal oxides for FQ. It should be noted that most of those studies were focused on the adsorption behavior of ciprofloxacin on pure-phase minerals such as montmorillonite or Al

and Fe oxides (Goyne et al., 2005; Trivedi and Vasudevan, 2007). However, naturally occurring soil colloids are multicomponent associations of minerals and organic matter. Clay mineral surfaces are usually coated with metal oxides and oxyhydroxides (Celis et al., 1999). The previous studies showed that aluminum- and Fe-pillared clays exhibited high affinity to some herbicides (Abate and Masini, 2005). But up to now, little is known about the adsorption behavior and mechanism of FQ on iron oxide and clay mineral composites.

Pillared clays (PLCs) are new porous materials, which can be prepared by intercalation of inorganic polycations into the interlayer of swelling clays followed by dehydration and dehydroxylation to form rigid cross-linked materials with uniform microporosity. In this regard, it is also an ideal candidate for a clay–metal oxide composite. Moreover, the increased surface area, pore volume, thermal stability and improved catalytic activity in comparison with their parent clays make them suitable as catalysts and adsorbents (Zuo and Zhou, 2008). Recently, Fe-pillared clays have been used as a heterogeneous Fenton catalyst to eliminate organic contaminants in water (De León et al., 2008). Similarly, it is expected that these materials could be used to remove the emerging FQ contaminants in aqueous solutions through adsorption or Fenton process. Nevertheless, to use these processes we need to understand the adsorption property of Fe-pillared clays to FQ as well.

Based on the above discussions, the purpose of this paper is to investigate the adsorption characteristic and mechanism of fluoroquinolone levofloxacin (LVX) onto the Fe-pillared montmorillonite (Fe-P-Mt). To our knowledge, there are few or no such studies so far. To this end, Fe-P-Mt was synthesized and characterized by XRF, XRD, N_2 adsorption and DRS UV–vis analyses. Considering the fact that previous studies on adsorption of FQ emphasized investigating the effect of pH, measuring adsorption isotherms and exploring adsorption mechanisms, little attention was paid to adsorption kinetics and thermodynamics, so this study aimed to determine the kinetics, isotherm and thermodynamic parameters for LVX adsorption on Fe-P-Mt. The effects of solution pH and addition of salt concentration on LVX adsorption were also examined. Simultaneously, FTIR was employed to find out the underlying adsorption mechanism at the molecular levels. This study would provide important information for accurate risk assessment and management of the emerging antibiotics in soil and aquatic environments.

2. Materials and methods

2.1. Materials

The KSF-montmorillonite was purchased from Aladdin (Shanghai) Reagents Co., Ltd. It contains >95% montmorillonite. The surface area of the sample is about 20 $m^2 \cdot g^{-1}$. Levofloxacin ($C_{18}H_{20}FN_3O_4$, >98%) was obtained from Xinchang Pharmaceutical Factory, China. Sodium chloride, ferric nitrate, sodium carbonate, sodium hydroxide, dibasic sodium phosphate, and hydrochloric acid were of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Xi'an, China). Deionized water was used throughout the study.

2.2. Synthesis and characterization of Fe-pillared montmorillonite

KSF-montmorillonite was initially saturated with sodium ions through washing twice with 1 $mol \cdot L^{-1}$ sodium chloride, followed by washing with deionized water. The obtained montmorillonite was labeled as Na^+-Mt. The Fe-pillared montmorillonite was synthesized according to procedures described in the literature (Chen and Zhu, 2006). Firstly, the pillaring solution was prepared as follows: Na_2CO_3 powder was slowly added into 200 mL of $Fe(NO_3)_3 \cdot 9H_2O$ solution (0.2 $mol \cdot L^{-1}$) under magnetic stirring for 2 h, until the final molar ratio of $[Na^+]/[Fe^{3+}]$ became 1:2. Then the solution was then aged at 25 °C for 1 day. Subsequently, the pillaring solution was added dropwise to 100 mL Na^+-Mt suspension (4 wt.%), and kept at 60 °C in a water bath, under vigorous stirring. The final Fe/clay ratio was set at

10 $mmol \cdot g^{-1}$ of dry Na^+-Mt. The mixture was allowed to react at room temperature for 48 h. Finally, the solid was separated, washed with deionized water to remove the excess of adsorbed ions, dried at 90 °C, then heated at 400 °C in a muffle furnace under air atmosphere for 3 h, and ground to 200-mesh, obtaining Fe-P-Mt.

The element content of raw montmorillonite and Fe-pillared montmorillonite were analyzed by X-ray fluorescence spectrometry (Magix PW2403, Panalytical, Holland). Power X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance diffractometer (Germany) using Cu Kα radiation. Specific surface area and pore volume were determined by N_2 adsorption at 77 K using a 3H-2000PS2 micromeritics apparatus (Beishide Instrument Technology (Beijing) Co., Ltd). BET surface areas were calculated by the multiple-point BET method in the relative pressure (P / P_0) range of 0.05–0.3; the total pore volume was determined at $P / P_0 = 0.98$. UV–vis diffuse reflectance spectra (DRS) were recorded on a UV–vis spectrophotometer (UV-2550, Shimadzu) equipped with an integrating sphere attachment, while $BaSO_4$ was used as a reference.

2.3. Adsorption experiments

All adsorption experiments were carried out using a batch mode. A certain amount of Fe-P-Mt was weighed into a 100-mL conical flask and contacted with 50 mL aqueous levofloxacin solution with a known initial concentration and the desired pH value. After the flask was sealed and wrapped with Al foil to prevent exposure to light, the suspensions were mechanically shaken in an air bath thermostatic at 150 rpm. At predetermined time intervals, samples were taken and centrifuged for 15 min at 12,000 rpm. The LVX concentration in the supernatant was determined. The pH value of the LVX solution was adjusted with 0.1 $mol \cdot L^{-1}$ NaOH or 0.1 $mol \cdot L^{-1}$ HCl and measured by a pH-meter (pH-S-2F, China). Unless otherwise stated, the pH values of LVX solutions were not regulated, which were ~6.8. All experiments were performed at least in duplicate, and the mean values were reported. The maximum errors were less than 3.0%.

In the kinetic experiments, 0.025 g of Fe-P-Mt was contacted with 50 mL of a series of LVX solutions with three different initial concentrations (20, 30, and 40 $mg \cdot L^{-1}$) at 25 °C for 0.25, 0.5, 1, 2, 4, 8, 12, 24, 48 and 96 h.

For isotherm studies, 0.025 g of Fe-P-Mt was mixed with 50 mL of LVX solutions with various initial concentrations (varying from 20 to 100 $mg \cdot L^{-1}$) for 48 h at 25, 35, and 45 °C.

The effect of pH on LVX adsorption was investigated in the initial pH values of LVX solutions varying from 3.0 to 10.0, while the sorbent dosage (0.5 $g \cdot L^{-1}$), LVX concentration (20 $mg \cdot L^{-1}$), reaction time (48 h), and temperature (25 °C) were constant. For the effect of salt concentration, different amounts of NaCl or NaH_2PO_4 were added into LVX solutions. Except where solution pH was natural, other experimental conditions were the same as those used in the effect of pH change.

Preliminary experiments showed that the loss of LVX due to sorption to the container walls and degradation catalyzed by clay was negligible under experimental conditions. Therefore, the amount of LVX adsorbed was calculated from the difference between the initial concentration and the equilibrium concentration as:

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where q is the amount of LVX adsorbed ($mg \cdot g^{-1}$); C_0 and C are LVX concentrations at the initial and t time ($mg \cdot L^{-1}$), respectively; V is the volume of the solution (L); and m is the mass of adsorbent (g).

2.4. Concentration and FT-IR analyses

The concentration of levofloxacin was analyzed by a UV–vis spectrophotometer (754PC, Shanghai Spectrum Instruments Co., Ltd., China).