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An insight into the removal of fluoroquinolones in activated sludge process: Sorption and biodegradation characteristics

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ABSTRACT

The detailed sorption steps and biodegradation characteristics of fluoroquinolones (FQs) including ciprofloxacin, enrofloxacin, lomefloxacin, norfloxacin, and ofloxacin were investigated through batch experiments. The results indicate that FQs at a total concentration of 500 μg/L caused little inhibition of sludge bioactivity. Sorption was the primary removal pathway of FQs in the activated sludge process, followed by biodegradation, while hydrolysis and volatilization were negligible. FQ sorption on activated sludge was a reversible process governed by surface reaction. Henry and Freundlich models could describe the FQ sorption isotherms well in the concentration range of 100–300 μg/L. Thermodynamic parameters revealed that FQ sorption on activated sludge is spontaneous, exothermic, and enthalpy-driven. Hydrophobicity-independent mechanisms determined the FQ sorption affinity with activated sludge. The zwitterion of FQs had the strongest sorption affinity, followed by cation and anion, and aerobic condition facilitated FQ sorption. FQs were slowly biodegradable, with long half-lives (>100 hr). FQ biodegradation was enhanced with increasing temperature and under aerobic condition, and thus was possibly achieved through co-metabolism during nitrification. This study provides an insight into the removal kinetics and mechanism of FQs in the activated sludge process, but also helps assess the environmental risks of FQs resulting from sludge disposal.

Introduction

Fluoroquinolones (FQs) are a class of broad-spectrum antibiotics with currently increasing use in human medical care and animal husbandry. Wastewater and solid waste originating from residential areas, hospitals, pharmaceutical manufacturers, livestock farms, and aquaculture facilities constitute the main sources of FQ contamination (Sukul and Spiteller, 2007; Lin et al., 2008). FQs are released into the natural environment along with wastewater discharge and waste disposal, and transport across multiple environmental media *via* various interactions, *e.g.*, runoff, percolation, partitioning, and bioaccumulation (Van Doorslaer et al., 2014). Therefore, residual FQs have been frequently detected in aqueous matrices, soils, sediments, and biota (Gothwal and Shashidhar, 2015). Although their environmental concentrations are very low, usually at ng/L to μg/L in water phases and ng/kg to mg/kg in solid phases, FQs have still attracted increasing attention because of their potential ecological risks arising from the selective formation of antibiotic-resistant bacteria over the long term (Van Doorslaer et al., 2014; Gothwal and Shashidhar, 2015).

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FQs originating from multiple sources are usually discharged with sewage into wastewater treatment plants (WWTPs), which are considered to be the last barrier to minimize FQ release to the environment. Hence, the behavior of FQs in WWTPs deserves great concern. The occurrence and fate of FQs in WWTPs have been investigated through field sampling (Verlicchi et al., 2012; Yuan et al., 2015). Mass balance has also been performed to determine FQ removal efficiencies and potential removal pathways in WWTPs (Golet et al., 2002; Lindberg et al., 2006). Furthermore, the effects of operational strategies, *e.g.*, sludge retention time (SRT), hydraulic retention time (HRT), and redox conditions, have also been evaluated by comparing the removal of FQs in WWTPs with varying designs and operations (Batt et al., 2007). Despite the well-known advantages, there are some difficulties in performing and controlling field investigations in WWTPs. For instance, the contributions of sorption and biodegradation to the overall removal of FQs may be overrated or underrated due to the fluctuations of sewage flow and excess sludge discharge. The solid-water sorption coefficient obtained by single-point calculation rather than sorption isotherms may not represent the FQs' sorption affinity appropriately at other concentrations (Stevens-Garmon et al., 2011).

To overcome the uncertainties of field sampling, well-controlled lab-scale reactors have been employed to evaluate the removal of FQs in the activated sludge process, and clarify the contributions and characteristics of different removal pathways, *e.g.*, sorption and biodegradation (Wu et al., 2009; Dorival-Garcia et al., 2013). To date, most studies concerning FQ sorption on activated sludge have focused on equilibrium time, isotherms, and effects of operational conditions (*e.g.*, concentrations of FQs and activated sludge, redox conditions, pH, and co-existing ions) on FQ sorption (Zhou et al., 2013; Polesel et al., 2015); whereas the detailed sorption steps (*e.g.*, film diffusion, intra-particle diffusion, and surface reaction) are rarely discussed. On the other hand, the role of biodegradation in the removal of FQs is not yet clear, and the limited studies on FQ biodegradation have yielded different results (Van Doorslaer et al., 2014).

Therefore, this study aimed to provide an insight into the removal of FQs in the activated sludge process, especially the roles and characteristics of FQ sorption and biodegradation. Ciprofloxacin (CIP), enrofloxacin (ENR), lomefloxacin (LOM), norfloxacin (NOR), and ofloxacin (OFL) were selected as target FQ antibiotics. Batch experiments were carried out to investigate the inhibition of sludge bioactivity by FQs, as well as the removal pathways and sorption isotherms of FQs in the activated sludge process. Moreover, different models were employed to clarify the rate-limiting step of FQ sorption on activated sludge, the effects of FQ speciation and sludge properties on sorption affinity, and the biodegradability of FQs under different redox conditions.

1. Materials and methods

1.1. Chemicals

The standards of caffeine (CAF) and LOM were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). NOR, OFL, CIP, and ENR were provided by Sigma-Aldrich (St. Louis, MO, USA). Caffeine-$^{13}C_3$ (Cerilliant, Round Rock, TX, USA) and ofloxacin-D_3 (Witega, Berlin, Germany) were used as internal standards (ISs). The purity of all the standards was ≥98%, and the major physicochemical properties of studied FQs and ISs are summarized in Appendix A. Table S1. HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Geel, Belgium), and formic acid (purity > 99%) from Dikma Technologies, Inc. (Lake Forest, GA, USA). NaN_3 was obtained from Sigma-Aldrich (St. Louis, MO, USA). Other chemicals of at least analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). The stock solutions of CAF (100 mg/L), FQs (100 mg/L each), and ISs (10 mg/L each) were used in batch experiments. Mill-Q water was produced by passing distilled water through a Milli-Q purification system (Advantage A10, Millipore, Billerica, MA, USA).

1.2. Batch experiments

Batch experiments were performed using activated sludge from a lab-scale sequencing batch reactor (SBR) fed with synthetic wastewater (Appendix A. Text S1). The activated sludge was repeatedly centrifuged and washed with Mill-Q water three times. After the last centrifugation, the remaining sludge was suspended in synthetic wastewater to reach a desired concentration of mixed liquor suspended solids (MLSS) (3.8 g/L), which is referred to as treated sludge hereafter. The treated sludges originating from the aerobic and anoxic stages of the SBR were used in the experiments carried out under aerobic and anoxic conditions, respectively.

Three series of batch experiments were carried out using 250-mL Erlenmeyer flasks (working volume: 200 mL), with experimental conditions shown in Table 1. CAF and NaN_3 were used to indicate the sludge bioactivity and inhibit the potential biodegradation of FQs in the activated sludge process, respectively. All the flasks were wrapped with aluminum foil to avoid possible photolysis. Comparisons of CAF biodegradation in Control A with that in Group I or II could indicate the inhibition degree of FQs or NaN_3 on sludge bioactivity, respectively. The potential removal pathways of FQs in the activated sludge process include hydrolysis, volatilization, sorption, and biodegradation (Kummerer, 2009). All four pathways could simultaneously occur in Group IV, while biodegradation was excluded in Group III with the addition of NaN_3. In Control B, only hydrolysis and volatilization accounted for the possible removal of FQs.

FQ or CAF stock solution was spiked into the flask to achieve the desired initial concentration (Table 1). Aerobic and anoxic conditions were provided by magnetic stirring in open and sealed flasks, respectively. The dissolved oxygen (DO) concentrations under each condition were 3.0–4.0 and <0.7 mg/L, respectively. Temperature was controlled by a thermostatic water bath. Initial pH was adjusted by HCl and NaOH solutions. For Control A and Groups I–IV, slurry samples were taken from the flask *via* syringe at the following times: 5, 10, 20, 30, 40, 50 min; and 1, 1.5, 2, 3, 4, 6, 8, 10, 12, 18, 24, 36, 48, 50 hr, respectively. For Control B, sampling times were 1, 2, 4, 6, 8, 10, 12, 24, 36, 48 hr. For Groups V and VI, samples were collected after 6 hr of exposure. All experiments were performed in duplicate, and duplicate samples (2 mL each) were taken from each parallel experiment.

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