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Partition and fate analysis of fluoroquinolones in sewage sludge during anaerobic digestion with thermal hydrolysis pretreatment

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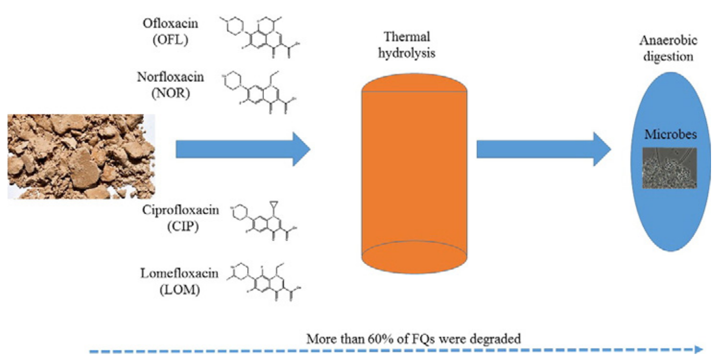
HIGHLIGHTS

- A SPE with HPLC-FLD method was successfully applied for analysis of FQs in sludge.
- Thermal hydrolysis did not remove FQs but increased their distribution in liquid.
- Anaerobic digestion alone removed >60% of FQs.
- The inhibitory effects of FQs to microbial community was mitigated.
- The individual FQ differs greatly in their fate and distribution.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluoroquinolones (FQs) are broad-spectrum synthetic antibiotics that play an important role in the treatment of serious bacterial infections. FQs can reach wastewater treatment plants from different routes, and eventually accumulate in activated sludge. In this study, a solid-phase extraction (SPE) with HPLC-FLD detection method was utilized to investigate the partition and fate of FQs in digested sludge when thermal hydrolysis was used as pretreatment. As a result, thermal hydrolysis showed minor effects on the fate of FQs in batch anaerobic digestion processes, while anaerobic digestion alone removed >60% FQs and finally assisted in the mitigation of the inhibitory effects to microbial communities.

1. Introduction

Fluoroquinolone (FQ) antibiotics, firstly synthesized in the 1980s, are capable of selectively inhibiting harmful bacteria and preventing infections (Hamad, 2010). The presence of fluorine in FQs confers biological resistance to human bodies, which renders these compounds as ubiquitous environmental contaminants. In general, 22–87% of consumed FQs are excreted in urine or feces from patients and resulted in domestic and hospital wastewaters with FQs ranging from ng/L up to μg/L (Larsson et al., 2007). FQs in effluents from pharmaceutical manufacturing facilities could even reach mg/L level (Kolpin et al., 2002). Since sludge retention time (SRT) in wastewater treatment

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plants (WWTPs) is shorter than the half-life of those pharmaceuticals (Carballa et al., 2004), >70% original FQs could not be completely removed by bioremediation, causing activated sludge to act as a reservoir of FQs (Lindberg et al., 2005). The enriched FQs in sludge are slowly released into soil and aquatic environment, rendering bacteria, aquatic organism, and insects tolerant to antibiotics (Lindberg et al., 2006; Amorim et al., 2014a; Li et al., 2015). After the introduction of FQs into agriculture, ciprofloxacin (CIP) resistance gene, as an example, was observed to be among several genera of bacteria: *Campylobacter*, *Salmonella*, and *Colibacter* (Navarro-Gonzalez et al., 2013). Thus, the investigation on the fate of many pharmaceuticals in the environment, especially in WWTPs, has gained interest over the last decade (Jia et al., 2012; Lindberg et al., 2006).

So far, anaerobic digestion processes have been applied in treating settled and dewatered sludge, providing superior stabilization of the contained organic wastes. In addition, thermal hydrolysis is commercially implemented and utilized to successfully accelerate the breakdown of cell walls and the solubilization of organic matters (Xue et al., 2015). During thermal hydrolysis pretreatment, sludge adsorptivity is greatly altered, which might also change partition coefficients of adsorbed FQs (Laurent et al., 2011). However, few studies have investigated the degradation and distribution of FQs during sludge treatment and subsequent disposal processes, especially in regards to the processes combining sludge pretreatment.

In this study, the robust and efficient SPE-HPLC-FLD method was conducted to determine the solid/liquid partitions of FQs compounds in digested sludge with thermal-hydrolysis pretreatment. Four representative FQs with fluorescent characteristics (Ofloxacin (OFL), Norfloxacin (NOR), CIP, Lomefloxacin (LOM)) were analyzed. The distribution of the FQs in thermal-hydrolyzed sludge, the effects of the FQs on batch anaerobic digestion performance, and the roles of anaerobic digestion in the FQs degradation were clarified.

2. Materials and methods

2.1. Chemicals and reagents

The physicochemical properties of the four standard FQs are shown in Table 1 (Ternes and Joss, 2006). The SPE cartridge HLB (6 mL, 500 mg) was purchased from Waters (USA). The HPLC grade methanol and acetonitrile were bought from Anpel (Shanghai, China).

The four FQ stocks were prepared as follows: 20 mg of each FQ was diluted to 200 mL using formic acid solution (pH 3) and stored at 4 °C in brown bottles. The FQ working solutions were prepared by diluting the stock solution to 10 mg/L and then different concentrations in the initial mobile eluent (phosphoric acid-triethylamine buffer: methanol ratio, 80:20). The phosphoric acid-triethylamine buffer was prepared by diluting phosphoric acid to 0.1% (v/v) and subsequently adding triethylamine to adjust the pH to 3.0.

2.2. FQs partitions in sludge before and after thermal hydrolysis

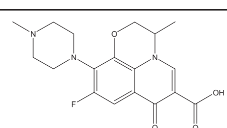
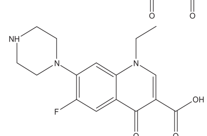
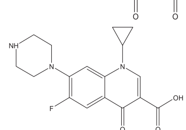
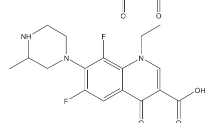
The hydrolysis effect on FQ degradation and distribution was evaluated by monitoring the changes of FQ concentrations before and after thermal hydrolysis. The initial pH was set to be 3, 7, and 11 in the original 20 mg/L standard samples. 40 mL of each were poured into a Teflon Jar and incubated at 160 °C for 1 h to avoid the insufficient heating time due to the heat absorption by the Teflon Jar. The samples were allowed to slowly return to room temperature and the Teflon Jar was then opened. A specific amount of each liquid sample was collected and the pH was adjusted to 3. Following the developed protocol, the samples were analyzed by HPLC to determine FQ concentrations in the liquid samples before and after thermal hydrolysis.

Meanwhile, in order to further homogenize FQs and ensure the composition of sewage sludge, the dewatered sludge (total solids (TS) = 16.69%, VS (volatile solids)/TS = 69.39%) was diluted 4-fold, decreasing TS to 4.17%. 2 mg/kgDS (ppm), 20 mg/kgDS (ppm), and 100 mg/kgDS (ppm) of FQs were added to the sludge samples, which represented the FQs concentrations ranging from typical sewage sludge samples (Golet et al., 2003) to pharmaceutical sludge samples (Kolpin et al., 2002). The samples were then shaken at 300 rpm for 20 min for FQs homogenization. Afterwards, the degradability of FQs in batch anaerobic digestion processes (28 days) with or without thermal hydrolysis was determined. All the determinations were conducted in triplicate.

2.3. Effects of FQs on biogas yield and FQs degradation in batch anaerobic digesters

The sludge samples spiked with 2, 20, and 100 ppm FQs were pretreated with or without thermal hydrolysis. The sludge samples were seeded by the digestate from a lab-scale thermophilic anaerobic digester of dewatered sludge with a 1:2 ratio on volatile solids (VS) base for the following biochemical methane potential (BMP) experiments (Table S1). The gas yield was periodically detected for 4 weeks and the TS and VS/TS were determined to evaluate the effects of different addition of FQs on the performance of anaerobic digestion with or without thermal hydrolysis pretreatment.

Table 1
Physicochemical properties of the four FQs investigated in the study.

Name	Structure	Molecular formula	Molecular weight	CAS	pKa	LogKow
Ofloxacin (OFL)		$C_{18}H_{20}FN_3O_4$	361.37	82,419–36-1	6.95; 7.65	−0.39
Norfloxacin (NOR)		$C_{16}H_{18}FN_3O_3$	319.33	70,458–96-7	6.3; 8.4	−1.03
Ciprofloxacin (CIP)		$C_{17}H_{18}FN_3O_3$	331.34	85,721–33-1	6.0; 8.8	0.28
Lomefloxacin (LOM)		$C_{17}H_{19}F_2N_3O_3$	351.35	98,079–51-7	5.8; 9.3	−0.3