Bioresource Technology 144 (2013) 644–651

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Adsorption, inhibition, and biotransformation of ciprofloxacin under aerobic conditions

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HIGHLIGHTS

- Ciprofloxacin (CIP) degraded in a poultry litter extract-fed aerobic culture.
- Aerobic culture was inhibited by CIP at 10 mg/L or higher.
- The degree of inhibition increased with increasing CIP concentration.
- A CIP biotransformation product was proposed based on HPLC/UV/MS analysis.
- The antibiotic quinolone moiety in CIP was not transformed under aerobic conditions.

ARTICLE INFO

Article history:
Received 25 May 2013
Received in revised form 4 July 2013
Accepted 8 July 2013
Available online 13 July 2013

Keywords:
Ciprofloxacin
Adsorption
Inhibition
Aerobic biotransformation
Mineralization

ABSTRACT

The adsorption, inhibition, and biotransformation of the fluoroquinolone antibiotic ciprofloxacin (CIP) under aerobic conditions were investigated in this study. The maximum adsorption capacity and the Langmuir constant were 37.9 mg CIP/g VSS and 37 L/g, respectively. A glucose-fed aerobic culture was inhibited by CIP at 10 mg/L or higher and the degree of inhibition increased with increasing CIP concentration. However, the microbial activity recovered to some extent with prolonged incubation under a semi-continuous feeding mode. A low extent of CIP biotransformation was observed in an aerobic, glucose-fed culture derived from poultry litter extract. LC/UV/MS analysis of the biotransformation product showed that only the piperazine ring was oxidized, while the antibiotic quinolone part of CIP was intact.
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1. Introduction

Ciprofloxacin (CIP) is a common human and veterinary broad-spectrum fluoroquinolone antibiotic which consists of a quinolone structure and a piperazine moiety. The core quinolone structure is the effective antibiotic site which prevents DNA from unwinding and duplicating (Hooper, 2001). CIP can exit the target organisms unaltered with up to 72% of the nonmetabolized form being excreted (Daughton and Ternes, 1999). CIP residues have been widely found in wastewater and surface water (Li et al., 2011). Furthermore, CIP strongly adsorbs on sewage sludge solids with concentrations up to 6.3 mg/kg dry matter (Golet et al., 2002) and accumulates in soils after application of CIP-bearing biosolids (Golet et al., 2003). The ubiquitous occurrence of antibiotics in the environment has been proposed as a leading cause of the rise in antibiotic resistance for both pathogenic and not pathogenic bacteria, which has tremendous implications in terms of both human and environmental health.

Previous studies have shown potential photosensitivity of CIP. Turiel et al. (2004) found CIP in river water was stable for at least two weeks at ambient temperature, but completely degraded after 3 months of storage. Lin et al. (2010) concluded that natural irradiation plays a major role in the degradation of CIP in pond water and even in the sediment slurry in a laboratory study. Nevertheless, it is generally assumed that CIP adsorbed to solids does not photodegrade. Notably, Cardoza et al. (2005) indicated that even low particulate organic carbon levels result in reduced photodegradation, but soluble CIP disappearance rates were accelerated due to adsorption.

CIP strongly adsorbs on sewage sludge solids and accumulates in soils. Based on data from the Zurich-Werdhölzli wastewater treatment plant (WWTP) in Switzerland, Golet et al. (2003) found that 83 ± 14% of CIP in raw sewage was ultimately found in the anaerobically digested sludge and may have resulted in the

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http://dx.doi.org/10.1016/j.biortech.2013.07.031

accumulation of antibiotics in the biosolids-treated soil. Similar results were also obtained in a WWTP in Umeå, Sweden (Lindberg et al., 2006). In a simulated activated sludge process, Li and Zhang (2010) reported that 90.8% and 52.8% of amended CIP was removed in the first 15 min while treating freshwater and saline sewage, respectively. The interaction of CIP with various materials, such as aerobically digested biosolids (Wu et al., 2009), goethite (Carrasquillo et al., 2008; Zhang and Huang, 2007), kaolinite (Li et al., 2011; Mackay and Seremet, 2008), hydrous aluminum oxides (Gu and Karthikeyan, 2005), and hydroxyapatite (Ivashchenko et al., 2011) has been investigated. Langmuir isotherms were generally employed to fit the adsorption data in previous studies.

The CIP biodegradation potential is important in order to better understand the fate of CIP in both engineered and natural systems, especially related to wastewater treatment processes. A few investigations have found that some fungus species could significantly transform CIP but at relatively low rates (Wetzstein et al., 1999; Parshikov et al., 2001; Prieto et al., 2011). However, systematic laboratory studies on CIP biotransformation under different redox conditions representative of WWTPs are still scarce. In an OECD closed bottle test performed with a mixed bacterial population from the effluent of a municipal WWTP, CIP was not biodegraded even after 48 days of aerobic incubation (Kümmerer et al., 2000). There was also no significant removal of CIP under methanogenic conditions in a field evaluation (Golet et al., 2003). The only observed CIP biodegradation in the activated sludge process was reported by Li and Zhang (2010) who found that 32.2% of CIP was biodegraded after 48 h of incubation in the mixed liquor obtained from the aeration tanks of a WWTP treating saline sewage. However, they noted that this incomplete CIP biodegradation needed higher retention times than those typically used in most WWTPs. Furthermore, the biodegradation of CIP observed in this study mainly related to some special fluoroquinolones-degrading bacteria which only existed in the saline activated sludge. Fluoroquinolones such as norfloxacin, ciprofloxacin, danofloxacin, and enrofloxacin are commonly used in animal production and residual fluoroquinolones were found in poultry litters at concentrations of 1.37–6.68 mg/kg (Khan et al., 2005; Sapkota et al., 2011; Leal et al., 2012). Thus, fluoroquinolone-resistant and CIP-degrading bacterial strains may exist in poultry litter.

The objective of this study was to investigate the inhibition and biotransformation potential of CIP under aerobic conditions. Adsorption of CIP onto biomass was also evaluated mainly for its effect on CIP biotransformation. Two aerobic cultures were used in this study for the biotransformation assays: a glucose-fed culture developed with inoculum from a contaminated river sediment, and a glucose-fed culture developed with inoculum from a poultry litter extract.

2. Methods

2.1. Chemicals

Ciprofloxacin hydrochloride monohydrate ($C_{17}H_{18}FN_3O_3 \cdot HCl \cdot H_2O$) was obtained at >98.0% purity from Tokyo Chemical Industry Co., Ltd. (TCI America) and a CIP stock solution of 1000 mg/L was prepared in deionized (DI) water.

2.2. Aerobic cultures

Two aerobic cultures were used in this study, a glucose-fed culture developed with inoculum from a contaminated river sediment (R_G), and a glucose-fed culture developed with inoculum from a poultry litter extract (R_{PL}). The original, two stock cultures had been maintained in the laboratory fed-batch dextrin/peptone or poultry litter water extract, respectively, for over 2 years with a 14 days retention time. The poultry litter which contained antibiotic residues was collected from a chicken farm in the State of Georgia, USA. Both cultures were washed with 10 mM phosphate buffered DI water three times to eliminate nitrate and other possible interfering substances in the original cultures before any use. The washed cultures were then placed in 2 L glass reactors along with culture media to a total liquid volume of 1.5 L. The two cultures were fed with 500 mg/L glucose and 26.7 mg NH_4 N/L twice a week corresponding to an average organic and ammonia nitrogen loading rate of 152.4 mg COD/L day and 7.6 mg NH_4 N/L day, respectively. Both cultures were aerated with pre-humidified compressed air passed through a fine pore diffuser, mixed with a magnetic stirrer and maintained at room temperature (22–24 °C). The culture media contained (in mg/L): K_2HPO_4, 1070; KH_2PO_4, 524; $CaCl_2 \cdot 2H_2O$, 68; $MgCl_2 \cdot 6H_2O$, 135; $MgSO_4 \cdot 7H_2O$, 268; and $FeCl_2 \cdot 4H_2O$, 68. In addition, 0.67 mL/L of a trace metal stock solution was also added (Misiti et al., 2013). Over 90% of the feed soluble COD (sCOD) was degraded within the first day after feeding in both cultures. The final sCOD at the end of each feeding cycle was between 70 and 120 mg/L. The steady-state volatile suspended solids (VSS) concentration of the R_G and R_{PL} cultures was 0.98 ± 0.03 and 1.05 ± 0.01 g/L (mean ± standard deviation), respectively.

2.3. Batch adsorption assay

A batch adsorption assay was performed to determine the partition coefficient of CIP to biomass obtained from an aerobic, glucose-fed CIP-free aerobic culture. In order to achieve a higher biomass concentration, 500 mL of culture waste was collected and settled for 2 h. The supernatant was discarded and the concentrated culture was centrifuged for 5 min at 4000 rpm. The culture pellet was then rinsed with 150 mL of 10 mM phosphate buffered DI water and then used in the adsorption assay. All samples were prepared in triplicate 40 mL Teflon centrifuge tubes with 20 mL liquid volume at initial CIP concentrations of 10, 30, 50, and 100 mg/L. Each tube was amended with about 200 mg VSS/L and 10 mM phosphate buffered CIP solution amended with 200 mg/L sodium azide (in the culture) to achieve the desired initial CIP concentration. Sodium azide was used as an inhibitor to suppress any biological activity and prevent possible biotransformation of CIP (Ismail et al., 2010). The pH was 7.0 in all tubes. An abiotic, control tube without biomass was also prepared at each CIP concentration. After measurement of initial CIP concentration in the control tubes, each tube was sealed with a Teflon cap and then shaken at 190 rpm on an orbital shaker at 22 °C for 24 h. After 24 h, the liquid-phase CIP concentration was measured and the CIP adsorbed to biomass was calculated by difference of total and aqueous CIP mass. It is noteworthy that a preliminary kinetic test showed that adsorption equilibrium was achieved in less than 24 h (data not shown).

2.4. Batch inhibition assays

The R_G culture was used in all batch inhibition assays considering that there was no significant difference in the rate of glucose degradation between the R_G and R_{PL} cultures in preliminary tests (data not shown). Glucose and ammonia chloride stock solutions were used in all inhibition and biotransformation assays (Section 2.5, below) to achieve initial concentrations of 500 mg glucose/L and 26.7 mg NH_4-N/L, respectively.

A batch glucose degradation assay was carried out to investigate the inhibitory effect of CIP on the glucose consumption in the R_G aerobic culture exposed to a range of CIP concentrations. This assay was conducted in duplicate 250 mL Erlenmeyer flasks with 150 mL liquid volume. A sample of 120 mL of the R_G culture was added to each flask along with 15 mL culture media. After glucose and ammonia addition, the Erlenmeyer flasks were amended

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