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Accelerated ciprofloxacin biodegradation in the presence of magnetite nanoparticles

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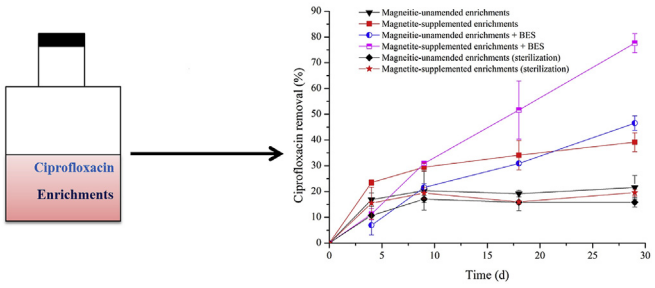
HIGHLIGHTS

- The magnetite-supplemented enrichments degraded ciprofloxacin rapidly.
- BES addition improved ciprofloxacin degradation by the enrichments.
- Addition of magnetite and/or BES shifted the bacterial community composition.

GRAPHICAL ABSTRACT



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ABSTRACT

Ciprofloxacin (CIP) biodegradation was investigated using enrichments obtained in the presence of magnetite nanoparticles, CIP and human fecal sewage. CIP addition inhibited methanogenic activity and altered the bacterial community composition. The magnetite-supplemented enrichments significantly promoted CIP biodegradation, especially in the presence of 2-bromoethanesulfonate (BES). When BES was added, CIP biodegradation in the magnetite-supplemented enrichments was 67% higher than in the magnetite-unamended enrichments. Fe (II) concentrations were also significantly increased in the BES and magnetite-supplemented enrichments. This indicated that there might be a positive relationship of CIP biodegradation with microbial reduction of Fe (III) to Fe (II). As for the magnetite-supplemented enrichments, DNA-sequencing analysis revealed that *Stenotrophomonas* was the dominant genus, while *Desulfovibrio* became the dominant genus in the presence of BES. These two genera might be related to Fe (III) reduction in the magnetite. The findings provide a strategy for improving CIP biodegradation during waste treatment.

1. Introduction

Ciprofloxacin (CIP) is a third generation fluoroquinolone commonly used in human and veterinary medicine. High proportions of CIP are usually incompletely metabolized in humans and livestock, and excreted as the parent substance (Daughton and Ternes, 1999). CIP residues can reach the soil-water ecosystem with effluents of wastewater treatment plant, manure, and sludge (Golet et al., 2003; Motoyama et al., 2011; Jia et al., 2012). This creates potential threats to ecosystem and human health due to potential development and spread of antibiotic resistance. Therefore, it is necessary to consider CIP removal prior to release into the environment.

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Over the past years, data have demonstrated that sorption and biodegradation were the main removal routes for CIP during wastewater treatment. Although CIP biodegradation has been observed in an aerobic sludge system (Li and Zhang, 2010; Dorival-García et al., 2013), a number of studies have documented that sorption ranging from 50% to 100% was the main route of CIP removal (Golet et al., 2003; Lindberg et al., 2005, 2006; Li and Zhang, 2010; Jia et al., 2012; Amorim et al., 2014). This indicated that sludge can act as the reservoir of CIP for releasing CIP into the environment, highlighting the importance of developing the sludge management strategies (Golet et al., 2003). Although anaerobic digestion (AD) is a common technology for sludge stabilization, it is often designed to eliminate organic matter without particular consideration for removal of antibiotics. The biodegradation efficiency due to resistance of CIP to digestion was only in the range of 0–40% during sludge treatment (Golet et al., 2003; Lindberg et al., 2006; Li et al., 2013; Liu et al., 2013). Most of CIP remained in the digested sludge. Therefore, it is imperative to develop a strategy to eliminate CIP residues when designing high efficiency of AD processes in biogas digesters.

Recently, much work reported that magnetite nanoparticles can accelerate biodegradation of organic matter (e.g. ethanol, acetate, propionate and butyrate) (Kato et al., 2012; Cruz Viggi et al., 2014; Li et al., 2015; Yang et al., 2015a, 2015b, 2016). In this process, it is thought that magnetite can function by facilitating interspecies electron transfer (IET) between syntrophic partners. Additionally, existing evidence has showed that magnetite can promote biodegradation of organic pollutants (e.g. trichloroethene and benzoate) (Aulenta et al., 2013; Zhuang et al., 2015). Thus, these findings led to a hypothesis that magnetite addition to anaerobic digested sludge might enhance CIP biodegradation during AD.

In testing this hypothesis, the digested sludge enrichments obtained in the presence of magnetite, CIP and fecal sewage were firstly established. Using the resulted enrichments, both CIP biodegradation and microbial community structure were subsequently investigated.

2. Materials and methods

2.1. Feedstock, seed sludge and enrichments

Human fecal sewage that used as feedstock was collected from community toilets in Qingdao. The total solids (TS) content of fecal sewage was 2.1% (w/w). Volatile solids (VS) are the solids in fecal sewage or sludge that are lost on ignition of dry solids at 550 °C. To calculate conveniently the organic content of fecal sewage or sludge, VS was used as an indicator to represent the organic content of fecal sewage or sludge. 61.3% of TS in fecal sewage was VS. Magnetite nanoparticles were prepared according to a previous method (Kang et al., 1996). Anaerobic granular sludge was obtained from a brewery facility in Qingdao. VS of sludge accounted for 90% (w/w) of TS. The sludge was used as inoculum and homogenized prior to use.

Enrichments were obtained via the repeated batch cultivation under anaerobic condition (37 °C). Three experimental conditions were designed: (1) control (named as C), which was performed in the absence of magnetite and CIP; (2) magnetite-supplemented bottles (named as M), and (3) magnetite-unamended bottles (named as MU). Groups (2) and (3) were performed in the presence of CIP. The enrichments were prepared by inoculating the seed sludge (1 g-VS/L) into 120 mL sealed bottles in the absence and presence of 20 mM magnetite. Each bottle contained 50 mL medium amended with 1.2 g-VS/L of fecal sewage and 200 mg/L (final concentration) of CIP. 25 mL of enrichments were periodically transferred into fresh medium. After three cycles of enrichment cultivation, the resulted enrichments were used to perform subsequent experiments for CIP biodegradation. The details of experimental conditions were shown in Table S1. The medium (pH 7.0) was prepared as described previously (Yang et al., 2015b).

2.2. CIP biodegradation

Two successive batch cultivations were performed at 37 °C in 120 mL of bottles with a working volume of 50 mL. Each test was performed in duplicate without shaking under anaerobic conditions. In the first feeding cycle, 5 mL of enrichments were inoculated into fresh medium containing 1.2 g-VS/L of fecal sewage and 50 mg/L CIP. When CIP removal reached a plateau, subcultures for the second feeding cycle were performed by inoculating 5 mL of enrichments from the first feeding cycle to fresh medium. In the second feeding cycle, 100 mM of 2-bromoethanesulfonate (BES) was used to investigate CIP biodegradation. To investigate the effects of sorption on CIP removal, the feedstock and inoculum were treated in an autoclave at 121 °C for 3 h to inactivate the microorganisms. The detailed experimental conditions were depicted in Table 1.

2.3. Analytical methods

Methane was periodically analyzed using a gas chromatograph as described previously (Yang et al., 2015b). TS was determined at 105 °C (Yang et al., 2015b). VS was measured after igniting at 550 °C for 2 h in a muffle furnace according to the standard method (APHA, 1998). CIP in the samples was analyzed using high performance liquid chromatography (Waters 2998) equipped with UV detection (280 nm) and ZORBAX SB-C18 column (Agilent). 0.05% H_3PO_4 (A) and acetonitrile (B) was used as the mobile phase at a flow rate of 1 mL/min at 30 °C. A linear gradient was listed as follows: 10 min, 90% A; 7 min, 80% A; 13 min, 90% A. The X-ray diffraction spectrum (XRD) was determined by a $2\theta/\theta$ method using X-ray diffraction (Bruker D8 Advance). XRD was used to check whether magnetite structure was maintained during CIP biodegradation.

The total genomic DNA extraction of samples, DNA quantification, PCR amplification, and construction of amplicon library targeted for V3-V5 region of 16S rDNA were carried out as described previously (Fu et al., 2016). Illumina sequencing was performed at GENEWIZ, Inc. (Suzhou, China). Sequence analysis and taxonomic classifications were performed as previously described (Yang et al., 2015b).

3. Results and discussion

3.1. Inhibitory effects of methane production

The methane yields during the repeated batch cultivation were shown in Table S2. The methane yield from control was average 146.9 mL/g-VS. When CIP was added into the bottles, the methane yields in group M and MU were average 47.4 mL/g-VS and 45 mL/g-VS, respectively. Table S2 also shows that the methane production rates in group M and MU were average 65.8% and 66.2% lower than in control, respectively. Additionally, as for the acclimated enrichments (Fig. 1b and d), less methane (<1 mL in the headspace of bottles) was produced during two successive feeding cycles. Although magnetite addition facilitated methane production during the first feeding cycle (Fig. 1b), the methane yield in the magnetite-supplemented enrichments was similar to that in the magnetite-unamended enrichments during the second feeding cycle (Fig. 1d). These findings indicated that CIP addition substantially inhibited methane production from the human fecal sewage. This was similar to a previous report that a significant