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Enhanced anaerobic degradation of amide pharmaceuticals by dosing ferroferric oxide or anthraquinone-2, 6-disulfonate

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ABSTRACT

Amide pharmaceuticals cannot be removed easily in conventional wastewater treatment processes, and the dosage of redox mediators may enhance their removals under anaerobic conditions. Anaerobic batch experiments were carried out for the removals of amide pharmaceuticals with the dosage of ferroferric oxide or anthraquinone-2,6-disulfonate. Factors of redox mediators, organic carbon and steps of anaerobic treatment on the removals of amide pharmaceuticals were evaluated. For primidone, carbamazepine and crotamiton, their removals were poor during anaerobic treatment, and the addition of redox mediators enhanced their removals. For sulfamethoxazole, it was effectively removed by anaerobic treatment (above 90%) and the dosage of redox mediator accelerated its removal. The cooperation of carbon source and redox mediators accelerated the removals of amide pharmaceuticals, but the types of organic carbon had little influence on the anaerobic degradation of amide pharmaceuticals. Furthermore, the hydrolysis/acidification step contributed significantly to the removal of amide pharmaceuticals during anaerobic treatment. For the control of amide pharmaceuticals in wastewater, the incorporation of anaerobic process into the wastewater treatment stream is a valuable strategy, especially with the dosage of redox mediators.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are widely used in the fields of medicine, farming industries and our daily life [1]. The existence of PPCPs has been widely reported in aquifer environments [2,3]. Among PPCPs, amide pharmaceuticals are compounds with the amide functional group (i.e., carbamazepine (CBM), primidone (PRM), and crotamiton (CRT)), and sulfamethoxazole (SMX) is a sulfonamide which can also be considered as an amide pharmaceutical. In municipal wastewater, these amide pharmaceuticals have been widely detected [4]. More specifically, high concentration of amide pharmaceutical was detected in the effluent from hospitals, i.e., 0.73 μg/L CBM and 4.2 μg/L SMX [5]. Conventional activated sludge (CAS) wastewater treatment processes and soil aquifer treatment could not remove amide pharmaceuticals easily [4,6,7], while effective removals of amide pharmaceuticals were observed during chlorination and ozonation [8–10], but high cost is disadvantage for the application of chlorination and ozonation for wastewater treatment. Therefore, the implementation of an effective technology is necessary for the removal of amide pharmaceuticals from wastewater to protect the safety of receiving water bodies. Previous studies reported that anaerobic treatment is a reliable and economically feasible alternative for treating high strength wastewater with antibiotics [11]. Thus, anaerobic treatment may be suitable for controlling amide pharmaceuticals.

Anaerobic treatment involves various types of microorganisms and many steps for converting organic matters to methane (CH_4) and CO_2. As a biological process, interspecies electron transfer plays an important role in anaerobic treatment. Interspecies electron transfer through hydrogen and/or formate has been investigated intensively and been considered as the main pathways [12]. Recently, direct interspecies electron transfer (DIET) has been shown to be dominant under some conditions, such as *Geobacter* dominated systems [13]. During DIET, redox mediators, such as ferroferric oxide (Fe_3O_4) and anthraquinone-2, 6-disulfonate (AQDS) have been proposed to be electron transfer media facilitating DIET [14–16]. By the present of redox mediator, the CH_4 production rate was significantly accelerated in anaerobic treatment processes [17,18]. Yin et al. [19] reported that Fe_3O_4 dosage could enhance the maximum CH_4 production rate, and shorten the lag phase in anaerobic treatment process. During anaerobic treatment, redox mediator might act as an 'electron shuttle' between

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the enzyme and the pharmaceuticals, resulting in enhanced anaerobic biodegradation of pharmaceuticals, and the enhancement of anaerobic degradation depends predominantly on the type of redox mediators and the structure of pharmaceuticals [20]. However, up to date, no study had been carried out for the removals of amide pharmaceuticals during anaerobic treatment, especially with the dosage of redox mediator.

In this study, Fe_3O_4 and AQDS were chosen as target redox mediators representing typical solid and dissolved redox mediators, respectively. The influence of redox mediators on anaerobic degradation of amide pharmaceuticals was investigated by factors of (i) types of redox mediators, (ii) types of organic carbon, and (iii) hydrolysis/acidification in anaerobic treatment processes. Finally, suggestions on enhanced removal of micropollutants were proposed based on the experiment results.

2. Materials and methods

2.1. Chemicals

PRM was purchased from TCI Development Co., Ltd (Shanghai, China). CBM, CRT, and SMX were purchased from Sigma-Aldrich, Inc (Shanghai, China). Formic acid and acetonitrile used in the LC–MS/MS analysis were also purchased from Sigma-Aldrich, Inc (Shanghai, China). Other chemicals for anaerobic reaction were reported in our previous work [19].

2.2. Synthetic wastewater

Referring to the works of Yin et al. [19], components of synthetic wastewater for batch reactors were as follows: organic carbon corresponding to 2000 mg/L of chemical oxygen demands (COD), 480 mg/L NH_4Cl, 100 mg/L $CaCl_2$, 200 mg/L $MgCl_2$, 120 mg/L Na_2HPO_4, 200 mg/L $KHCO_3$ and 1 mL/L trace elements. Trace elements consisted of 1 g/L $FeCl_2{\cdot}4H_2O$, 100 mg/L $CoCl_2{\cdot}6H_2O$, 200 mg/L $NiCl_2{\cdot}6H_2O$, 100 mg/L $MnCl_2{\cdot}4H_2O$, 100 mg/L $NaMoO_4{\cdot}2H_2O$, 100 mg/L H_3BO_3, 100 mg/L $NaWO_4{\cdot}2H_2O$ and 100 mg/L $NaSeO_3$.

2.3. Batch experiments

Batch experiments were carried out in replications (n = 2) to examine the removals of amide pharmaceuticals during anaerobic treatment under different conditions. 250 mL of sludge was taken from the anaerobic sequencing batch reactor after effluent discharging, and placed in 600 mL (an effective volume of 500 mL) glass bottles. Following, 250 mL of synthetic wastewater was fed into these glass bottles. Next, stock solution of amide pharmaceuticals (CBM, PRM, CRT and SMX) was spiked into each reactor to achieve the initial concentration of 10 μg/L for each PPCP. Finally, the glass bottles were sealed with rubber stoppers and mixed in an air bath shaker at 170 rpm and 35 °C. Liquid and gas samples were periodically collected to analyze concentrations of amide pharmaceuticals, COD, volatile fatty acids (VFAs) and CH_4, respectively. The experiments were divided into three main parts as follows.

Firstly, for the effect of dosage of Fe_3O_4 or AQDS on the removal of amide pharmaceuticals in the anaerobic treatment process, reactors were additionally dosed with Fe_3O_4 and AQDS. Referring to the works of Yin et al. [19] and Liu et al. [21] on enhanced anaerobic degradation, the dosage of Fe_3O_4 was 1, 5 and 10 g/L, and the dosage of AQDS was 0.01, 0.1 and 1 mmol/L, respectively. Control reactors without the redox mediator dosage were also operated. In these experiments, soluble starch was used as the organic carbon with the concentration of 2000 mg/L COD.

Secondly, for the effect of organic carbon on the removals of amide pharmaceuticals in anaerobic treatment process, peptone, soluble starch and the mixture of peptone and soluble starch were used as the organic carbon with the COD concentration of 2000 mg/L. In addition, Fe_3O_4 and AQDS were dosed into reactors with concentrations of 5 g/L and 0.1 mmol/L, respectively.

Thirdly, the contributions of hydrolysis and acidification on the removals of amide pharmaceuticals were investigated. During the study, 10 mmol/L of 2-bromethanesulfonic acid sodium salt (BES) was dosed to inhibit the activity of methanogens [21]. Soluble starch was used as organic carbon with the COD concentration of 2000 mg/L. In addition, AQDS was dosed into reactors with the concentration of 0.1 mmol/L.

2.4. Analytical methods

COD was measured according to standard methods [22]. Gas pressure inside the bottles was determined by a differential pressure meter (Testo 512, TESTO, Germany) to calculate the biogas production. CH_4 was measured by a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a thermal conductivity detector and a 2 m packed column (Porapak N, Agilent, USA) [19]. The temperatures of injector, detector and column were kept at 90, 100 and 35 °C, respectively. Helium gas was used as the carrier gas at a flow rate of 25 mL/min. VFAs (including acetic acid, propionic acid, iso-butyric acid, butyric acid, iso-valeric acid and valeric acid) were determined by a gas chromatograph (GC-2014, Shimadzu, Japan) equipped with a flame ionization detector and a capillary column [23].

In the study, four amide pharmaceuticals (CBM, PRM, CRT and SMX) were selected, and their characteristics are shown in Table S1. Samples for the measurement of amide pharmaceuticals were filtered by glass fiber membrane filters, and the pH of filtrates was adjusted to 3 by adding hydrochloric acid. Acidified filtrates were concentrated by the method of solid-phase extraction (SPE) using Strata-X cartridges (200 mg/6 mL, Phenomenex, USA). Strata-X cartridge was conditioned with 5 mL of methanol and 5 mL MQW at pH of 3. Samples were pumped through the cartridges at the flow rate of 5 mL/min for 10 min with a concentrator (Sep-Pak, Waters, USA). Strata-X cartridges were cleaned by 5 mL of MQW at pH of 3. The SPE cartridges were dried with nitrogen gas. After drying, Strata-X cartridges were eluted with 5 mL of methanol. The elute from Strata-X cartridges was evaporated to dryness under a gentle stream of nitrogen gas by a dry thermo bath. The residues of samples were re-dissolved in 2 mL of mixture of MQW and acetonitrile (92/8, v/v), respectively. The concentrations were determined by LC–MS/MS with testing conditions shown in Tables S2 and S3.

3. Results and discussion

3.1. Effect of the dosage of Fe_3O_4 and AQDS on performance of anaerobic reactors

Dynamics of CH_4 by dosing Fe_3O_4 or AQDS in anaerobic reactors are shown in Fig. 1, and dynamic of VFAs by dosing Fe_3O_4 or AQDS in anaerobic reactors are shown in Figs. S1 and S2 in Supplementary information. CH_4 production was improved with the addition of Fe_3O_4 or AQDS. The maximum CH_4 production in the control reactor, the reactor with Fe_3O_4 (1 g/L), and the reactor with AQDS (1 mmol/L) were 39.6, 58.8, and 61.1 mL, respectively. Li et al. [18] found that the maximum CH_4 production rate was improved by the addition of nano-Fe_3O_4 in paddy soil enrichments. Total VFAs concentrations in the control reactor, the reactor with Fe_3O_4 (1 g/L), and the reactor with AQDS (1 mmol/L) were initially increased to the maximum of 915, 951 and 977 mg/L, respectively. In summary, dosage of redox mediators (Fe_3O_4 and AQDS) could enhance the production of CH_4 and VFA during anaerobic treatment.