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Cathodic degradation of antibiotics: Characterization and pathway analysis

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ABSTRACT

Antibiotics in wastewaters must be degraded to eliminate their antibacterial activity before discharging into the environment. A cathode can provide continuous electrons for the degradation of refractory pollutants, however the cathodic degradation feasibility, efficiency and pathway for different kinds of antibiotics is poorly understood. Here, we investigated the degradation of four antibiotics, namely nitrofurazone (NFZ), metronidazole (MNZ), chloramphenicol (CAP), and florfenicol (FLO) by a poised cathode in a dual chamber electrochemical reactor. The cyclic voltammetry preliminarily proved the feasibility of the cathodic degradation of these antibiotics. The cathodic reducibility of these antibiotics followed the order of NFZ > MNZ > CAP > FLO. A decreased phosphate buffered solution (PBS) concentration as low as 2 mM or utilization of NaCl buffer solution as catholyte had significant influence on antibiotics degradation rate and efficiency for CAP and FLO but not for NFZ and MNZ. PBS could be replaced by Na_2CO_3–$NaHCO_3$ buffer solution as catholyte for the degradation of these antibiotics. Reductive dechlorination of CAP proceeded only after the reduction of the nitro group to aromatic amine. The composition of the degradation products depended on the cathode potential except for MNZ. The cathodic degradation process could eliminate the antibacterial activity of these antibiotics. The current study suggests that the electrochemical reduction could serve as a potential pretreatment or advanced treatment unit for the treatment of antibiotics containing wastewaters.

1. Introduction

Pharmaceuticals and personal care products (PPCPs), as emerging contaminants, have attracted growing attention worldwide in recent years, which would pose potential threats to aquatic life and even human health (Liu and Wong, 2013). As one cluster of the most important pharmaceuticals, antibiotics have been excessively abused in humans and domestic

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animals. However, because of the relatively lower removal efficiency, effluents of urban wastewater treatment plants are among the main sources of antibiotics' releasing into various environments (Michael et al., 2013). Antibiotics discharged into the environments (e.g., soil and aquatic ecosystems) could result in evolution of novel antibiotic resistant genes and bacteria, making these ecosystems reservoirs of antibiotic resistance (Andam et al., 2011; Davies and Davies, 2010; Jechalke et al., 2014; Marti et al., 2014). Thus, antibiotic resistance problems have become a global concern.

Nitrofurazone (NFZ) and metronidazole (MNZ) belong to nitrofurans and nitroimidazole antibiotics, respectively. NFZ was mainly used in livestock and aquaculture production, as it could effectively treat gastrointestinal diseases caused by bacteria and protozoans (Yu et al., 2013). MNZ was abused for treating infections caused by anaerobic bacteria, bacteroides and protozoa, including amoebiasis, trichomoniasis and gingivitis (Dong et al., 2014). Chloramphenicol (CAP) and florfenicol (FLO) were broad-spectrum chloramphenicols antibiotics, which were against diverse Gram-positive and Gram-negative bacteria including most of anaerobic organisms. Due to potential carcinogenicity and genotoxicity of CAP and NFZ to human health, the European Union and U.S. Food and Drug Administration have banned their use in food-producing animals (Liang et al., 2013; Vass et al., 2008). However, in some developing countries, they are still used owing to their low production cost and easy availability. As a result, at the worldwide scale including China, South Korea, UK, Germany, Poland and Spain, trace levels of CAP (3–47,400 ng/L), FLO (3.55–4610 ng/L) and MNZ (17–9400 ng/L) were frequently detected in diverse water environments such as sewage treatment plant effluent, animal wastewater effluent, hospital effluent and surface water (Table S1), while NFZ residues and its toxic metabolite semicarbazide were monitored in some aquatic species and products (Vass et al., 2008; Yu et al., 2013). Thus, the elimination of the antibacterial activity of these antibiotics is very important during wastewater treatment.

Powerful cathode can provide continuous electrons for the reductive degradation of refractory pollutants such as nitroaromatics, azo-dye and halogenated compounds (Aulenta et al., 2011; Liang et al., 2013, 2014; Mu et al., 2009a,b, 2011; Radjenovic et al., 2012; Shen et al., 2013; Wang et al., 2011). This emerging cathodic reduction technology has great potential utilization in the wastewater treatment with the features of higher efficiency and selectivity of the reduction process (cathode providing continuous electrons), environmental friendliness (adding no chemicals and applying tiny voltage) and low-cost (without expensive catalyst) (Huang et al., 2011; Zhang and Angelidaki, 2014). Previous studies have showed that antibiotics CAP could be efficiently reduced to antibacterial inactivity products by cathode. Moreover, biocatalyzed cathode had higher CAP reduction efficiency than that of the abiotic cathode (Liang et al., 2013; Sun et al., 2013). However, under the cathode potential around −0.7 V (vs. SHE), reductive dechlorination of the nitro-group reduced product of CAP (aromatic amine product AMCl2) to AM (dechlorinated product of AMCl2) was not achieved. Kong et al. (2015) reported the cathodic degradation efficiency and pathway of nitrofurans furazolidone. Nevertheless, the underlying mechanism and pathway of the cathodic degradation of different kinds of antibiotics is poorly understood. Antibiotics CAP, NFZ, MNZ, and FLO have been frequently employed in livestock and aquaculture in China, which has led to environmental pollution. These antibiotics in wastewaters must be partially (nitro group reduction and dehalogenation) and/or completely degraded in order to eliminate their antibacterial activity. Thus, it is necessary to explore reasonable and easily controlled electrochemical reduction technology for the treatment and detoxification of these antibiotics in wastewaters before discharging into the environment.

This study investigated the effects of different cathode potentials, cathode buffer solutions and initial antibiotics concentrations on the degradation of NFZ, MNZ, CAP and FLO by cathode, which was poised by a fixed potential in an electrolysis cell with separated anode and cathode chamber. The cyclic voltammetry (CV) characterization, degradation pathways, and toxicity analysis of degradation products were studied. The objectives of this study were to (i) demonstrate the feasibility of the cathodic degradation of four antibiotics; (ii) reveal the linkages between antibiotics degradation products and applied cathode potentials and (iii) confirm the elimination of the antibacterial activity of four antibiotics during the cathodic degradation process.

2. Materials and methods

2.1. Chemicals

MNZ (99% purity), NFZ (98% purity) and FLO (98% purity) were purchased from Aladdin (Shanghai, China). CAP (>98% purity) and high performance liquid chromatography (HPLC) grade methanol were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ultrapure water used throughout the study was obtained from a Milli-Q Academic water purification system (Millipore, Bedford, MA, USA).

2.2. Experimental setup

The electrochemical reactors were constructed by two equal-volume Lexan cubic chambers (4 cm × 4 cm × 3 cm) with a cylindrical cavity (3 cm in diameter and 4 cm in length) as described previously (Kong et al., 2014a). The internal volume for each chamber was 28 mL and they were separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International, Ringwood, NJ, USA). The cation exchange membrane was immersed in saturated NaCl solution and subsequently in deionized water for pretreatment. Graphite fiber brush (2.5 cm in diameter and 2.5 cm in length, TOHO TENAX Co., Ltd., Tokyo, Japan) twisted by titanium wire (2 mm in diameter) (BaoJi XinLiTong Group Co., Ltd., China) worked as electrodes. They were pretreated with 1 M hydrochloric acid for 24 h and then immersed in deionized water for another 24 h, finally baked using muffle furnace (SX2-4-10G, Jinan Precise. Sci. Instru. Co., Ltd., China) at 450 °C for 30 min. Cathode potential was poised by a potentiostat (WMPG1000K8 multichannel potentiostat, WonATech Co., Ltd, Seoul, South Korea). Saturated calomel electrode (SCE) (0.247 V vs. standard hydrogen electrode (SHE), model-217, Shanghai Precise. Sci. Instru. Co., Ltd., China) was inserted into the cathode

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