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Electrochemical degradation of nitrofurans furazolidone by cathode: Characterization, pathway and antibacterial activity analysis

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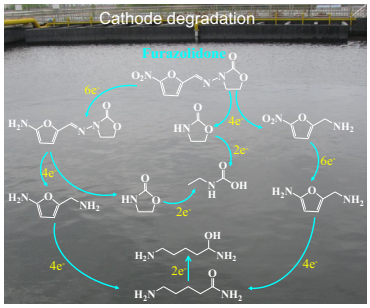
HIGHLIGHTS

- The cathodic degradation of nitrofurans furazolidone (FZD) was achieved.
- The cathodic degradation pathway of FZD including open loop degradation was proposed.
- Different applied cathode potentials were associated with FZD degradation products composition.
- The cathodic degradation of FZD eliminated its antibacterial activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Antibiotics existing in wastewaters must be degraded to eliminate its antibacterial activity before discharging into the environment. Electrochemical reduction by continuous electrons supply can degrade various refractory pollutants, however, the information about the feasibility and characterization of the cathodic degradation of nitrofurans antibiotic furazolidone (FZD) is scarce. Here, we investigated the degradation of FZD using a poised cathode electrochemical reactor. The cyclic voltammetry (CV) preliminarily proved the feasibility of FZD degradation on cathode. In contrast to the different buffer solutions concentrations, buffer types, and initial FZD concentrations which only had obvious impact on the FZD degradation efficiency, different cathode potentials had significant effects both on the FZD degradation efficiency and degradation products composition. Catholyte PBS could be replaced by Na_2CO_3–$NaHCO_3$ and NaCl buffer solution for the FZD degradation. The cathodic degradation pathway of FZD was proposed based on intermediate products analysis. When the cathode potential was lower than −0.75 V, both the furan ring and oxazole ring of FZD were destroyed to generate linear chain products after N–N bond disconnection, suggesting that the high toxic biological metabolite of FZD, 3-amino-2-oxazolidinone (AOZ) could be detoxified by cathodic degradation. This study suggests that the electrochemical reduction could serve as a potential strategy for the treatment of FZD and AOZ containing wastewater.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) have been classified as emerging contaminants ubiquitously found in the aquatic environment in China and other countries [1,2]. As one of the most important pharmaceuticals, antibiotics have been widely

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used for human and animals since last century. China, the world's largest producer and consumer of pharmaceutical products, consumes more than 25,000 tons antibiotics annually [3]. Furazolidone (FZD), namely 3-(5-nitrofurfurylideneamino)-2-oxazolidinone, is a typical example of nitrofurans antibiotics, has been widely used for more than 30 years as an antibacterial and antiprotozoal feed additive for poultry, cattle and farmed fish as well as human medicine for the eradication of *Helicobacter pylori* [4]. Long-term studies with experimental animals indicated the mutagenic, genotoxic and potentially carcinogenic characteristics of FZD and its metabolite 3-amino-2-oxazolidinone (AOZ) [5]. Thus, its utilization has been banned in food-producing animals by European Union and Ministry of Agriculture of China in 1995 and 2002, respectively. However, due to the low production cost and high effectiveness of FZD, it is still being illegally used in a relatively large scale across the world, particularly in developing countries [6]. In general, animals and human had a very low assimilation rate of the FZD, thus a majority of the FZD used in farms and aquaculture was finally released into the environments [4]. As a result, FZD residues and its high toxic biological metabolite AOZ were frequently detected in some aquatic species, aquatic products, pond water and sediments [5,7–9]. Thus, it is necessary to detoxify FZD and AOZ in contaminated environments or municipal wastewaters.

Generally, bacterial degradation of FZD suffered from lower degradation rates due to its antimicrobial nature [4,10], while physical–chemical methods such as electron irradiation are needed to provide more energy required for FZD degradation [11]. The electrochemical reduction is an emerging technology that could reductively degrade various refractory pollutants with features of higher removal efficiency, environmental friendly and low-cost [12–18]. The existence of FZD in the wastewaters or surface water environments must be degraded to eliminate its antibacterial activity. The electrochemistry based method for the removal of various antibiotic chloramphenicol, sulfonamides, trimethoprim, tetracycline, ceftriaxone, penicillin, and metronidazole by abiotic anode, bioanode, abiotic cathode or biocathode in electrochemical system has been studied extensively [19–25]. However, regarding the electrochemical degradation of nitrofurans FZD by cathode has not been well understood yet. Thus, it is necessary to conduct more experiments to elucidate the mechanisms involved in the detoxification of FZD and its high toxic metabolite AOZ in various wastewaters before their discharging into the environment.

This study discussed the effects of different cathode potentials, cathode buffer solutions and initial antibiotics concentrations on the degradation of antibiotics FZD by a poised cathode electrochemical reactor. Meanwhile, the cyclic voltammetry (CV) characterization, degradation pathways, and toxicity analysis of degradation products were also described. The aims of this study were to (i) characterize the cathodic degradation of FZD under different conditions; (ii) reveal the linkages between FZD degradation products and cathode potentials and (iii) confirm the cathodic degradation process which would eliminate the antibacterial activity of FZD. The results verified that the cathode providing electrons microenvironment could efficiently degrade and detoxify antibiotics FZD by applying tiny voltage, suggesting that the electrochemical reduction could serve as a potential pre-treatment or advanced treatment unit for antibiotics containing wastewaters.

2. Materials and methods

2.1. Experimental setup

The electrochemical reactors were constructed by assembling 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 [26]. The chambers each had a 28 mL of internal volume and they were separated by a pretreated cation exchange membrane (Ultrex CMI-7000, Membranes International, Ringwood, NJ, USA). 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. The electrodes 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). About 28 mL phosphate buffer solution (PBS, 50 mM, 11.55 g/L Na_2HPO_4 and 2.77 g/L NaH_2PO_4) was added into the counter electrode chamber, while for working electrode chamber, 50 mM PBS amended with 35 mg/L FZD was supplied, unless otherwise stated. Saturated calomel reference electrode (SCE) (0.247 V vs. standard hydrogen electrode (SHE), model-217, Shanghai Precise. Sci. Instru. Co., Ltd., China) was inserted into the cathode chamber. All of the potentials reported herein were already against SHE. The schematic diagram of the dual chamber electrochemical reactor used in this study has been shown in Fig. 1.

2.2. Chemicals

Furazolidone (FZD, >98% purity) and high performance liquid chromatography (HPLC) grade methanol were purchased from Aladdin (Shanghai, China) and Sigma–Aldrich (St. Louis, MO, USA), respectively. GC derivatization regent *N*,*O*-Bis(trimethylsilyl) trifluoroacetamide (BSTAF, ⩾99% purity) and catalyst pyridine (>99.9% purity) were purchased from Sigma–Aldrich (St. Louis, MO, USA) and Aladdin (Shanghai, China), respectively. Other chemicals used in this study were of analytical grade. Ultrapure water used throughout the study was obtained from a Milli-Q Academic water purification system (Millipore, Bedford, MA, USA).

2.3. Analytical methods

Effluent samples from the cathode chamber (at 0th, 3rd, 9th, 24th and 48th h) were filtered through a 0.22 μm filter prior to HPLC analysis. The concentrations of FZD and its transformation products were measured using a reverse-phase HPLC system (model-2695, Waters, Milford, MA, USA) equipped with a C18 analytical column (5 μm 4.6 × 250 mm, Waters Co., USA) and a UV detector (250 nm). The separation was achieved by using mobile phase (methanol/H_2O, 50:50; Vol/Vol) at a flow rate of 0.8 mL/

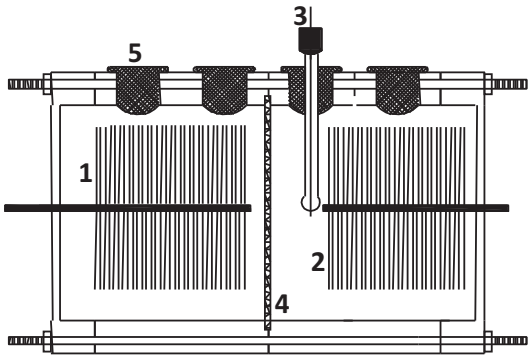

Fig. 1. The schematic diagram of electrochemical reactor used in this study. (1) Carbon brush anode; (2) carbon brush cathode; (3) saturated calomel reference electrode; (4) cation exchange membrane; (5) rubber stopple.

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