



Degradation of Chloramphenicol with Novel Metal Foam Electrodes in Bioelectrochemical Systems



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ABSTRACT

Bioelectrochemical system (BES) has been considered as one of the efficient methods for recalcitrant organic pollutant removal. This study compared three different cathodes, i.e. carbon rod (CR), copper foam (Cu), nickel foam (NF), for chloramphenicol (CAP) removal in BESs, while Cu and NF have not been used as cathodes for CAP degradation before. The results demonstrated that with 0.3 V applied voltage, 100% removal of 32 mg L⁻¹ CAP was observed after 36 h and 24 h with CR and Cu electrodes respectively, while amines were the main intermediate products. The performance of Cu cathode was 15.13 times better than NF electrode under 0.3 V applied voltage. When the applied voltage increased to 0.5 V, CAP could be completely removed within 12 h with Cu electrode, while complete CAP removal was found after 24 hours for CR and more than 120 hours for NF respectively. With 0.5 V applied voltage in 24 h degradation period, the final degradation products were found to be CO₂ and H₂O for Cu electrode, while nitrobenzene and 4-Nitrobenzyl alcohol were the main products for CR and NF electrodes respectively. The results demonstrated that Cu was the most efficient cathode for CAP degradation.

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1. Introduction

Widespread of antibiotics in the open environment has become an emerging concern in recent years [1]. A variety of antibiotics were detected in pharmaceutical manufacturing wastewater [2]. The wastewater, once entering the environment, will impose a potential environmental risk and threaten human health. Among the commonly used antibiotics, chloramphenicol (CAP) is a popular antibiotic compound for human and animals due to its excellent antimicrobial properties and low price [3,4]. It has a broad-spectrum and can effectively deactivate most of Gram-positive and Gram-negative bacteria [5,6]. Therefore, many researchers have looked into their impact on the environment and explored the methodologies to effectively remove this compound.

It was reported that chlorinated nitro aromatic antibiotics could be removed by conventional biological wastewater treatment system with a long solids retention time (SRT) (10–70 days) [7,8].

However, the degradation cannot be completed and 4-nitro-mandelic acid, 4-nitrobenzyl alcohol, 4-nitrobenzoic acid, 4-aminobenzoic acid, are commonly found in the treated effluent, and long SRT also leads to sludge accumulation [9]. On the other hand, electrolysis can reduce CAP efficiently and completely, while the high energy consumption is a major concern to deploy such technology [5].

CAP can exhibit reduction peak current when the potential is below -0.4 V in electrochemical test [10], hence microbial electrolysis cell (MECs) with a 0.5 V applied voltage have been explored for CAP reduction [3,10–13]. Lower applied voltage has not been tested according to our best knowledge. In most of these studies, conventional carbon-based materials, e.g. carbon rod, carbon fiber, graphite felt, carbon cloth, graphite blush, were selected as cathodes. In spite of non-corrosive and biocompatibility characteristics of carbon materials, the conductivity is not as good as metal materials [14]. Metal materials are commonly used in some conventional electrolysis process to enhance electrochemical catalytic activity [15,16]. Compared to normal metal electrodes, metals foam has highly open porous walls and larger specific surface area [17,18]. The unique characteristics of metal foams can accept the electrochemical deposition. The excellent performance of copper nanofoams in the CO₂ reduction in an electrochemical cell indicated that the high surface roughness,

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hierarchical porosity, and confinement of reactive species of the material contributed to both final products and faradaic efficiencies [18]. Nickel foam as the cathode was studied in an electrocoagulation device for boron removal and results revealed nickel foam removed 99.2% of 10 mg L^{-1} boron acid in 120 min at particular onset potential of 0.8 V [19]. Nickel foam has also been considered as the best cathode material for hydrogen generation [20].

In this study, for the first time, the metal foam was used as the cathode to degrade toxic and recalcitrant organic compounds in a bioelectrochemical system. CAP was chosen as a model antibiotic to investigate the efficiency of carbon rod, copper foam and nickel foam as electrodes. The effect of applied voltage and electrochemical activity of these materials were elucidated by cyclic voltammetry (CV) test and electrochemical impedance spectroscopy (EIS). The degradation mechanism of CAP in the electrochemical oxidation system was analyzed and a possible degradation pathway of CAP was proposed.

2. Methods and materials

2.1. Reactor setup

All bioelectrochemical reactors were made of dual cubic chambers, which were separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International, Ringwood, NJ, USA). The working volume of each chamber was 28 mL. A carbon rod (CR, Chijiu Duratight Carbon Co., China) and graphite fiber ($1.5 \times 1.5 \times 1.0 \text{ cm}$, Sanye Co., Beijing, China) were used as the anode electrode. During the acclimation period, carbon rod was also used as the cathode electrode. Carbon rod (CR, diameter of 0.8 cm, length of 3.2 cm), copper foam (Cu, $2.0 \times 2.0 \text{ cm}$, 99%, Jiashide Co. Suzhou, China) and nickel foam (NF, $2.0 \times 2.0 \text{ cm}$, 99.9%, Jiashide Co. Suzhou, China) were applied as cathode materials for comparison during experiment stage. The working area for all these three cathode electrodes was 8 cm^2 . During the electrochemical tests, all current density were normalized by the working area of electrodes. These materials were cleaned before tests using $0.5 \text{ M H}_2\text{SO}_4$. Three reactors with different cathodes were operated in parallel to compare the performance of CAP removal. All reactors were operated under open circuit condition with different applied voltage (0.3 V and 0.5 V in sequence).

2.2. Inoculation and operation

The microbial community in anode chambers was inoculated from a bioelectrochemical reactor with acetate as feed [21,22]. The anolyte composed of (g L^{-1}) sodium acetate, 1.0; KH_2PO_4 , 4.4; K_2HPO_4 , 3.4; NH_4Cl , 1.3; KCl, 0.78; MgCl_2 , 0.2; CaCl_2 , 0.0146; NaCl, 0.5; trace vitamins and minerals [23–25]. The feed was sparged with N_2 for 15 min before fed into the anode chamber. During anode acclimation period, DI water with dissolved oxygen was used as electrons acceptor in cathode chamber [14], and an external resistor of 1000Ω was used [23]. After eight-cycle feeding, the catholyte was replaced by aqueous CAP (32 mg L^{-1} , $\text{pH} = 6.0$ and $3.83 \pm 0.04 \text{ mg L}^{-1}$ dissolved oxygen). The pH and conductivity of catholyte were adjusted with 1 M HCl and 1 M NaCl respectively.

Microbial fuel cell (MFC) mode was applied during the acclimation period. From day 18, three reactors were operated under applied voltage of 0.3 V (MEC mode) to investigate the removal efficiencies. In order to compare the performance with the literature [10], a higher applied voltage of 0.5 V, which was commonly used for CAP degradation, was investigated from day 30 to day 60. Open circuit conditions (OCCs) as control experiments for three cathodes were carried out separately to examine changes

of CAP in the absence of current generation. All reactors were operated in fed-batch mode and maintained at room temperature. All experiments were carried out in duplicates.

2.3. Measurements and analysis

Total chemical oxygen demand (COD) in the anolyte was determined according to the standard method [22,26]. Total organic carbon (TOC) was analyzed by a TOC auto analyzer (Shimadzu TOC-VCPH; Japan). Solid-phase extraction (SPE) (Strata-X, Phenomenex Co. Singapore) was conducted to detect CAP degradation products. After filtered through $0.22 \mu\text{m}$ filter, the purified samples were analyzed by a High-Performance Liquid Chromatography (HPLC 1260, Agilent) coupled with a C18 column (Gemini-NX $3 \mu\text{m}$, 110A, $100 \times 2.0 \text{ mm}$, Phenomenex). The mobile phase was methanol and water (55/45; V V^{-1}). The eluent was delivered at a flow rate of 0.3 mL min^{-1} and the absorbance at 275 nm was measured. To identify the products of CAP degradation, LC-MS/MS (G6460C, Agilent) equipped with an electrospray ionization source were used. The LC/MS was operated under negative [27] polarity mode with the same C18 column. The mobile phases were gradient distilled water and acetonitrile with 0.1% acetic acid, at a 0.25 mL min^{-1} flow rate. The scanned range was from 60 m/z (mass to charge) to 400 m/z.

An automatic data collection system (PISO-813, Hongge Co., Taiwan) was used for collecting potential of anode and cathode. The power density of microbial cells was tested with a potentiostat (SP-150, BioLogic, Singapore) using the anode as a counter electrode and cathode as the working electrode. Before the linear sweep voltammetry measurement, the cell was in open circuit mode until the potential was stabilized and then tested from 0.0 V to the open circuit potential (OCP) at a scan rate of 0.1 mV s^{-1} [23]. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests for cathode were conducted with the same potentiostat. A three-electrode system using cathode electrode as working electrode, an Ag/AgCl as the reference (195 mV vs. SHE) near the working electrode and a Pt filament as a counter electrode was set-up for EIS and CV tests. The Pt filament was used to replace the anode biofilm to avoid any possible effect of anode bacteria on the analysis of the cathode. During the analysis, the anolyte was 50 mM PBS buffer solution while the catholyte was 32 mg L^{-1} CAP solution. The electrodes were characterized electrochemically by CV tests in a NaCl solution without (same conductivity as 32 mg L^{-1} CAP) and with 32 mg L^{-1} CAP. EIS analysis was conducted under polarized conditions, which was close to MFC cathodic operating potentials of -0.1 V and 0 V (vs. SHE, for different cathodes), with a frequency range of 100 kHz to 1 mHz and a sinusoidal perturbation of 10 mV reference amplitude [28]. The equivalent circuit and detailed value of different resistances were conducted through Zsimpwin software [29].

2.4. Calculation

Reduction efficiency of CAP in MEC, anodic coulombic efficiencies (CE_{an}), reaction rate constant k (h^{-1}), half-life time ($t_{1/2}$) and overall system efficiency for CAP degradation ($\text{mol CAP mol}^{-1} \Delta\text{COD}$) were calculated using Eqs. (1)–(5):

$$\text{CAP reduction}(\%) = \frac{\text{CAP}_i - \text{CAP}_t}{\text{CAP}_i} \times 100\% \quad (1)$$

$$\text{CE}_{\text{an}} = \frac{\sum_{i=1}^n I_i \Delta t}{F \times \frac{4 \times \Delta\text{COD}_{\text{an}} \times V_{\text{an}}}{M_{\text{O}_2}}} \times 100\% \quad (2)$$

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