



Self-Driven Bioelectrochemical Mineralization of Azobenzene by Coupling Cathodic Reduction with Anodic Intermediate Oxidation



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ABSTRACT

Bioelectrochemical systems have been intensively studied as a promising technology for wastewater treatment and environment remediation. Coupling of the anodic and cathodic electrochemical reactions allows an enhanced degradation of recalcitrant organics, but external power supply is usually needed to overcome the thermodynamic barrier. In this work, we report a self-driven degradation of azobenzene in a microbial fuel cell (MFC), where the cathodic reduction of azobenzene was effectively coupled with the anodic oxidation of its reduction degradation intermediate (i.e., aniline). The anodic degradation rate of aniline, as the sole carbon source, was significantly higher than that under open-circuit conditions, suggesting a considerable bioelectrochemical oxidation of aniline. Output voltages up to 8 mV were obtained in the MFC. However, a shift of cathodic electron acceptor from oxygen to azobenzene resulted in a decreased aniline degradation rate and output voltage. The present work may provide valuable implications for development of sustainable bioelectrochemical technologies for environmental remediation.

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1. Introduction

Efficient and energy-effective treatment of refractory organic wastewater (e.g., dyeing wastewater) remains a big challenge today [1,2]. Conventional physicochemical methods generally suffer from high costs and intensive energy consumption [3], while biological processes are usually slow and susceptible to inhibition [4,5]. Recently, bioelectrochemical system, which combines the advantages of microbial metabolism and electrochemistry, has been proposed as a promising alternative [6–9]. By utilizing the electrons generated from the bioanode, an efficient reductive dechlorination of azo dyes at the cathode of a microbial fuel cell (MFC) can be readily achieved [8,10]. However, many reduction products could be more toxic than the original dyes [4,5], hence energy-intensive aerobic post-treatment is typically needed. Meanwhile, extra biodegradable substrate is usually added as substrate to enhance bioelectricity generation and cathodic dye reduction.

Both problems are supposed to be resolved if the reduction products of dye can be further utilized as anodic fuels, thereby realizing a self-driven degradation process. Previous studies have demonstrated the concept of sequential reduction and oxidation of chlorinated organics and nitrobenzene [11,12] in electrochemical systems at appropriately applied voltage. Therefore, it is interesting to see whether such a coupled process can also be accomplished for azo dye mineralization and, more importantly, whether a self-driven process can be achieved. In fact, a variety of organic substrates, including some refractory compounds, have been demonstrated to be effectively oxidized at MFC anodes [13,14]. Thus, it is expected that the reduction products of azo dyes can also be utilized as carbon and energy sources at MFC anodes, but this is yet to be demonstrated.

In this study, we demonstrated the feasibility for a self-driven bioelectrochemical mineralization of azobenzene in MFCs. The individual processes of cathodic reduction of azobenzene and anodic oxidation of its reduction product (i.e., aniline) as well as a coupled reduction-oxidation process were studied. This work may provide valuable implications for development of sustainable bioelectrochemical processes for degradation of azo dyes or other recalcitrant organic matters in anoxic subsurface environments.

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2. Experimental

2.1. Experimental design and operation

2.1.1. Reactor configurations

Two types of MFC reactors were used in this work: dual-chamber MFC (hereafter denoted as MFC-A) and single-chamber MFC (denoted as MFC-B). For both MFCs, the electrode chambers were made of cubic-shaped plexiglass cells, with a working volume of 130 ml each. Proton exchange membrane (PEMs, Nafion 117, Dupont Inc. USA) was used as the electrode separator. The electrodes were connected via electric circuit with a 100 Ω external resistor. A carbon felt (6 mm thick and $4.5 \times 4.5 \text{ cm}^2$ projected area, purchased from Sanye Carbon Co., China) was used as the anode without modification. However, different cathode materials were used in the two MFCs. While the cathode of MFC-A adopted the same material as the anode, a $4.5 \times 4.5 \text{ cm}^2$, platinumized (0.5 g/m^2) carbon paper (Sanye Carbon Co., China) was employed in MFC-B to constitute an air-cathode.

2.1.2. Inoculum and synthetic wastewater

The bioanodes of all the MFCs were pre-acclimated for three months in another single-chamber MFC fed with a mixture of acetate and aniline as substrate. Previous studies have demonstrated that aniline could be degraded by mixed cultures with oxygen or nitrate as the electron acceptor [15]. Therefore, to enrich aniline-degrading microorganisms, 5 mL of activated sludge (from a municipal wastewater treatment plant) and 5 mL of anaerobic sludge (from a full-scale anaerobic reactor treating food-processing wastewater), both with a sludge concentration of approximately 5.0 g/L, were mixed and co-incubated in the MFC anodic chamber. The acclimation was performed in a batch-fed mode. Briefly, the total organic carbon (TOC) concentration was maintained at about 500 mg/l, and the aniline concentration was gradually increased from 150 to 450 mg/l in each batch cycle during the acclimation.

After acclimation, the bioanodes were installed into the anodic chamber of each MFC that was filled with the synthetic wastewater anolyte. The anolyte was buffered with 20 mM phosphate buffer solution (PBS, pH = 7.0) and contained the following components (per liter): 1.0 g acetate or 150–400 mg aniline (according to the experimental design below), 310 mg NH_4Cl , 130 mg KCl, 10 mg CaCl_2 , 20 mg $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 2 mg NaCl, 5 mg FeCl_2 , 1 mg $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, 1 mg $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 0.5 mg AlCl_3 , 3 mg $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, 1 mg H_3BO_3 , 0.1 mg $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 1 mg ZnCl_2 . For the catholyte of MFC-A, a 0.1 mM azobenzene solution, buffered with 20 mM PBS (pH = 7.0), was used.

2.1.3. Experimental design and operation

To understand the individual anodic and cathodic reactions in the MFCs, three sets of experiments were conducted (detailed in Table 1). Experiment 1 aimed to evaluate the feasibility of azobenzene reduction at an MFC cathode, for which azobenzene and acetate were added in the cathodic and anodic chambers, respectively. Experiment 2 investigated the degradation of aniline, as the sole substrate and electron donor for microorganisms, at an MFC anode. In Experiment 3, simultaneous cathodic reduction of azobenzene and anodic oxidation of aniline were performed

Table 1
MFC experimental design.

Experiment No.	MFC type	Anodic substrate	Cathodic oxidant
1	A (dual-chamber)	acetate	azobenzene
2	B (single-chamber)	aniline	oxygen
3	A (dual-chamber)	aniline	azobenzene

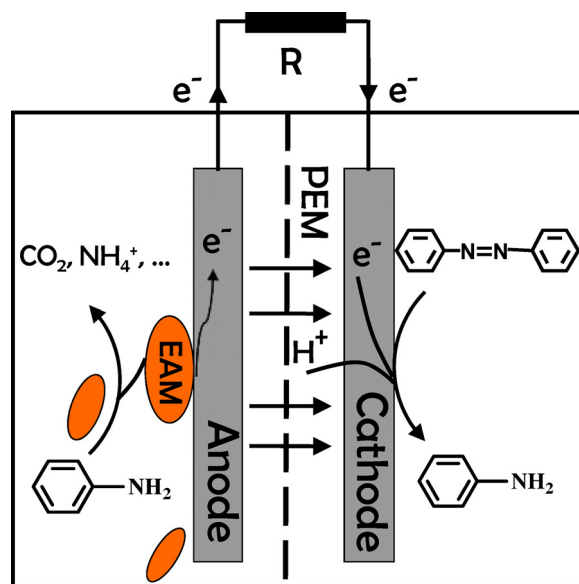


Fig. 1. Schematic of MFC-A for coupling cathodic azobenzene reduction with anodic aniline oxidation. EAM refers to electrochemically-active microorganisms.

(illustrated in Fig. 1). Here, MFC-A was adopted for Experiments 1 and 3, while MFC-B was used for Experimental 2. For Experiment 2, extra electrochemical tests with specific poised potentials (from -0.2 to 0.6 V versus Ag/AgCl) were also conducted by using a potentiostat (CHI 1030A, Chenhua Instrument Co., China).

All the MFCs were run in a batch-fed mode at ambient temperature. In Experiment 2, passive oxygen supply was employed for the cathode. The electrolytes of the MFCs were constantly mixed using magnetic stirrers. All experiments were conducted in triplicates and the mean values were reported. During the operation, 10 ml of water sample was collected from each reactor every two days and subjected to analysis after filtering through 0.45 μm filter membrane.

2.2. Analysis and calculation

The concentrations of azobenzene and aniline were measured using a high-performance liquid chromatograph (HPLC, Alliance 2695, Waters Co., USA) equipped with a polar embedded C18 reversed phase column (Phenomenex Co., USA) and diode array detector. A mixture of 35% methanol and 65% water was used as the mobile phase with a flow rate of 0.6 ml/min. Acetate concentration in the anode was determined by a gas chromatograph (Model 6890NT, Agilent Inc. USA) equipped with a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ fused-silica capillary column (DP-FFAP) and a flame ionization detector. The UV-vis spectra of catholytes were obtained by a UV-vis spectrophotometer (UV-2550, Shimadzu Co., Japan). To analyze the reduction products of azobenzene at the cathode, the catholyte was extracted by ethyl acetate for GC-MS (gas chromatography – mass spectra) detection. A GC system (Trace GC Ultra, Thermo Electron Co., USA) with a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ HP-5 capillary column coupled to a single quadrupole mass filter (DSQ II, Thermo Electron Co., USA) through an EI interface was used. Helium was used as the carrier gas at a flow rate of 1.0 ml/min. The oven temperature was initially held at 40 $^\circ\text{C}$ for 5 min, ramped at a rate of 10 $^\circ\text{C}/\text{min}$ to 280 $^\circ\text{C}$, and held for 5 min. The TOC concentration was measured by a TOC analyzer (Elementar Liqui TOC, Elementar Inc. Germany). Ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) was analyzed using Nessler's reagent colorimetric method (EPA Method

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