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Short communication

Enhanced vanadium (V) reduction and bioelectricity generation in microbial fuel cells with biocathode

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HIGHLIGHTS

- Enhanced V(V) reduction and power generation are realized in MFCs with biocathode.
- Synergistically electrochemical and microbial reductions occur for V(V) removal.
- Biocathode promotes electron transfers and reduces charge transfer resistance.
- High-throughput 16S rRNA gene sequencing analysis is performed.
- *Dysgonomonas* and *Klebsiella* are mainly functional species in MFCs with biocathode.

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ABSTRACT

Microbial fuel cells (MFCs) represent a promising approach for remediation of toxic vanadium (V) contaminated environment. Herein, enhanced V(V) reduction and bioelectricity generation are realized in MFCs with biocathode. Synergistically electrochemical and microbial reductions result in the nearly complete removals of V(V) within 7 d operation with initial concentration of 200 mg L^{-1}. Maximum power density of 529 ± 12 mW m^{-2} is obtained. Electrochemical tests reveal that biocathode promotes electron transfers and reduces charge transfer resistance. XPS analysis confirms that V(IV) is the main reduction product, which precipitates naturally under neutral conditions. High-throughput 16S rRNA gene sequencing analysis indicates that the newly appeared *Dysgonomonas* is responsible for V(V) reduction and *Klebsiella* contributes mainly to bioelectricity generation in MFCs with biocathode. This study further improves the performance of remediating V(V) contaminated environment based on MFC technology.

1. Introduction

Vanadium (V) contaminant attracts widespread attentions due to its intensive applications in modern industries as catalysts [1]. It is moderately toxic and V(V) is the most hazardous state which is known to cause oxidative cell damage [2,3]. Physical-chemical methods such as adsorption and precipitation are often involved in V(V) removals from water/soil with questionable cost-effectiveness [4,5]. Microbial reduction of V(V) to less toxic and mobile V(IV) by pure or mixed cultures represents an economical way [1], while its efficiencies need further improvement.

Microbial fuel cells (MFCs), which use bacteria as catalysts to oxidize organics for bioelectricity generation [6], offer an efficient pathway to safe treatment of heavy metal ions with higher electrochemical redox potentials, by employing them as the alternative cathode electron acceptors, such as representative Cr(VI), Hg(II) and Cu(II) [7–9]. V(V) is also firstly tested in our previous research and is realized to be electrochemically reduced to V(IV) and immobilized due to favorable half cell redox potentials of 0.99 V (vs standard hydrogen electrode) [10], while the performance of this pH-dependent V(V) reduction gets worse in neutral condition where microbial V(V) reduction can take place favorably [2]. The use of biocathode reduces electrode overpotentials free of expensive catalysts and biocatalyzed cathodic reduction is an emerging technology combining electrochemical and microbial functions for detoxifing various pollutants as Cr(VI) [8], while rare reports have been published on the behaviors of V(V) removals and bioelectricity generation in MFCs with biocathode.

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This study aims at revealing the feasibility of V(V) reduction with energy recovery in biocathode MFCs. Accelerated V(V) removals and improved power outputs were demonstrated with abiotic cathode and bioreactor as controls. Reduction products as well as the invoved microbial communities were also examined. The results prove the effectiveness of removing V(V) from aqueous solution and generating bioelectricity using MFCs with biocathode.

2. Materials and methods

2.1. MFCs constructions and operations

Four double chamber MFCs with cylindrical geometry chambers were employed [10]. Carbon fiber felt with dimensions of 40 × 40 × 10 mm served as both anodic and cathodic electrodes, which were connected through 100 Ω external resistance. The MFCs were connected to the data acquisition system (Measurement Inc, USA) to record voltage outputs at 5 min intervals. Each anode chamber was fed with 250 mL anolyte with chemical oxygen demand (COD) of 800 mg L^{-1} (acetate). 250 mL solution with the same components as anolyte and extra addition of 200 mg L^{-1} V(V) in the form of $NaVO_3$ acted as catholyte as the typical concentration of V(V) in vanadium matallurgical wastewater ranged from 200 mg L^{-1} to 400 mg L^{-1} [11]. All solutions were prepared based on 50 mM phosphate buffer solution (pH = 7). All MFCs were inoculated with 25 mL anaerobic sludge in the anode chambers. The four MFCs were divided into two groups equally. Two of them with inoculation of 25 mL anaerobic sludge in the cathode chamber to form biocathode were designated as MFC-BC. Another two with abiotic cathode were specified as MFC-AC for comparison. Furthermore, two 250 mL glass bottles sealed by silica gel stoppers for anaerobic condition with the same inoculation and solution condition as the cathode chamber of MFC-BC were served as control sets (Bioreactor).

Successful start-up of all MFCs and domestication of microbes in Bioreactor were achieved by refreshing all solutions every three days. Then V(V) reductions and bioelectricity generation were comparatively evaluated in 7 d fed-batch mode. Subsequently, the precipitate generated in the cathode chamber of MFC-BC were collected and analyzed. After that, microbes on the cathodic electrodes of MFCs were examined by high-throughput 16S rRNA gene sequencing. Two MFCs in each group were operated under identical conditions and the average results were recorded. All experiments were carried out at room temperature (22 ± 2 °C). Each test was repeated three times and average results were reported.

2.2. Analytical methods

Spectrophotometric method was chosen to measure the concentration of V(V) [7]. Total vanadium was determined by ICP-MS (Thermo Fisher X series, Germany). COD was measured by fast airtight catalytic decomposition method. Catholyte conductivity was monitored by a conductivity meter (DDS-11A, Shanghai Lei Yun test equipment Manufacturing Co., Ltd., Shanghai, China). Cathodic half-cell potentials were monitored by placing Ag/AgCl reference electrodes in cathode chambers. Polarization curves and power outputs were performed as reported previously [8]. Current density and power density were normalized by the cathode area (the single-side projected surface area) for comparisons with existing studies [12,13]. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests of biocathode and abiotic cathode were performed using an electrochemical workstation (VMP3, Bio-Logic Science Instruments, France) based on methods from Li et al. [14].

Precipitates were characterized by X-ray photoelectron spectroscopy (XPS) (Axis Ultra, Kratos Analytical Ltd., Manchester, UK). Microbes on the biocathode and in Bioreactor were ultrasonically collected and total genomic DNA was extracted and purified. The mixture of amplicons was used for high-throughput 16S rRNA gene sequencing on MiSeq (Illumina, the USA) and data were analyzed according to Hao et al. [15].

3. Results and discussion

3.1. Performance of MFCs with biocathode

Gradually V(V) removals were observed in the cathode chamber of MFC-AC (Fig. 1). Electrons generated from organics oxidation in the anode chamber were transferred to cathode through external circuit and then consumed for electrochemical V(V) reduction, while the efficiency was lower than that obtained in previous study, due to unadjusted pH [12], as lower pH facilitated electrochemical reductions of V(V) in cathode chamber of MFCs through Eq. (1).

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \; E^\Theta = 0.991 \text{ V} \quad (1)$$

Regarding Bioreactor, obvious V(V) removals with comparable efficiency occurred with time through anaerobic metabolisms with the consumption of organics [16]. When Biocathode was employed, significant enhancement of V(V) removals were realized in MFC-BC because of the synergistic electrochemical and microbial reductions (Fig. 1). During the first 3 days, all MFCs possessed higher cathode potentials under higher V(V) concentration (Fig. S1). Electrochemical oxidation was responsible for V(V) removal and MFC-BC performed better than MFC-AC since the accelerated electron transfers in the cathode chamber with the accumulated electrochemically active microorganisms as they could transfer electrons from cathode to metal ions with high valences efficiently [8]. Though more organics were consumed in Bioreactor, V(V) was removed more slowly than that in MFC-BC during this period as the slight toxic suppression of V(V) with higher concentration. Then microbial reduction dominated V(V) removal in the rest of whole operating cycle. Owing to relatively higher organics concentration saved within the first 3 days, MFC-BC maintained more efficient V(V) removals than Bioreactor (Fig. 1). After 7 d operation, V(V) was nearly completely removed in MFC-BC. Previous report revealed that approximate 500 mg L^{-1} of COD was consumed for electrochemically stimulated microbes to reduce 75 mg L^{-1} of V(V) [17]. These suggested that MFCs with biocathode could support

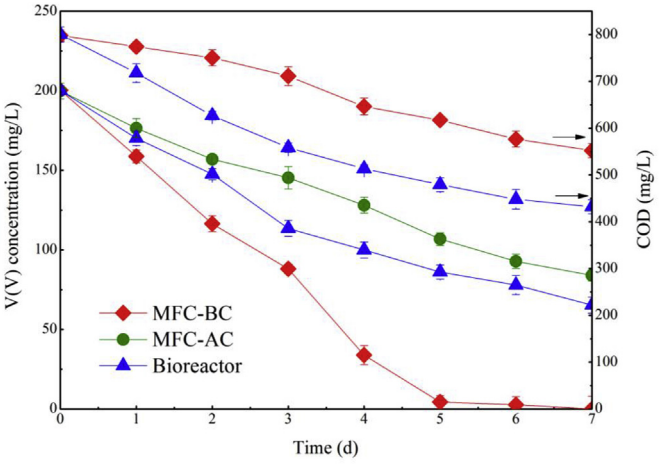

Fig. 1. Time histories of V(V) and COD concentrations in MFCs with biocathode as well as in control sets.