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Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production

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ARTICLE INFO

Article history:
Received 2 July 2013
Received in revised form
20 September 2013
Accepted 26 October 2013
Available online 7 November 2013

Keywords:
Microbial fuel cell
Electricity
Heavy metal removal
Cadmium
Zinc

ABSTRACT

Simultaneous high power generation (3.6 W/m^2) and high Cd (90%) and Zn (97%) removal efficiencies were demonstrated in a single chamber air-cathode microbial fuel cell (MFC). The maximum tolerable concentrations (MTCs) were estimated as 200 μM for Cd and 400 μM for Zn. Increasing the concentrations of Cd to 300 μM and Zn to 500 μM resulted in voltage drops by 71 and 74%, respectively. Feeding the MFCs with incrementally increased Cd and Zn concentrations resulted in much slower reduction in voltage output. Biosorption and sulfides precipitation are the major mechanisms for the heavy metal removal in the MFCs.

1. Introduction

Heavy metal pollution is one of the most important environmental issues nowadays. Heavy metals present a serious danger to the environment and public health because of their toxicity, non-biodegradability and bio-accumulation (Guo et al., 2010). Physical, chemical and biological technologies are available for removing metals from wastewaters (Wang and Chen, 2009). The physical and chemical methods, such as chemical precipitation ion exchange, electrochemical treatment, reverse osmosis and evaporation recovery can be ineffective or very expensive especially if the metals concentrations are as low as 1–100 mg/L (Ahluwalia and Goyal, 2007). Biological materials including bacteria, algae, yeasts and fungi are available in large quantities and have demonstrated good performance in removing heavy metals (Volesky and Holan, 1995).

Microbial fuel cell (MFC) is a novel technology that can convert organic matter in wastewater into electricity (Liu and Logan, 2004; Cheng et al., 2006; Logan et al., 2006). Removal of metals, such as chromium, copper, vanadium and mercury has been studied using two-chamber MFCs, in which, heavy metals were removed in the anaerobic cathode chamber through cathode metal reduction while organics in the anodic chamber were used as carbon sources and electron donors (Wang et al., 2008; Li et al., 2008; Tandukar et al., 2009; Li et al.,

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http://dx.doi.org/10.1016/j.watres.2013.10.062

2009; Huang et al., 2010; Heijne et al., 2010; Tao et al., 2011; Wang et al., 2011; Zhang et al., 2012a, 2012b; Lefebvre et al., 2013). The cathodic medium solutions in these studies contained only heavy metals without organic compounds. Many waste streams, however, contain both heavy metals and organic substances such as those from animal farms, petrochemical factory and rayon industry (Price et al., 2001; Pathak et al., 2009; Malakahmad et al., 2011; Ghosh et al., 2011). While it is well-known that electricity can be generated from various organic substances in wastewater using MFCs, it is still not clear how the presence of heavy metals affects power output and whether and how the heavy metals can be removed in the anodic chamber.

In this study, two heavy metals (Cd and Zn) were selected as representatives of hazardous heavy metals to investigate their impacts on power generation of single chamber membrane-less air-cathode MFC, an MFC type that has great potential to be scaled-up for practical wastewater treatment. These two heavy metals were selected due to their different toxicity levels and redox potentials. Cd is one of the most toxic heavy metals while Zn is one of the least toxic ones. The World Health Organization (WHO) and the US EPA limits for Cd and Zn in drinking water are 0.005 and 5 mg/L, respectively (Cazón et al., 2012). The heavy metals removal efficacies and mechanisms in the MFCs were also examined and discussed.

2. Material and methods

2.1. MFC construction

Single chamber air cathode MFCs were constructed as described previously (Catal et al., 2008). The MFC consisted of a plastic (Plexiglas) cylindrical chamber (12 mL). The anode and cathode were placed in parallel on the opposite sides of the chamber with a spacing of 1.7 cm. The anode (1.8 cm^2) was made from type A carbon cloth (no wet proofing: E-Tek, USA) while the cathode (7 cm^2) was made from type B carbon cloth (30% wet proofing; E-Tek, USA). The smaller anode surface area was selected in order to reduce the cathode limitation (Fan et al., 2008). The cathode was prepared by coating 1 mg/cm^2 Pt catalyst on carbon cloth following the method previously reported (Cheng et al., 2006).

2.2. MFC inoculation and operation

The MFCs were inoculated with a mixed bacterial culture originally enriched from sewage sludge obtained from Corvallis Wastewater Treatment Plant (Corvallis, OR) and were operated in a batch fed mode using the medium with the following composition: 60 mM sodium acetate, 200 mM PIPES (piperazine-N,N′-bis(2-ethanesulfonic acid) buffer, and nutrients as described previously (Liu and Logan, 2004).

A series of tests were conducted to investigate the effects of Cd and Zn on the MFC performance and the removal of the heavy metals. Cadmium chloride and zinc sulfate were dissolved in the medium solution described above to obtain final concentrations of 200 μM, 300 μM, 400 μM and 500 μM of Zn and Cd. In the first set of experiments, the medium solutions containing different metal concentrations were added to individual MFCs and each MFC was operated for 10 batches to investigate the effects of the heavy metals (at a fixed concentration) on electricity generation and to determine the maximum tolerable concentrations (MTCs), the highest metal concentrations that do not inhibit the microbial culture for electricity generation. In the second set of experiments, heavy metal concentrations were increased gradually in an increment of 100 μM for the same MFC. The addition of heavy metal solutions continued until the maximum voltage output was reduced to 0.1 V. Subsequently, the initial medium was added without heavy metals to investigate the possibility for voltage recovery. Some MFCs with mature biofilms on the anodes were autoclaved to investigate the heavy metal removal by biosorption. Control experiments were also conducted by feeding MFCs with solutions only without adding the inoculum. All experiments were conducted in a temperature controlled chamber (32 ± 1 °C).

2.3. Analyses

Cell voltages were recorded every 5 min using a multimeter with a data acquisition system (2700, Keithly, Cleveland, OH, USA). MFC voltages were assumed to be constant between readings. The power density was calculated according to $P=I^*V/A$, where I is the current, V voltage, and A the projected area of the anode. Coulombic efficiency (CE) was determined by the ratio of total recovered coulombs to the theoretical amount of coulombs from acetate (Liu and Logan, 2004). Cd and Zn concentrations were analyzed using Inductively Coupled Plasma (ICP) Spectroscopy (Prodigy spec, Leeman Labs Inc., Hudson, NH, USA). Removal efficiencies of the heavy metals were calculated according to (Ci − Ce)*100/Ci, where Ci and Ce are the metal concentrations in MFC influent and effluent, respectively.

3. Results and discussion

3.1. Determination of external resistance for heavy metal experiments

To evaluate the anode at its optimal performance, the performance of the single chamber MFC was first evaluated at various external resistances. A maximum power density of 3.7 W/m^2 (based on anode surface area) was achieved at a current density of 11.7 A/m^2 when the external resistance was 150 Ω (Fig. 1). Since the power output did not change significantly while varying the external resistance from 200 Ω to 100 Ω and to avoid overshoot at high current density when heavy metals were added, 200 Ohms was selected for the subsequent experiments.

3.2. Effects of Cd and Zn concentrations on MFC voltage output

The MTCs of Cd and Zn for the mixed culture at 200 Ω were estimated as 200 μM and 400 μM, respectively (Figs. 2 and 3). The slight decrease in voltage output for the multiple batches operated under the same condition (Figs. 2a, 3a and 3b and 3c) was possibly due to the formation of cathodic biofilm that reduces the cathode performance overtime, which was