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Substrate removal and electricity generation in a membrane-less microbial fuel cell for biological treatment of wastewater

Haiping Wang [a,c], Sunny C. Jiang [a,*], Yun Wang [b], Bo Xiao [c]

[a] Civil and Environmental Engineering, University of California, Irvine, CA 92697, USA
[b] Renewable Energy Resources Laboratory, Mechanical and Aerospace Engineering, University of California, Irvine, CA 92697, USA
[c] School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

HIGHLIGHTS

- A new membrane-less MFC with a biocathode was developed.
- A power density of 30 mW/m^2 and 75.9% substrate degradation efficiency were achieved.
- Pyrosequencing identified Bacteroidia as electron donors in the anode.
- Coulombic efficiencies varied from 19.8% to 58.1%.

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ABSTRACT

Microbial fuel cells have gained popularity in recent years due to its promise in converting organic wastewater into renewable electrical energy. In this study, a membrane-less MFC with a biocathode was developed to evaluate its performance in electricity generation while simultaneously treating wastewater. The MFC fed with a continuous flow of 2 g/day acetate produced a power density of 30 mW/m^2 and current density of 245 mA/m^2. A substrate degradation efficiency (SDE) of 75.9% was achieved with 48.7% attributed to the anaerobic process and 27.2% to the aerobic process. Sequencing analysis of the microbial consortia using 16S rDNA pryosequencing showed the predominance of Bacteroidia in the anode after one month of operation, while the microbial community in the cathode chamber was dominated by Gamma-proteobacteria and Beta-proteobacteria. Coulombic efficiencies varied from 19.8% to 58.1% using different acetate concentrations, indicating power density can be further improved through the accumulation of electron-transferring bacteria.

1. Introduction

Microbial fuel cells (MFCs) have attracted attention for their capability to produce renewable energy from the treatment of organic wastewater (Pant et al., 2012). In an MFC, organic substrates are biologically oxidized by anaerobic bacteria at the anode. The electrons generated during the microbial oxidation reaction are transferred to the anodic electrode and subsequently conducted through an external circuit to the cathode, while protons migrate from the anode chamber to the cathode chamber (Lovley, 2006). On the cathode, the protons combine with electrons and oxygen to form water. The flow of electrons and the positive potential differences between the electrodes give rise to the generation of electrical power (Zhang et al., 2008).

Conventional MFCs consist of biological anodes and abiotic cathodes. The abiotic cathode usually requires a catholyte (e.g., hexacynoferrate or acidic permanganate) to achieve high electron transfer (You et al., 2006) or a metal catalyst (e.g., platinum, pyrolyzed iron (II) phthalocyanine (FePc) or cobalt tetramethylphenylporphyrin (CoTMPP)) with O_2 or air as the cathodic electron acceptor (Cheng et al., 2006; Zhao et al., 2005). However, a catalyst that deactivates with time requires continuous replacement and metal catalysts are easily poisoned by components in the substrate solution and need to be constantly regenerated (Zhao et al., 2006), leading to increased costs and decreased operational sustainability. These systems are therefore impractical and unsustainable for the long-term operation. Such challenges can be overcome by biocathodes, which use microorganisms to assist cathodic reactions (He and Angenent, 2006). Biocathodes have the potential for sustainable operations, but so far few studies have investigated them (Zhang et al., 2008; Huang et al., 2012; Zhuang et al., 2012).

The use of a chemical catholyte or metal catalyst requires the physical separation of the anode and cathode chambers by an ion

* Corresponding author. Address: 716E Engineering Tower, University of California, Irvine, CA 92696, USA. Tel.: +1 949 824 5527.
E-mail address: sjiang@uci.edu (S.C. Jiang).

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exchange membrane (IEM) to prevent substrate diffusion from the anode to the cathode that leads to a rapid deactivation of the cathode and deterioration of MFC performance (Tartakovsky and Guiot, 2006). IEM inhibits substrate diffusion but permits proton migration from the anode to the cathode. Yet, the application of IEM results in a high internal resistance (Cheng and Liu, 2006) and a retarded transfer of protons from the anode to the cathode, which leads to pH splitting and thus lowers the system stability and bioelectrochemical performance (Kim et al., 2007; Rozendal et al., 2006). Therefore, there exists a counterbalance between higher proton migration and lower substrate diffusion. Another problem for the use of an IEM is biofouling. Membranes used over a period of 50 days were fouled and the biofilm on the membrane caused adverse effects on mass transport through the membrane (Chae et al., 2008). Here again, the use of an IEM increases the overall internal resistance and the overall cost of the MFC.

A membrane-less MFC that uses aerobic microorganisms as a cathodic catalyst was designed and tested in this study. The design, by introducing a unidirectional flow, improves protons and substrate transport from the anode to cathode while reduces oxygen diffusion from the cathode to anode (Fig. 1a). Anolyte mixing is promoted by continuously feeding influent from the bottom of the anode chamber. The organic carbon in medium functions as an electron donor in the metabolic process resulting in the breakdown of the substrate to CO_2 and water in concurrence with the electron generation as a by-product. The unidirectional flow of the remaining organic substrates from the anode to cathode allows further degradation of organic carbon in the cathode chamber by aerobic microbial processes to accomplish the second step of biological oxygen demand (BOD) removal. The vertical stack of two chambers combined with unidirectional flow also prevents the oxygen downward-diffusion. This study demonstrates electricity generation from substrate degradation in the membrane-less MFC with a biocathode and reports the substrate degradation efficiency (SDE), the bacterial morphologies and community composition in each chamber.

2. Methods

2.1. MFC design and construction

The MFC was consisted of two cylindrical polysulfone chambers (Nalgene Co., New York USA) with different volumes (Fig. 1b). The cathode chamber (600 mL total volume) was stacked on top of the anode chamber (800 mL total volume) and the two chambers were separated by a rigid porous plastic spacer, allowing solution to pass from the anode to cathode chamber in a unidirectional flow. For an efficient accumulation of the electrogenesis microflora, ~40 pieces of small carbon felts (~1 cm × 1 cm × 0.6 cm) were filled into the anode chamber as biofilm growth supporters. A graphite rod of 1.27 cm in diameter and 7.62 cm in length (32.9 cm^2 surface area) was used as anode to collect electrons. Cathode was made of a roll-up sheet of carbon felt (15 cm × 3 cm × 0.6 cm). The distance separating anode and cathode electrodes was 4.8 cm. The anode and the cathode were connected by an external copper wire.

2.2. MFC operation

The anode and cathode chambers were inoculated with digested sludge and activated sludge, respectively, collected from a local wastewater treatment plant (Irvine, CA, USA). Synthetic wastewater medium containing 2 g/L acetate as a carbon source (Cao et al., 2009) was pumped into the anode using a peristaltic pump (Barnant Co., lL, USA) at a flow rate of 1 L/day. Synthetic medium contained the following constituents per liter of deionized water: 4.4 g KH_2PO_4; 3.4 g $K_2HPO_4{\cdot}3H_2O$; 1.5 g NH_4Cl; 0.1 g $MgCl_2{\cdot}6H_2O$; 0.1 g $CaCl_2{\cdot}2H_2O$; 0.1 g KCl; 0.1 g $MgSO_4{\cdot}7H_2O$; 0.005 g $MnCl_2{\cdot}4H_2O$ and 0.001 g $NaMoO_4{\cdot}2H_2O$. The effluent from the anode flowed unidirectionally into the cathode by pumping. Air was bubbled into the cathode continuously to provide a dissolved oxygen concentration of 6–7 mg/L. All the experiments were conducted at least in duplicates and at room temperature (24 °C) and atmospheric pressure. To evaluate the influence of the organic nutrient on the performance of MFC, two feeding regimes were tested. The first regime pumped synthetic medium at an acetate-loading rate of 2 g/day at 12-h-on and 12-h-off intervals. The second feeding regime pumped nutrient medium continuously at the same loading rate into the anode and subsequently flow through to the cathode.

2.3. MFC performance, substrate degradation, and microbial colonization

The voltage (V) in the MFC was monitored continuously at 2 min intervals using a multimeter with a data acquisition system (Sinometer instruments, Shenzhen, China). The current (I), power (P), current density (CD), power density (PD) and coulombic efficiency (CE) were calculated as previously described (Liu et al., 2005). PD and CD were normalized to the anode surface area (32.9 cm^2). The polarization and power density curves were obtained by changing external circuit resistances. The dissolved oxygen and pH were measured using a bench top pH meter (Accumet Instruments, Vernon Hills, IL, USA).

Acetate feeding concentration was varied between 1–3 g/L at a constant flow rate of 1 L/day in order to determine SDE and CE as a

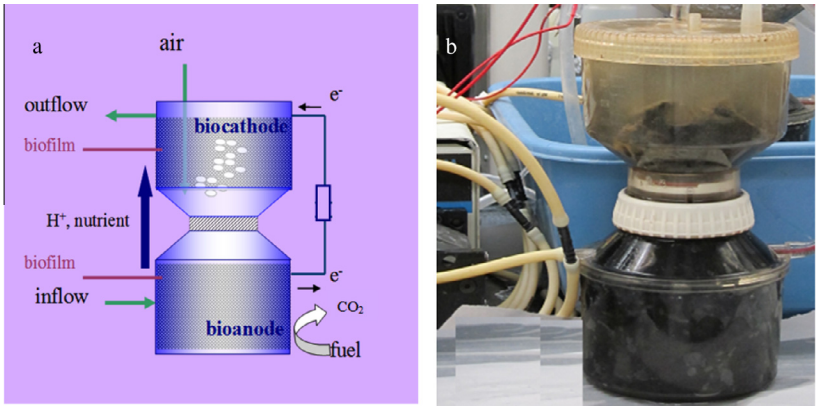

Fig. 1. Schematic (a) and picture (b) of the lab-scale membrane-less MFC.