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Treating refinery wastewaters in microbial fuel cells using separator electrode assembly or spaced electrode configurations

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HIGHLIGHTS

- Using RW in MFCs produced relatively good power with high organics removal.
- RW had lower power than the DW due to poorer biodegradability/toxicity of RW.
- Oxygen crossover was more important for organics removal in the RW than the DW.
- Organics removals were improved in MFCs compared to previous MEC results for RW.
- SEA had lower organics removals as a result of reduced oxygen intrusion.

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ABSTRACT

The effectiveness of refinery wastewater (RW) treatment using air–cathode, microbial fuel cells (MFCs) was examined relative to previous tests based on completely anaerobic microbial electrolysis cells (MECs). MFCs were configured with separator electrode assembly (SEA) or spaced electrode (SPA) configurations to measure power production and relative impacts of oxygen crossover on organics removal. The SEA configuration produced a higher maximum power density (280 ± 6 mW/m^2; 16.3 ± 0.4 W/m^3) than the SPA arrangement (255 ± 2 mW/m^2) due to lower internal resistance. Power production in both configurations was lower than that obtained with the domestic wastewater (positive control) due to less favorable (more positive) anode potentials, indicating poorer biodegradability of the RW. MFCs with RW achieved up to 84% total COD removal, 73% soluble COD removal and 92% HBOD removal. These removals were higher than those previously obtained in mini-MEC tests, as oxygen crossover from the cathode enhanced degradation in MFCs compared to MECs.

1. Introduction

A microbial fuel cell (MFC) is a microbial electrochemical technology (MET) that is being investigated to recover energy from wastewater in the form of electricity (Logan et al., 2006; Logan and Rabaey, 2012; Rabaey and Verstraete, 2005; Rozendal et al., 2008). The potential advantages of MFCs compared to traditional technologies such as activated sludge are reduced operational costs, due to passive oxygen diffusion to the cathode (no wastewater aeration), reduced sludge production, and electricity production. Tremendous advances have been made in recent years in increasing power densities by improving reactor configurations and developing new electrode materials. The use of inexpensive materials, such as activated carbon cathodes and graphite fiber brush anodes, has substantially decreased the cost of MFC electrodes (Dong et al., 2012; Logan et al., 2007; F. Zhang et al., 2009), which could enable cost-effective systems at larger scales.

Although many different types of wastewaters have been used to produce electricity in MFCs, performance has substantially varied depending on the specific wastewater and reactor configuration (Ahn and Logan, 2013; Feng et al., 2008; Lu et al., 2009; Pant et al., 2010; Puig et al., 2011; Sun et al., 2009). Treatability studies are therefore needed to evaluate a specific wastewater in an MFC in terms of power generation and the extent of organics removal. Mini microbial electrolysis cells (mini-MECs) were recently proposed as a method to rapidly evaluate wastewaters for current generation and chemical oxygen demand (COD) removal (Call and Logan, 2011), and have been used to examine treatment efficiencies (COD removal) and current generation of different types of wastewaters (Ivanov et al., 2013; Ren et al., 2013). The mini-MEC is a completely anaerobic test as both electrodes are sealed in the same gas-tight vial.

Recently, mini-MECs were used to evaluate treatability of six different refinery wastewaters (RWs) (Ren et al., 2013). The best correlation between the organics removal and current production with different RWs was found to be between the headspace biochemical oxygen demand (HBOD) removal and total recovered

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coulombs in one cycle. The de-oiled RW samples produced good current densities and organics removals in the mini-MEC tests. However, there is often less COD removal in an MEC compared to an MFC test (Cusick et al., 2010). COD removal in an MEC occurs under completely anaerobic conditions, while dissolved oxygen is used in a biochemical oxygen demand test. COD removal in MFCs therefore occurs both through anaerobic processes (by exoelectrogenic microorganisms on the anode) and aerobic degradation sustained by oxygen crossover through the cathode (Cusick et al., 2010). Dissolved oxygen can be important for biodegradation of certain organic compounds, particularly those derived from oil and fossil fuels which are relatively recalcitrant under anoxic conditions. In addition, hydrogen gas is produced at the cathode in MECs, and the oxidation of hydrogen could increase current production and compete with organic matter as an electron donor for exoelectrogenic microbes (Call and Logan, 2011). For these different reasons, the extent of COD removal can vary between MECs and MFCs, and therefore treatability in an MFC could be quite different from that obtained in an MEC.

Power produced in an MFC is a function of both solution chemistry and reactor configuration, as these can alter internal resistance. For example, adding a phosphate buffer (50 mM) into a brewery wastewater increased power production by 136% (Feng et al., 2008). However, the use of phosphate buffers or making wastewaters more saline by adding salt to increase solution conductivities are not sustainable approaches for improving power production. Internal resistance due to low solution conductivity can partly be overcome by changing the reactor configuration, for example by reducing electrode spacing. Separators (placed between the anode and cathode) are used with very closely spaced electrodes to avoid direct electrode contact. The use of separator electrode assembly (SEA) MFC designs can reduce internal resistance compared to more widely spaced electrode (SPA) designs (Zhang et al., 2013; Zhang et al., 2009). However, the separator reduces overall oxygen transfer into the anode chamber, which could affect overall COD removal. The effect of the SEA and SPA designs on the rate and extent of COD removal with wastewaters which contain organics that are only slowly degraded under anoxic conditions, such as refinery wastewaters, has not been previously examined.

In this study, the power production and organics removal of a refinery wastewater (RW) sample were compared with a domestic wastewater (DW) sample in MFCs using either the SEA (separator) or the SPA (no separator) configuration. A de-oiled RW sample that showed good performance and organics removal (58% COD removal and 61% HBOD removal) in mini-MECs was selected for testing in the MFCs. Domestic wastewater (DW) was also examined here using the two different MFC configurations as a positive control. COD removal (72%) and HBOD removal (>90%) for the DW sample were higher in the mini-MECs than those obtained using the RW (Ren et al., 2013), indicating its improved biodegradability. The use of the RW and DW samples therefore provided a good contrast in performance of the two different MFC configurations for wastewaters that differed in terms of biodegradability, current generation, and COD removal efficiencies in mini-MECs. In order to investigate if there was cathode degradation with the wastewaters in these two MFC configurations, used cathodes were tested in the electrochemical cell to evaluate the extent of degradation during MFC operation.

2. Methods

2.1. Wastewater samples

Refinery wastewater (RW) samples were collected from a refinery facility in Hawaii, placed on ice in coolers, and delivered to the Pennsylvania State University within three days. Upon arrival, the samples were stored at 4 °C. The RW samples were obtained from the effluent of an oil–water separator at the refinery [previously identified as DOW3 (Ren et al., 2013)], so that most of the oil phase and suspended solids were removed prior to MFC and HBOD tests. Domestic wastewater (DW) samples were obtained from the primary clarifier effluent at the Pennsylvania State University wastewater treatment plant. Fresh DW samples were obtained every one to two weeks and stored at 4 °C. Although wastewaters may have slightly changed during storage, the influent CODs remained relatively constant during all tests.

2.2. MFC construction and operation

MFCs were single-chamber, cubic-shaped reactors with a cylindrical anode chamber 2 cm long and 3 cm in diameter (Liu and Logan, 2004). The empty bed volume was 13 mL. The anodes were graphite fiber brushes (PANEX 35 50 K, Zoltek, total bristle surface area of ~0.056 m^2) that were pre-treated at 450 °C for 30 min. Reference electrodes (Bioanalytical Systems, Inc., RE-5B; +0.209 V versus a standard hydrogen electrode, SHE) were inserted through the hole in the middle of the chamber, with the frit ~3 mm away from the brush edge. Cathodes were made of carbon cloth as previously described (Cheng et al., 2006), with a diffusion layer made of PTFE on the air facing side, and a Pt catalyst layer (Pt loading of 0.5 mg/cm^2) on the solution side.

MFCs were constructed with either the SPA or SEA configurations (Fig. S1). The cathode in the SPA MFC was placed 1.5 cm away from the anode brush core, which removed the possibility of a direct electrical contact between electrodes. The cathode in the SEA MFC was placed 0.5 cm away from the anode brush core, with two layers of a porous cloth separator (DuPont Sontara, style 8864; also known as Amplitude ProZorb Wipers) to prevent electrode short circuiting. All the reactors were initially inoculated and acclimated to DW with the external resistance of 1000 Ω (2–3 weeks), and then half the reactors were switched to the RW samples. This acclimation procedure was previously shown to be an effective method for reactor acclimation and operation with mini-MECs (Ren et al., 2013). During MFC operations, the RW was always used as received without any addition of the DW. With each type of wastewater and configuration, MFCs were operated in fed-batch mode, in duplicate, at 30 °C. The wastewater was replenished when the voltage dropped to less than 30 mV.

2.3. Calculations and measurements

Voltage (U) across the external resistor in the MFC circuit was measured at 20 min intervals using a data acquisition system (2700, Keithley Instrument, OH) connected to a personal computer. Current ($I = U/R$) and power ($P = IU$) were normalized by the projected surface area of the cathode (7 cm^2). Anode potentials were measured respect to the reference electrode, and the cathode potentials were calculated based on the anode potentials and the whole cell voltages. Polarization tests were performed using the multi-cycle method (a different resistance for each complete fed batch cycle), in order to obtain the treatment efficiencies at different current conditions, and to minimize the possibility of power overshoot (Watson and Logan, 2011). All the reactors were left open circuit for a cycle, and then the external resistances were varied from 5000 Ω to 250 Ω (DW) or 5000–300 Ω (RW) in a decreasing order over successive fed-batch cycles. Small resistances were repeated for two cycles, while large resistances (>1000 Ω) were tested for only one cycle to avoid changes of wastewater characteristics during storage over the duration of the multi-cycle tests. Coulombic efficiencies (CEs) were calculated as the ratio of recovered coulombs to the theoretical amount of