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Scaled-up dual anode/cathode microbial fuel cell stack for actual ethanolamine wastewater treatment

Byung-Min An, Yoon Heo, Hubdar-Ali Maitlo, Joo-Yang Park *

Department of Civil and Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Republic of Korea

HIGHLIGHTS

- The batch test showed that the MFC unit is an advanced system for ETA treatment and electricity generation.
- The MFC power density decreased while the corresponding internal resistance increased in actual ETA-fed.
- Stack MFCs in series connection showed a gradual increase in COD and ammonia removal.

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ABSTRACT

The aim of this work was to develop the scale-up microbial fuel cell technology for actual ethanolamine wastewater treatment, dual anode/cathode MFC stacks connected in series to achieve any desired current, treatment capacity, and volume capacity. However, after feeding actual wastewater into the MFC, maximum power density decreased while the corresponding internal resistance increased. With continuous electricity production, a stack of eight MFCs in series achieved 96.05% of COD removal and 97.30% of ammonia removal at a flow rate of 15.98 L/d (HRT 12 h). The scaled-up dual anode/cathode MFC stack system in this research was demonstrated to treat actual ETA wastewater with the added benefit of harvesting electricity energy.

1. Introduction

Ethanolamine (ETA) is an organic chemical compound consisting of amino and alcohol functional groups. It is used in various industrial applications as feedstock in the production of detergents, emulsifiers, polishes, pharmaceuticals, and chemical intermediates (Ndegwa et al., 2004; Wang et al., 2013). ETA has also been utilized as a substitute to the ammonia that was used to prevent metal pipes from corrosion in secondary systems (water/steam circuit) of nuclear power plants because it is less volatile than ammonia (Nordmann, 2004). In secondary systems, the condensate polishing plant (CPP) is installed to blow down excess ETA and impurities from the steam cycle before the condensate is fed back to the steam generators. Ion exchange resin columns are used in CPP. ETA is captured onto ion exchange resins during treatment of secondary water. ETA remains in high concentration in discharged regeneration wastewater. ETA is difficult to naturally degrade, and its intermediates (such as ethanol and ammonia) can cause water pollution of chemical oxygen demand (COD) and total nitrogen (Lee, 2013). Although ETA has been treated by electrodialysis reversal with bipolar electrolysis (Yeon et al., 2007; Malovanyy et al., 2013) and Fenton oxidation (Anotai et al., 2012), these methods generally require large amounts of energy and chemicals with long degradation times.

Microbial fuel cells (MFCs) are a promising technology to treat wastewater while recovering bioenergy and have been studied to remove wastewater (Logan and Rabaey, 2012; Koók et al., 2016). MFCs utilize microorganisms as the catalysts for directly converting the chemical energy available in the biomass into electricity. Only those microorganisms capable of transferring electrons outside the cell to insoluble electron acceptors, called "exoelectrogens", contribute to electricity generation in MFCs (Logan, 2009). Currently, the most studied exoelectrogens belong to the α-, β-, γ-, and δ-proteobacteria (e.g., *Geobacter sulfurreducens*, *Geobacter metallireducens*, *Shewanella oneidensis*) (Bond and Lovley, 2003; Min et al., 2005; Ringeisen et al., 2006).

In the past years, the performance of MFCs has increased exponentially. Though it has been accepted that the power density generally decreases with increasing scale, the efforts to challenge MFC

* Corresponding author. Tel.: +82 2 2220 0411.
E-mail address: jooypark@hanyang.ac.kr (J.-Y. Park).

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scaling are still ebullient. The main challenges for a scalable design are increasing power, increasing power recovery, and reducing material cost. For the realistic application of wastewater treatment, the continuous flow is more suitable than batch culture systems, which have the disadvantage of discontinuity. Connecting multiple MFCs in continuous flow requires the units to be fluidly joined to an inflow and an outflow stream. Aelterman et al. (2006) connected six MFCs in parallel, which resulted in a current equal to the sum of the individual MFCs, while the voltage was similar to the average of the individual MFCs. Furthermore, the maximum power density of parallel-connected MFCs can be several times greater than that of the single MFC unit (Wang and Han, 2009). Recently, Ledezma et al. (2013) reported MFC-cascades as an uncomplicated and effective way to reduce >96% COD from high-load effluents to acceptable environmental standards with concomitant electricity production. They are both very similar concepts to the existing wastewater treatment processes; nevertheless, their studies were conducted with acetate (Wang and Han, 2009; Ledezma et al., 2013) as substrate instead of real wastewater. To date, there are only few significant studies using actual wastewater in MFC stack research (Zhuang et al., 2012), especially under continuous operating mode.

As mentioned above, knowledge about MFC technology is reaching the edge of practicality for many engineering processes. To keep pace with the rapid growth of this technology and improve its practical applications, the first step is to investigate whether a target organic contaminant is suitable. Our previous study showed that the use of ethanolamine as a substrate in air cathode single-chamber MFCs allows energy recovery and ethanolamine removal (Shin et al., 2014; Song et al., 2015). The second step is to transfer this promising and challenging MFC technology into the field, we evaluated the applicability of scaled-up dual anode/cathode microbial fuel cell stacks using actual ETA wastewater. Prior to stacking, we evaluated the performance of MFC units with different ratios of synthetic medium and actual wastewater in a continuous mode based on current output.

2. Methods

2.1. MFC design and construction

Dual electrode MFCs were made of rectangular acrylic ($28 \times 32 \times 6$ cm) with a working volume of 1000 mL, as shown in Fig. 1. Each electrode pair was placed on both sides of the chamber. This reactor contained five equally spaced baffles, forming six channels. Each baffle had a slot (side edge) to allow the next channel and water to go through the reactor. Non wet-proof type carbon cloth (1071 HCB, AvCarb®) and 30% wet-proof type carbon cloth (1071 HCB, AvCarb®) were used as the anode and cathode electrodes, respectively. The projected surface areas of electrodes were 360 cm^2 for one side of each electrode. The cathode electrode was coated with a carbon base layer and four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side. Then, Nafion (5 wt%, Sigma–Aldrich) binder mixed with 0.35 mg cm^{-2} Pt (10% Pt on Vulcan XC 72, Premetek) was applied to the solution-facing side as a catalyst layer (Cheng et al., 2006). A cation exchange membrane (Ultrex CMI-7000, Membranes International) was placed between the anode and cathode electrodes. Prior to use, the cation exchange membrane was treated with NaCl solution (5%) at 40 °C for 24 h and then rinsed with deionized water. A silicon gasket inserted between the supporter and chamber ensured sealing. The rubber O-ring was installed along the chamber outline to prevent water leakage. Titanium wires were fitted and then sealed to the body of the MFCs and an end plate with conductive silver epoxy to collect electrons.

2.2. MFC operation and actual ETA wastewater preparation

The inoculum for scaled-up dual electrode MFCs was obtained from a small scale MFC operated for about one year with 1000 mg/L ethanolamine. The MFC was first operated under fed-batch mode. The objective of batch mode was to adapt microbial communities to an anode electrode by feeding medium into the chamber. The MFC anode chamber was fed with artificial wastewater consisting of 1000 mg/L ethanolamine ($H_2NCH_2CH_2OH$, >99.0%, JUNSEI) as the organic substrate. The medium also contained (per liter) KCl, 0.13 g; Na_2HPO_4, 8.19 g; $NaH_2PO_4{\cdot}2H_2O$, 6.6 g; Wolfe's mineral solution (12.5 mL); and Wolfe's vitamin solution (12.5 mL) (Lovley and Phillips, 1988). This medium solution feed was replaced every 3 days. Before feeding these solutions into the chamber, nitrogen gas was sparged for 30 min to remove any oxygen. Actual ETA wastewater was collected from a condensate polishing system (CPP) in the nuclear power plant (NPP) and then stored in a bottle at 4 °C before each use. The actual ETA wastewater had total solids (3.8 mg/L), COD_{cr} (544 mg/L), Cl^- (2.2 mg/L), Ca (0.06 mg/L) Mg (0.02 mg/L) as well as NH_3-N (19.5 mg/L), NO_3-N (0.23 mg/L). The pH and the conductivity of the actual wastewater were 2.2 and 0.97 mS/cm, respectively. All experiments were carried out in a temperature-controlled room at 25 ± 2 °C.

2.3. Analysis and calculations

Cell voltages were measured at a predetermined time with a voltage recorder (VR-71, T&D Corporation). External resistance was established by a resistance decade box (380,400, Extech Instruments). Samples were immediately filtered through a 0.2 μm syringe filter before analysis. COD was measured by standard method 5220 (Hach COD system, Hach Company). Nitrate, nitrite, and ammonium were also measured with a HACH (DR-2800) spectrophotometer. The pH and conductivity of solution were analyzed by a pH meter (Orion 720A+, Thermo) and conductivity meter (Orion three star, Thermo), respectively. Current, I (in milliamperes; mA), was calculated according to $I = V/R_{ex}$, where V (in millivolts, mV) is voltage and R_{ex} (in ohms, Ω) is external resistance. Power, P (in milliwatts, mW), was calculated according to $P = IV$. Current and power density were normalized by the area of the anode electrode. Polarization curves were obtained by a multi-cycle method (from 5 to 2000 Ω).

3. Results and discussion

3.1. Performance of MFC unit

In the chamber of the MFC, ETA is biologically degraded into acetaldehyde and ammonium, respectively. Acetaldehyde can be hydrolyzed to ethanol and acetate (Mrklas et al., 2004), and then these two products are used as substrates. Electrons and hydrogen are produced by bacteria. The electrons and the hydrogen transfer to the cathode through the external circuit and cation exchange membrane and this then creates a current. At the cathode, oxygen acts as the terminal electron acceptor, and reacts with electrons and hydrogen to produce water. Upon replacement of the ETA substrate solution, the MFC produced electric currents. After one cycle of replacement, a stable and repeatable voltage of 0.75 ± 0.04 V was obtained with external resistance of 500 Ω (Fig. 2A). This voltage generation indicated that bacteria attached to the electrode surface were responsible for power generation (Bond and Lovley, 2003). The batch-fed mode was repeated until stable voltage generation was obtained for one month.