



Short Communication

Performance of low cost scalable air–cathode microbial fuel cell made from clayware separator using multiple electrodes



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HIGHLIGHTS

- Developed low cost air cathode MFC of 26 L capacity with clayware separator.
- Fourteen months stable performance reveals viability of MFC for field applications.
- Internal resistance decreased from 19 Ω (series) to 8 Ω by parallel connection.
- Maximum power of 17.85 mW achieved at 0.375 V (47.25 mA) with 78% COD removal.
- 5.1% Coulombic efficiency is among the higher value reported for larger volume MFC.

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ABSTRACT

Performance of scalable air–cathode microbial fuel cell (MFC) of 26 L volume, made from clayware cylinder with multiple electrodes, was evaluated. When electrodes were connected in parallel with 100 Ω resistance (R_{ext}), power of 11.46 mW was produced which was 4.48 and 3.73 times higher than individual electrode pair and series connection, respectively. Coulombic efficiency of $5.10 \pm 0.13\%$ and chemical oxygen demand (COD) removal of $78.8 \pm 5.52\%$ was observed at R_{ext} of 3 Ω . Performance under different organic loading rates (OLRs) varying from 0.75 to 6.0 g COD L⁻¹ d⁻¹ revealed power of 17.85 mW (47.28 mA current) at OLR of 3.0 g COD L⁻¹ d⁻¹. Internal resistance (R_{int}) of 5.2 Ω observed is among the least value reported in literature. Long term operational stability (14 months) demonstrates the technical viability of clayware MFC for practical applications and potential benefits towards wastewater treatment and electricity recovery.

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1. Introduction

A microbial fuel cell (MFC) is a bioreactor incorporated with electrochemical system that converts chemical energy stored in the chemical bonds of organic compounds to electrical energy through catalytic reactions of microorganisms under anaerobic conditions (Logan, 2008). Although there has been marked improvement in the performance of MFC through research efforts, large scale practical application of MFCs is yet to be achieved. Double chambered MFC using proton exchange membrane is difficult to implement on a large scale due to large volume and more area requirement. Hence, researchers are focusing on simple MFC design like a single chambered air–cathode MFC (Logan, 2008; Duteanu et al., 2010).

To reduce the capital cost of MFCs, it is necessary to develop economical electrodes and produce cheaper separator material which is effective in proton transfer, offer negligible substrate loss from anodic chamber, offer minimum oxygen diffusion and resist fouling to support long term stable operation. The major disadvantage of using Nafion membrane in MFC is high cost and low stability as it contains sulfonic acid groups which get easily combined with ammonia present in wastewater (Rabaey et al., 2005). Behera et al. (2010) used clayware ceramic separator as a membrane to reduce fabrication cost of MFC and obtained a maximum power density (P_{max}) of 16.8 W/m³. Although higher P_{max} (2.15 kW/m³) has been reported for MFC of 0.335 ml capacity (Nevin et al., 2008), significant decrease in P_{max} was observed when volume of anodic chamber is increased from few milliliter to liter (Feng et al., 2014; Ter Heijne et al., 2011; Jiang et al., 2011; Sonawane et al., 2013).

While operating MFC of large volume, use of multiple electrodes is suggested to enhance rate of bioelectrochemical reaction by

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providing multiple electron pathways (Jiang et al., 2011; Kim et al., 2013). A MFC of 16 L volume operated using domestic wastewater with 12 anodes–cathodes achieved better chemical oxygen demand (COD) removal efficiency ($80 \pm 8\%$) but demonstrated lower power output of 0.17 W/m^3 due to large internal resistance (R_{int}) of $175\text{--}225 \Omega$ (Jiang et al., 2011). Ter Heijne et al. (2011) replaced oxygen with ferric iron as electron acceptor and reported 38% increase in power output (200 W/m^3); which is highest value reported for a larger volume MFCs so far. However, use of such chemical catholyte in MFC is not a sustainable solution. Zhuang et al. (2012) designed a serpentine-type MFC (10 L volume) stack using 40 tubular air–cathodes and observed P_{max} of 6.3 W/m^3 under series–parallel connection. However, operating too many smaller MFC units in reality attracts higher operational and maintenance cost. Sonawane et al. (2013) proposed a hexagonal MFC design with multi-electrodes system and reported a P_{max} of 4.66 W/m^3 while treating distillery effluent. A stackable horizontal MFC of 250 L produced P_{max} of 0.39 W/m^3 using sewage as feed and it was noticed that the R_{int} is largely dependent on the contact resistance (Feng et al., 2014).

Effect of various operating parameters such as effect of organic loading rate (OLR), external resistance (R_{ext}) and electrode connection influences the performance of MFC. Effects of these parameters have been investigated using only MFCs of smaller anodic chamber volume (Ren et al., 2014). However, influence of these parameters on the performance of MFC having larger anodic chamber volume has not been evaluated so far. Therefore, the aim of this investigation was to observe the long term operational performance of a low cost scalable air cathode MFC, made up of clayware cylinder provided with multiple electrodes. Effect of applied OLR and R_{ext} on power production and COD removal was investigated. Influence of presence of multi-electrode system was explored by connecting the electrodes in series and in parallel.

2. Methods

2.1. Cell configuration and operation

Air cathode MFC was constructed using a baked clayware cylinder of height 0.69 m and inner diameter of 0.23 m, making working volume of 26 L (Fig. 1A). The cylinder served as the anodic chamber and the wall material of cylinder (8 mm thick) worked as a separator. Three pairs of anode and cathode were provided, which converted this single MFC actually into three different hydraulically connected MFCs as MFC-1 (lower portion), MFC-2 (middle part) and upper part as MFC-3 (Fig. 1B). Three ports were provided for sample collection, first at 0.23 m from bottom, second at 0.46 m and last at 0.67 m, which was also used for taking effluent out of the anodic chamber. For effective utilization of substrate, anode of each MFC was made with two concentric cylinders of 5 mm thick Carbon felt (Panex[®] 35, Zoltek Corporation) having total projected surface area of 0.44 m^2 . The outer surface of the ceramic cylinder was coated with conductive carbon ink prepared from Vulcan XC-72R carbon powder with MnO_2 catalyst, both at a loading of 0.5 mg/cm^2 , forming three different cathodes called separator electrode assembly (SEA) corresponding to each anode. Polyvinyl alcohol was used as binder at a loading of 0.5 mg/cm^2 . Carbon felt was tightly wrapped thus making close contact with conductive carbon surface and acted as current collector for oxygen reduction reaction. Stainless steel wires (T-316L) were wrapped tightly over carbon felt to establish electrical connection between carbon felt and concealed copper wires of external circuit. The electrical connections between MFCs were either set with completely individual circuits between the paired anode and cathode, or they were combined into single circuit (series or parallel)

using concealed copper wire through an R_{ext} of 100Ω (if not mentioned otherwise).

2.2. Inoculation and MFC operation

Anaerobic sludge collected from the bottom of a septic tank was used as inoculum in the anodic chamber of the MFC. After giving combined pretreatment using heat and acid (Behera et al., 2010), 4.87 L volume of sludge was added in anodic chamber. Acid treatment was given to sludge inoculum using $0.05 \text{ N H}_2\text{SO}_4$ to keep its pH in the range of 5.5–6.0. Synthetic wastewater containing sucrose as carbon source with COD ranging from 0.5 to 2.0 g L^{-1} was prepared following the composition given by Behera et al. (2010).

Experiments were performed in five cycles under different operating conditions in continuous mode. In the first four cycles, synthetic wastewater was fed to the anodic chamber at an OLR of $0.75 \text{ g COD L}^{-1} \text{ d}^{-1}$. First cycle was performed for a period of 30 days, wherein performance of MFC-1, MFC-2 and MFC-3 was evaluated by connecting individual pair of electrode through separate R_{ext} of 100Ω . For combined circuit connections, performance of MFC was investigated by connecting electrodes in parallel and in series across R_{ext} of 100Ω (Fig. 1B) in the second and third cycles, respectively, for each cycle duration of 20 days. In the fourth cycle of operation, effect of R_{ext} was evaluated by using R_{ext} of 100, 50, 30, 20, 15, 10, 8, 5 and 3Ω . In this cycle, performance of MFC was measured by keeping electrodes under parallel connection for a period of 14 days at each of these R_{ext} . Effect of applied OLR on the performance of MFC was evaluated in the fifth cycle for a duration of 30 days under each OLR. The OLR of $0.75 \text{ g COD L}^{-1} \text{ d}^{-1}$ was applied with influent COD of 0.5 g L^{-1} ; OLRs of 1.5 and $3.0 \text{ g COD L}^{-1} \text{ d}^{-1}$ were applied with influent COD of 1.0 g L^{-1} ; and for OLRs of 4.5 and $6.0 \text{ g COD L}^{-1} \text{ d}^{-1}$ influent COD concentration of 2.0 g L^{-1} was used.

2.3. Analysis and calculations

Influent and effluent COD concentrations and pH were measured according to Standard Methods (APHA, 1998). The performance of MFC was evaluated in terms of voltage (V) and current (I), measured using a data acquisition unit (PicoLog data logger, UK), and converted to power according to $P = V * I$, where P = power (W), I = current (A), and V = voltage (V). Volumetric power and current density were obtained by normalizing power and current to net liquid volume of anodic chamber, respectively. Polarization study was carried out by varying R_{ext} from 30,000 to 10Ω using the resistance box (GEC 05 R Decade Resistance Box, Renown Systems, Kolkata, India). The voltage across the resistor was recorded at every 30 min using a data acquisition unit and polarization was performed after attaining a stable cell potential (Watson and Logan, 2011). Coulombic efficiency (CE) was calculated as per Eq. (1) given by Logan (2008).

$$\text{CE} = \frac{M_s * I}{F * b_{\text{es}} * q * \Delta C} \quad (1)$$

where, M_s is the molecular weight of substrate added, I is the circuit current, F is the Faraday's constant, b_{es} is the number of electrons exchanged per mole of oxygen, q is the flow rate, ΔC is the difference in the influent and effluent COD. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with oxford detector (ZEISS, EVO 60, UK). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were carried out using CompactStat (IVIUM technologies, Netherlands).

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