

Performance Of Earthen Pot Microbial Fuel Cell Using Anodic Effluent As Cathodic Electrolyte

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Abstract

Performance of single chambered earthen pot Microbial fuel cells (MFC) was investigated to treat synthetic wastewater under continuous mode of operation using air and anode effluent as a cathode electrolyte. Stainless steel (SS) mesh with surface area 100 cm² was used as a both electrodes. Under continuous mode of operation, maximum power density of 12.0 and 16.44 mW/m²; maximum current density of 126 and 160.6 mA/m² and maximum volumetric power of 929 and 1096 mW/m³ were obtained using air and anode effluent as a cathode electrolyte respectively. Under continuous mode of operation, maximum chemical oxygen demand removal efficiency and maximum coulombic efficiency using air as a cathode electrolyte were 67-72% and 6.89%, respectively; whereas maximum chemical oxygen demand removal efficiency and maximum coulombic efficiency using anode effluent as a cathode electrolyte were 76-80% and 10.98%, respectively. Internal resistance of a cell changed with cathode electrolyte as well as with day of operation. Minimum internal resistance of the cell was 178 and 82 Ω using air and anode effluent as a cathode electrolyte respectively. Maximum potential difference developed using both stainless steel electrodes was 0.344 and 0.329 V using air and anode effluent as a cathode electrolyte respectively.

1. Introduction

The current technologies used to produce electric power are changing the climate due to increase in emission of the greenhouse gases such as CO₂, N₂O. In addition, due to limited amount of fossil fuels and considering the global warming effect, there is an increasing urge to develop more renewable energy sources, which are environmental friendly and clean energy source, with minimal or zero use of hydrocarbons. Fuel cells convert chemical energy

directly into electricity without an intermediate conversion into mechanical power [1]. The energy available in the organic matter present in the wastewater can be recovered as direct electricity through microbial metabolism oxidizing the organic matter under anoxic condition.

In a microbial fuel cell (MFC), the biochemical energy contained in the organic matter is directly converted in to electricity in what can be called as a microbially mediated "incineration" reaction [2]. This implies that overall conversion efficiencies that can be reached are potentially higher for MFCs compared to other biofuel processes. MFC uses bacteria to catalyze the organic matter in to electricity. Unlike a battery, fuel cell converts energy from one form to another (much like an engine) and will continue to operate as long as fuel is fed to it. They are mainly of two different types: biofuel cells that generate electricity from the addition of artificial electron shuttles (mediators) and MFCs that do not require mediator for electrons shuttles. Therefore, MFCs can use sustainable source of energy, apart from effective treatment of wastewater.

Performance of a MFC is affected by the substrate conversion rate, overpotentials at the anode and at the cathode, the proton exchange membrane performance, and internal resistance of the cell [3]. The optimization of MFCs requires extensive exploration of the operating parameters that affect the power output. A sound body of literature supports the exploration of different parameters such as surface area of electrode, different materials as electrodes, use of special aerobic culture of *Shewanella oneidensis* DSP10 as the active electrochemical species in the anode chamber [4], sedimentary bacterium [5], *Geobacter sulfurreducens* [6], sedimentary bacterium [5]; cathode performance with different electron acceptor such as a permanganate, oxygen [7; 8]; and Hexacyanoferrate [8]; spatial arrangement of effluent with respect to PEM [7]; electrode distance [9]; cathode surface area

and cathode mediator [10]; operating parameters such as pH, temperature [11] etc.

Performance of cathode, one of the governing factors in harvesting energy, is governed by the kinetics of reduction of oxygen, or other oxidant supplied, at the cathode [12]. Rate of reduction of oxygen at cathode is governed by the concentrations of proton, electron, and oxygen [13]. The proton transfer rate through the PEM is also affected by the concentration gradient across the PEM, which depends upon the reduction rate of oxygen, or other oxidant, supplied in the cathode chamber.

In traditional MFC, substrate is oxidized by bacteria in the anode chamber, generating electrons and protons. According to principle of MFCs, protons from an anode chamber are allowed to flow to a cathode chamber through a proton-exchange membrane (PEM) with electrons going in the same direction via a conductive wire externally [14]. The electrons, transferred to the cathode through external circuit, and the protons diffused through PEM in cathode chamber are combined with oxygen to form water. Oxygen is usually supplied by aeration in cathode chamber to act as oxidant.

The main disadvantage of a two chamber MFC is that the cathode solution must be aerated to provide oxygen to the cathode [1]. The power output of a MFC can be improved by increasing the efficiency of the cathode, e.g. power is increased by adding hydrogen peroxide, ferricyanide, hexacyanoferrate, oxygen and permanganate to the cathode chamber. Using permanganate as the cathode's electron acceptor the maximum power density of 3986.7 mW/m^2 was achieved in the MFC [8]. The present study was aimed to investigate the performance of single chambered earthen pot MFC using air and anode effluent as a cathode electrolyte which reduces operating cost of MFC.

2. Materials and methods

2.1. Microbial fuel cell

The study was carried in single chambered laboratory scale up-flow microbial fuel cell with air and anode effluent as a cathode electrolyte. The anode chamber in the MFC was made up of earthen spherical pot and the wall (4 mm thick) of the earthen pot itself was used as the medium for proton exchange [15]. The working volume of anode chamber of MFC was 125 ml and 150 ml for air and anode effluent as a cathode electrolyte respectively. The MFC was operated under continuous mode. The wastewater was supplied to the MFC from the bottom of the anode chamber (12.5 ml/h). Stainless steel mesh having total surface area of

100 cm^2 and 95 cm^2 was used as anode and cathode respectively. Stainless steel wire mesh wrapped around outer side of spherical pot was used as cathode electrode. The electrodes were connected externally with concealed copper wire.



Figure 1. Photo view of experimental setup

2.2. MFC Operation

Synthetic wastewater containing sucrose as a source of carbon was used in this study. The synthetic wastewater was prepared by adding 445 mg/l sucrose, 750 mg/l NaHCO_3 , 159 mg/l NH_4Cl , 13.5 mg/l K_2HPO_4 , 4.5 mg/l KH_2PO_4 , 125 mg/l $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 32 mg/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Trace metals like Fe, Ni, Mn, Zn, Co, Cu, and Mo were added as per the composition suggested by Ghangrekar et al. 2005 [16]. The operating chemical oxygen demand (COD) of synthetic wastewater was in the range of 600 to 610 mg/l. The influent feed pH was in the range of 7.2 to 7.6 throughout the experiments.

During start up, MFC was inoculated with anaerobic sludge collected from septic tank bottom after giving heat pre-treatment and required amount of sludge was added to the reactors to maintain the sludge loading rate at $0.1 \text{ kg COD /kg VSS/d}$. This MFC was operated at room temperature varying from 20 to 34°C . MFC was operated under continuous mode at hydraulic retention time (HRT) of 10 h using air as cathode electrolyte, HRT of 12 h using anode effluent as cathode electrolyte and organic loading rate (OLR) of $1.0 \text{ kg COD} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$.

2.3. Analyses and calculations

The suspended solids (SS), volatile suspended solids (VSS), influent COD, effluent COD and pH were monitored according to APHA standard methods [17]. The potential and current were measured using a digital

multimeter (MECO 603, India) and converted to power according to $P = I \cdot V$, where, P = power (W), I = current (A), and V = voltage (V). Internal resistance of the MFC was measured from the slope of line from the plot of voltage versus current [18]. The coulombic efficiency (CE) was estimated by integrating the measured current relative to the theoretical current on the basis of consumed COD, $CE = (C_E/C_T) \times 100$. The theoretical current production ' C_T ' was estimated as $C_T = (F \times n \times w)/M$, where ' F ' = Faraday constant (96485 C/mol), ' n ' = no. of moles of electrons produced per mole of substrate, $n = 4$ for wastewater COD, ' w ' = daily COD load removed in gram, ' M ' = molecular weight of substrate. The actual current production ' C_E ' was integrated as $C_E = I \times t$, where, ' t ' is time duration (sec). Polarization study was carried out at variable external resistances (1000-10 Ω) using resistance box. Internal resistance of the MFC was measured from the slope of line from the plot of voltage versus current.

3. Results and discussion

3.1. Waste water treatment and electricity generation

MFC was operated under continuous mode of operation at HRT of 10 h for first 20 days and later at HRT of 12 h for next 15 days Synthetic wastewater containing sucrose as a carbon source was used in the study, unless specified, having COD concentration 600-610 mg/l. In early stage of continuous mode of operation, short current, voltage, and power got increased with time, with subsequent decrease in internal resistance of cell. After reaching the peak, on 14th day, on later days of operation, slight decrease in current, voltage, and power density have been noticed. This might be due to increase in internal resistance on later days of operation after reaching the peak.

During early days of operation, performance of MFC in terms of energy harvesting got improved with increase in COD removal efficiency. Maximum power density of 12.0 mW/m^2 and coulombic efficiency of 6.89% was observed on the 14th day using air as a cathode electrolyte with corresponding COD removal efficiency of 70%. The corresponding short current was 1.263 mA. The maximum current densities, with respect to anode and cathode surface area, were 126.3 and 132.94 mA/m^2 , respectively. After reaching this peak value, a decrease in short current was noticed on the later days, although improvement in COD removal efficiency occurred. The current was stabilized at around 1.1 mA after 14. After stabilization, at 10 h HRT, the COD removal efficiency was in the range of 67-72%.

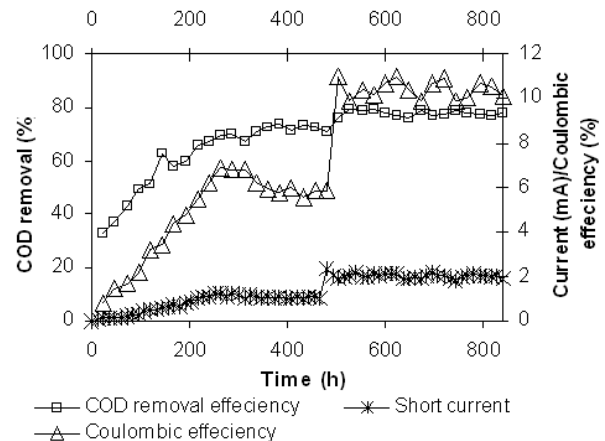


Figure 2. Variation of COD removal efficiency, coulombic efficiency and current with time

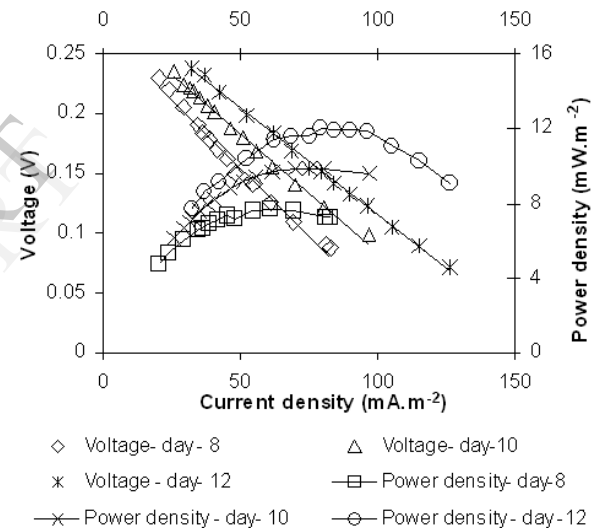


Figure.3. Polarization curves for MFC using air as a cathode electrolyte.

Later 21 day onwards anode effluent from top of pot was used as a cathode electrolyte, which increased the HRT and working volume of MFC. Sudden increase in current from 1.017 to 5.13 mA and decrease with time and stabled around 2.31mA after 1 hour; performance of MFC in terms of energy harvesting got improved due to change in cathode electrolyte. Maximum power density of 16.44 mW/m^2 and coulombic efficiency of 10.96% was observed on the 21st day using anode effluent as a cathode electrolyte with corresponding COD removal efficiency of 70%. The corresponding short current was 2.31 mA. The maximum current densities, with respect to anode and cathode surface area, were 245 and 258 mA/m^2 ,

respectively. After reaching this peak value, a decrease in short current was noticed on the later days, although improvement in COD removal efficiency occurred. The current was stabilized at around 2.0 mA after 21st day onwards, at 12 h HRT, the COD removal efficiency was in the range of 76-80 %.

Maximum potential difference developed using both stainless steel electrodes was 0.344 and 0.329 V using air and anode effluent as a cathode electrolyte respectively.

In both cases after reaching peak, a decrease in short current was observed. This reduction in current might be due to increased concentration of sludge in anode chamber and hence increased activity of methanogens with time, contributing to enhance COD removal.

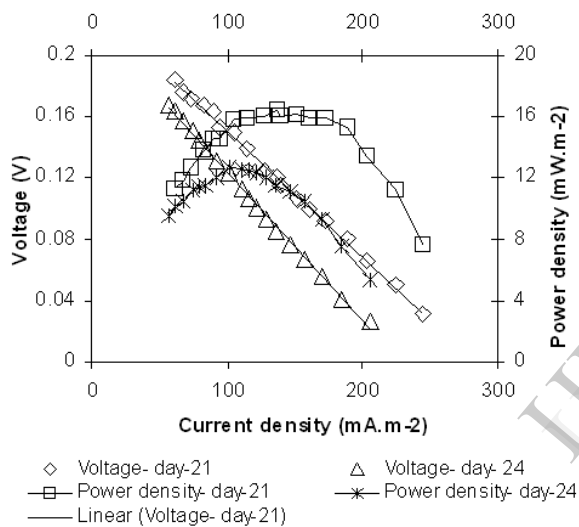


Figure 4. Polarization curves for MFC using anode effluent as a cathode electrolyte.

3.2. Polarization and internal resistance

Polarization studies was carried out for the MFC by varying external resistance from 1000 Ω to 10 Ω . Internal resistance of the MFC measured from the slope of line from the voltage versus current plot. Internal resistance of the MFC was initially decreased with time. It was 228.7 Ω , 196.6 Ω and 178.1 Ω on day of 8, 10, and 12 using as air as a cathode electrolyte respectively. On day 21st anode effluent was used as cathode electrolyte, it was observed that internal resistance of MFC suddenly decreased and it was 82.4 Ω on day 21st. later internal resistance was increased with time and it was 98.2 Ω on day 24th. Initially decrease in internal resistance with time might be due to increase in electron concentration in anode chamber

and increasing proton concentration in percolated water, which increases reaction rates at electrodes due to higher negative and positive charges at electrodes. Further increase in internal resistance might be due to decrease in water percolation through the wall, because percolation of water through wall is proportional to dryness on external wall surface. Under similar reactor configuration, the MFC showed higher internal resistance with air cathode electrolyte might be due to limiting rate percolation of proton to support cathode reaction. The internal cell differs with time; this might be due to blockages in voids, change in proton concentration in anode chamber and proton flux rate.

3.3. Earthen pot wall as PEM

The MFC performance will be optimum, when the proton diffusion through PEM is equal to the formation rate of protons in the anode chamber by biochemical reactions. Thus, the amount of protons produced in an anode chamber should penetrate through the PEM and they should be consumed at cathode at the same rate for cathodic reaction [11]. In this study, earthen pot was used as a MFC and wall of the earthen pot itself acts as a medium for proton exchange [15]. Under continuous mode of operation 300 ml/d feed was supplied to the anode chamber; and 50 ml/d was percolated through the wall of earthen pot during air as a cathodic electrolyte. In other words 16.67 % protons were available for cathodic reaction. Performance of MFC using earthen pot will be optimum, percolation rate of water through wall equal to the feed supply rate of water.

4. Conclusion

From the present study, it was observed that in earthen pot microbial fuel cell air can be used as cathodic electrolyte, which reduces operating cost of MFC. Performance of MFC in terms of energy harvesting improved when anode effluent was supplied as a cathodic electrolyte this might be due to increase in proton concentration at cathode. The internal resistance of cell differs with time; this might be due to blockages in voids, change in proton concentration in anode chamber and proton flux rate.

5. References

[1] A Liu, H., & Logan, B. E., "Electricity generation using an air cathode single chamber microbial fuel cell in the

absence of proton exchange membrane”, *Environmental Science and Technology*, (2004). 38, 4040–4046.

[2] Lens P., Wesermann P., Haberbauer M., Moreno A., “Biofuels for fuel cells”, IWA, Publishing, London, (2005).

[3] Rabaey, K., Verstraete, W., “Microbial fuel cells: Novel biotechnology for energy generation”, *TRENDS in Biotechnol.*, (2005). 23(6), 291–298.

[4] Ringeisen, B.R., Rayb, R., Little, B “A miniature microbial fuel cell operating with an aerobic anode chamber”, *J. Power Source*, (2007). 165, 591–597.

[5] Zhang, E., Xu, W., Diao, G., Shuang, C., “Electricity generation from acetate and glucose by sedimentary bacterium attached to electrode in microbial-anode fuel cells”, *J. Power Source.*, (2006). 161, 820–825.

[6] Dumas, C., Basseguy, R., Bergel, A., “Microbial electrocatalysis with *Geobacter sulfurreducens* biofilm on stainless steel cathodes”, *Electrochimica. Acta.*, (2008). 53, 2494–2500.

[7] A G.S. Jadhav, M.M., “Improving performance of MFC by design alteration and adding cathodic electrolytes”, *Appl. Biochem. Biotechnol.*, (2008). 151, 319–332.

[8] You S., Zhao Q., Zang J., Jiang J. and Shen P., “A microbial fuel cell using permanganate as a cathodic electron acceptor”, *Journal of power sources*, (2006). 162, 1409–1415.

[9] M.M. Ghangrekar, V.B. Shinde., “Simultaneous sewage treatment and electricity generation in membrane-less microbial fuel cell”, *Water Sci. Technol.*, (2008). 58, 37–43.

[10] Kim, B.H., Chang, I.S., Gadd, G.M., “Challenges in microbial fuel cell development and operation”, *Appl. Microbiol. Biotechnol.*, (2007). 76, 485–494.

[11] A G.S. Jadhav, M.M., “Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration”, *Bioresour. Technol.*, (2008). 100, 717–723.

[12] Cheng, S., Liu, H., & Logan, B. E., “Increased performance of single-chamber microbial fuel cells using an improved cathode structure”, *Electrochemistry Communications*, (2006). 8, 489–494.

[13] Gil, G. C., Chang, I. S., Kim, B. H., Kim, M., Jang, J. K., Park, H. S., & Kim, H. J., “Operational parameters affecting the performance of mediator-less microbial fuel cell”, *Biosensors and Bioelectronics*, (2003). 18, 327–334.

[14] Angenent, L. T., Karim, K., Al-Dahhan, M. H., Wrenn, B. A., & Domiguez, E. R., “ Production of bioenergy and biochemicals from industrial and agricultural wastewater”, *Trends in Biotechnology*, (2004). 22(9), 477–485.

[15] Manaswini Behera, Partha S. Jana, Tanaji T. More, M.M. Ghangrekar., “Rice mill wastewater treatment in microbial fuel cells fabricated using protonexchange membrane and earthen pot at different pH”, *Bioelectrochemistry*, (2010). 79, 228–233.

[16] Ghangrekar, M.M., Joshi, S.G., Asolekar, S.R., “Characteristics of sludge developed under diVerent loading conditions during UASB reactor start-up”, *Water Research*, (2005). 39 (6), 1123–1133.

[17] APHA, AWWA, WPCF, “Standard Methods for examination of water and wastewater, 20th edn. 364 Washington, DC”, *American Public Health Association*,

[18] Picoreanu, C., Head, I.M., Katuri, K.P., van Loosdrecht, M.C.M., Scott, K., “A 514 computational model for biofilm-based microbial fuel cells”, *Water Res.*, (2007). 41, 2921–2940.