Performance Of Dual-Chambered Membrane Less Microbial Fuel Cell With Anaerobic Cathode

Y. D. Jagtap* and G. S. Jadhav

Rajgad Dnyapeeth's Shri Chhatrapati Shivajiraje College of Engineering, Pune, India.

Abstract

Performance of dual-chambered membrane less microbial fuel cell (MFC) with anaerobic cathode was investigated to treat synthetic wastewater under continuous mode of operation with anaerobic cathode compartment. Stainless steel (SS) mesh with surface area 100 cm^2 was used as an anode electrode; whereas a graphite rod with surface area 75 cm^2 was used as a cathode electrode. Under continuous mode of operation, maximum power density of 0.52 mW/m^2 ; maximum current density of 3.8 mA/m^2 and maximum volumetric power of 12.78 mW/m³ were obtained using anode effluent as a cathodic electrolyte under anaerobic condition. Under continuous mode of operation, maximum chemical oxygen demand removal efficiency and maximum coulombic efficiency with respect to anode chamber were 65-69% and 0.363%, respectively; whereas maximum chemical oxygen demand removal efficiency with respect to total volume of the MFC was 92%. Internal resistance and potential difference of a cell was changed with day of operation. Minimum internal resistance of the cell was 13700 Ω ; whereas maximum potential difference developed was 0.583 V with both anaerobic compartments.

1. Introduction

Considerable attention has been paid to develop microbial fuel cells (MFCs) as a sustainable energy source because of their capability to simultaneously generate electricity and treat organic wastewaters [1]. This technology enables the direct capture of the energy contained in biodegradable organic matter in the form of electricity. MFC is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [2].

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 [3-4]. 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 possible reaction in cathode chamber using aerated water is shown below [5, 6, 7, and 8].

 $4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad E^\circ = 1.23 V$ (1.1)

The main disadvantage of a traditional two chamber MFC is that the cathode solution must be aerated to provide oxygen to the cathode [9]. The power output of a MFC can be improved by increasing the efficiency of the cathode, e.g. power is increased by adding ferricyanide, hexacynoferrate, hydrogen peroxide, oxygen and permanganate to the cathode chamber. Using permanganate as the cathode's electron acceptor the maximum power density of 3986.7 mW/m² was achieved in the MFC [10]; but use of different cathode electrolyte operating cost of MFC increases.

Based on the facts mentioned above, the main aim of the present work was an attempt to produce electricity using mixed culture and anaerobic cathode compartment. Moreover, this study may pave way to meet the demand of electricity and wastewater treatment in future by cost-effective method.

2. Materials and Methods

2.1. Microbial fuel cell

The study was carried in dual chambered completely anaerobic laboratory scale up-flow microbial fuel cell. Both chambers of was MFC made by using plastic bottles; both chambers was connected by 4 cm pipe. No proton exchange medium was used; anode effluent itself was used as a medium to bring proton at cathode for cathodic reaction. The working volume of anode chamber and cathode chamber of MFC was 100 ml and 75 ml 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 cm² and graphite rods having surface area of 75 cm² were used as anode and cathode respectively. 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 NaHCO₃, 159 mg/l NH₄Cl, 13.5 mg/l K₂HPO₄, 4.5 mg/l KH₂PO₄, 125 mg/l CaCl₂.2H₂O, and 32 mg/l MgSO₄.7H₂O. Trace metals like Fe, Ni, Mn, Zn, Co, Cu, and Mo were added as per the composition suggested by Ghangrekar and Shinde 2007 (2007). The

operating chemical oxygen demand (COD) of synthetic wastewater was in the range of 500 to 510 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 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 24 h and organic loading rate (OLR) of 1.0 kg COD $\cdot m^{-3} \cdot d^{-1}$.

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 [11]. The potential and current were measured using a digital multimeter (MECO 603, India) and converted to power according to P = I 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 [12]. 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 x n x 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 $C_E = I x t$, where, 't' is time duration (sec). Polarization study was carried out at variable external resistances, using resistance box. Internal resistance of the MFC was measured from the slope of line from the plot of voltage versus current.

3. Result and Discussion

3.1. Waste water treatment and electricity generation

MFC was operated under continuous mode of operation at HRT of 20 h for 50 days. Synthetic wastewater containing sucrose as a carbon source was used in the study, unless specified, having COD concentration 500-510 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 16th 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.



Figure 2. Variation of current and coulombic efficiency with time.



Figure 3. Variation of COD removal efficiency with time.

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 0.523 mW/m² and coulombic efficiency of 0.363 % was observed on the 14th day with corresponding anode chamber and overall COD removal efficiency of 60 and 75.5 % respectively. The corresponding short current was 38 μ A. The maximum current densities, with respect to anode and cathode surface area, were 3.8 and 5.01 mA/m², respectively;

whereas maximum volumetric power with respect to anode chamber of 52.306 mW/m³ was observed on 16th day. 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 15 μ A after 14. After stabilization, at 20 h HRT, the anode chamber and overall COD removal efficiency was in the range of 67-69 and 88-92 % respectively.Maximum potential difference developed was 0586 V using both anaerobic compartments.

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

In traditional MFC, oxygen is reduced at cathode as a result of potential difference developed between anode and cathode. In this study cathode was used under anaerobic conditions, potential difference between electrodes developed might be due to another bacterial redox reactions which acts as an electron accepter. Bacteria use a reduced compound as substrate, and oxidize during their metabolism. During oxidation, electrons are transferred from a low to a high potential, hence a voltage difference is generated [14]. An overview of common possible redox reactions are given in Table 3.1.

theoretical E0 varaes	
Redox reaction	E_0
	(mV)
$2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{H}_2$	-420
$Ferredoxin(Fe^{3+}) + e^{-} \rightarrow Ferredoxin(Fe^{2+})$	-420
$\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{NADH}$	-320
$S + 2H^+ + 2e^- \rightarrow H_2S$	-274
$\mathrm{SO_4}^{2-} + 10\mathrm{H}^+ + 8\mathrm{e}^- \rightarrow \mathrm{H}_2\mathrm{S} + 4\mathrm{H}_2\mathrm{O}$	-220
$Pyruvate^{2-} + 2H^{+} + 2e^{-} \rightarrow Lactate^{2-}$	-185
$FAD + 2H^+ + 2e^- \rightarrow FADH_2$	-180
$Fumarate^{2-} + 2H^{+} + 2e^{-} \rightarrow Succinate^{2-}$	+31
Cytochrome $b(Fe^{3+}) + e^- \rightarrow Cytochrome b$	+75
$({\rm Fe}^{2+})$	
Ubiquinone + $2H^+$ + $2e^- \rightarrow UbiquinoneH_2$	+100
Cytochrome $c(Fe^{3+}) + e^- \rightarrow Cytochrome$	+254
$c(Fe^{2+})$	
$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	+421
$\mathrm{NO_2}^- + 8\mathrm{H}^+ + 6\mathrm{e}^- \rightarrow \mathrm{NH_4}^+ + 2\mathrm{H_2O}$	+440
$\mathrm{Fe}^{3+} + \mathrm{e}^- \rightarrow \mathrm{Fe}^{2+}$	+771
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+840
[Source: Rabaey and Verstaete., 2005]	

3.2. Polarization and internal resistance

Table 3.1 Various redox reactions and possibletheoretical E_0 values



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 44500 Ω , 36100 Ω and 13700 Ω on day of 6, 9, and 16 respectively. Later internal resistance was increased with time and it was 27100 Ω on day 28th. Initially decrease in internal resistance with time might be due to increase in ion concentration in water, which increases conductivity of water. Further increase in internal resistance might be due to decrease in ion concentration due consumption by the bacteria for their metabolism.

4. Conclusion

Microbial fuel cell (MFC) as a sustainable energy source of electricity, should harvest energy with minimal operating cost. In traditional MFC require aeration for cathodic reaction which increases operating cost. In this study effluent from anodic chamber was successfully used as a cathodic electrolyte under anaerobic condition, to produce electricity using mixed culture. Moreover, this study may pave way to meet the demand of electricity and wastewater treatment in future by cost-effective method.

5. References

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