

Dual-Chambered Membrane Microbial Fuel Cell: Limitation On Potential Difference

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Abstract

Performance of two microbial fuel cells (MFCs) was investigated under batch mode of operation using aerated distilled water as cathodic electrolyte. Stainless steel (SS) mesh anode was used in both the MFCs with surface area of 100 and 170 cm² in MFC-1 and MFC-2, respectively. Stainless steel (SS) mesh cathode with surface area of 33.9 cm² was used in MFC-1, where as graphite rods cathode with surface area of 150 cm² was used in MFC-2. Under batch mode of operation, these MFCs gave chemical oxygen demand removal efficiency in the range of 85-87 % and about 87-92 %, respectively. Anodic electrolyte pH was decreased for both MFCs, where as cathodic electrolyte pH was increased in MFCs. Carbonate alkalinity, bicarbonate alkalinity, hardness and TDS (total dissolved solids) of cathodic electrolyte were increased in both MFCs.

1. Introduction

Microbial fuel cell (MFC) provides new opportunity for the sustainable production of energy, in the form of direct electricity from biodegradable compounds present in the wastewater. MFC is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms [1]. The MFC system often consists of two compartments normally separated by a PEM. In the anaerobic compartment microorganisms oxidize substrate [2]. The generated protons migrate from the anaerobic compartment to the aerobic compartment through the PEM. The produced electrons are transferred to the anode and then pass through an external electric circuit to the cathode, where they reduce oxygen to form H₂O. [3-4].

Performance of a MFC is affected by the substrate conversion rate, over-potentials at the anode and at the cathode, the PEM performance, and internal resistance of the cell [5]. 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 [6], sedimentary bacterium [7], *Geobacter sulfurreducens* [8], sedimentary bacterium [7]; cathode performance with different electron acceptor such as a permanganate, oxygen [9-10]; and Hexacyanoferrate [10]; spatial arrangement of effluent with respect to PEM [9]; electrode distance [11]; cathode surface area and cathode mediator [12]; and operating parameters such as pH, temperature [13] etc.

This study was aimed to investigate the effect on cathodic electrolyte of MFC and to investigate factors affecting reduction of potential difference, under batch mode of operation using dual chambered membrane MFC.

2. Materials and methods

2.1. Microbial fuel cell

Two dual-chambered MFCs were constructed from acrylic sheet, with difference of anode surface area, anode orientation, cathode material and cathode area. MFC-1 was provided with L-shaped stainless steel (SS) mesh anode electrode, having surface area of 100 cm². Stainless steel (SS) wire mesh square cage of side 7×7 cm and length of 7 cm as anode electrode, offering total surface area of 170 cm², was used in MFC-2. Stainless steel was used as a cheaper replacement to the graphite electrode and as an easily available material in mesh form to offer more surface area per unit volume [9]. Total working volume of each anode and cathode chamber was 1,330 ml for MFC-1 and 1,310 ml for MFC-2. Proton exchange membrane of 0.007 inch thickness (Nafion[®] 117, Aldrich) was used to separate both chambers. Membrane surface area of 25.0 and 24.01 cm² was used in MFC-1 and MFC-2,

respectively. SS mesh cathode electrode having surface area of 33.9 cm^2 was used in both the MFCs, placed close to the PEM. The electrodes were connected externally with concealed copper wire through external load resistance of 50 ohms.

2.2. Wastewater

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 and Shinde [11]. The operating chemical oxygen demand (COD) of synthetic wastewater was in the range of 480 to 510 mg/l. The influent feed pH was in the range of 7.2 to 7.6 throughout the experiments.

2.3. MFC Operation

The MFC was inoculated with the adapted anaerobic culture collected from the anode chamber of the existing MFC under operation [9]. This existing MFC was initially inoculated with preheated mixed anaerobic sludge and operated for four months. In the present experiments, MFC was operated under fed batch mode of operation for total 28 days, with aerated distilled water as cathodic electrolyte and using synthetic wastewater as a feed in anode chamber. The feed cycle time of 48 h was adopted throughout the batch mode of study. Effect of sodium ions in cathode electrolyte on open circuit voltage was studied using 10 gm/l NaCl with aerated distilled water as cathodic electrolyte.

2.4. Analyses and calculations

The suspended solids (SS), volatile suspended solids (VSS), influent COD, effluent COD and pH were monitored according to APHA standard methods [14]. 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 [15]. 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

Under batch mode of operation, at feed cycle time of 48 h, both MFCs took a period of ten days to reach stable conditions. It was observed that at steady state conditions the COD removal efficiency was around 85-87 % and 87-92 % for MFC-1 and MFC-2, respectively.

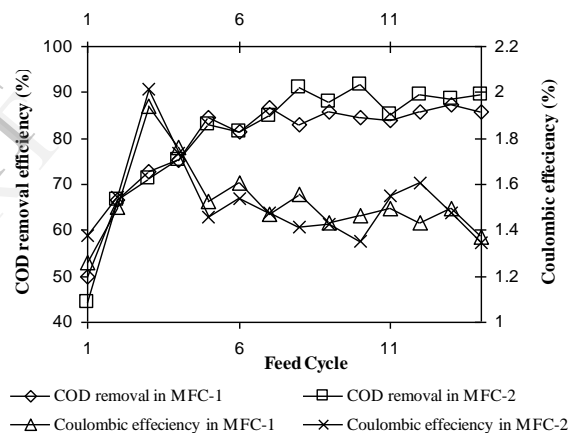


Figure 1. Variation of COD removal efficiency and Coulombic efficiency with time under batch operation.

After start-up, the coulombic efficiency started increasing with duration of operation and reached to the maximum value of Afterwards, coulombic efficiency decreased with time. The maximum coulombic efficiency 1.94 % and 2 % was observed for 3rd feed cycle with corresponding COD removal efficiency 73% and 71 % for MFC-1 and MFC-3, respectively [Fig. 1]; where as current density was 63.2 mA/m² and 186.5 mA/m² for MFC-1 and 37.5 mA/m² and 42.5 mA/m² for MFC-2 with respect to anode and cathode area, respectively [Fig. 2]; Later decrease in coulombic efficiency and increase in COD removal efficiency was observed for both the MFCs. Corresponding coulombic efficiency from 1.34 to 1.76% and 1.34 to 1.73% for MFC-1 and MFC-2, respectively. This reduction in coulombic efficiency and increase in COD removal

efficiency might be due to reason that initially electrochemically active bacteria were more active than the methanogenic bacteria. Later favorable conditions, such as, near neutral pH (6.8–7.2) and temperature, promoted the growth of methanogenic bacteria and resulted in reducing coulombic efficiency and increasing COD removal efficiency. Lesser electricity generation is reported earlier in MFC enriched with methanogens as compared to MFC enriched with electrogenic population [16]. Favorable conditions promoted the growth of methanogens faster than those of the electrochemically active bacteria in a mixed culture [5, 13,17, 18, 19]. Low coulombic efficiencies of MFC imply that the electron-transfer bacteria are incapable of converting all of the available organics into electricity, so the excessive substrate creates niche for the growth of methanogens under favorable environment [20]. This finding is consistent with earlier reports of methane production in a dual-chamber MFC [21] and MFC operated in up flow mode [20]. Increase in methane production with duration of operation is reported in MFC [21].

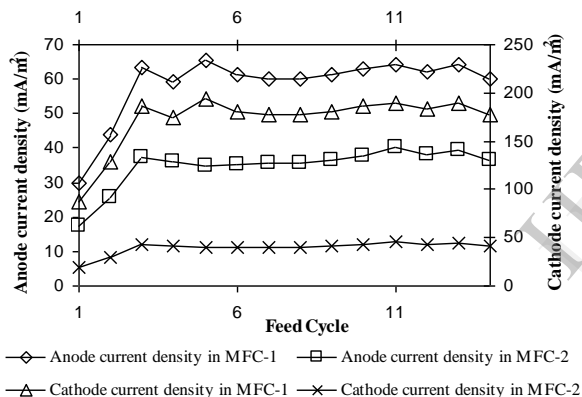


Figure 2. Variation of current density with time under batch operation.

Maximum current density was observed on 22nd day and it was 64.2 mA/m² and 189 mA/m² for MFC-1 and 40.17 mA/m² and 45.53 mA/m² for MFC-2 with respect to anode and cathode, respectively. Increase in current on 22nd day might be due to decrease in temperature on that day, the growth of methanogens got suppressed and resulted in lowering of the substrate utilization by methanogens and hence larger fraction of the substrate was available to electrogenic population and resulted in increase in current [13].

3.2. Effect on anodic electrolyte

During the batch mode experiment, the pH of anodic solution decreased with time, when the pH of the fresh feed was 7.4±0.1, the pH of anode solution

reached to the minimum value of about 6.7±0.1 for both the MFCs [Fig.3 and Fig. 4]. This indicates that the proton transport through the membrane is slower than its production rate in the anode chamber.

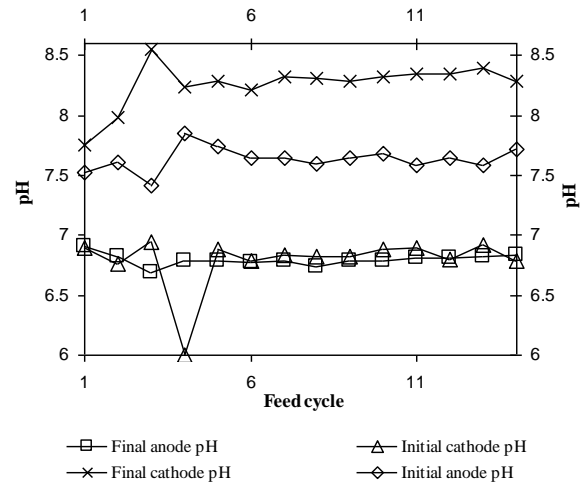


Figure 3. Variation of anode and cathode pH with time under batch operation in MFC-1.

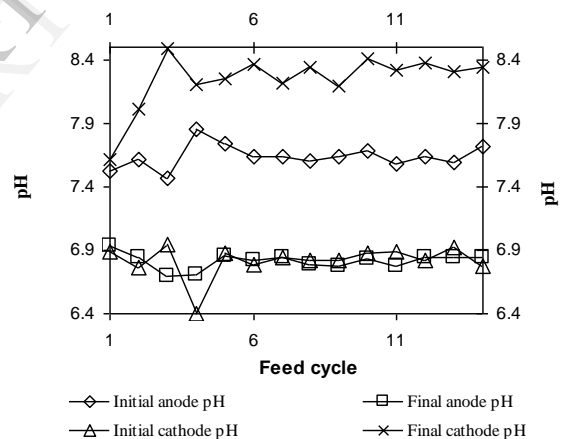
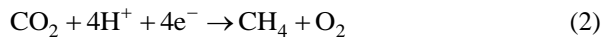


Figure 4. Variation of anode and cathode pH with time under batch operation in MFC-2.

The MFC performance will be optimum when constant pH is obtained in the anode chamber without buffer. This is possible 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 [13]. Decrease in pH, high COD removal efficiency and lower coulombic efficiency supports that electrochemically active bacteria convert sucrose in to proton and electron and become part COD removal

efficiency, but due to limitation of MFC as a whole system these end products are not utilized either by methanogens or for electricity generation.

Basic reactions occurring in anode chamber of MFCs, in the case of sucrose fed wastewater using mixed culture inoculums, considering complete conversion of sucrose into protons and electrons it first step of anaerobic digestion, further favorable conditions promotes growth of methanogens with time, [13] which produces methane from proton electron and carbon dioxide, and presence of hydrogen producing bacteria are as follows



3.3. Effect on Cathodic electrolyte

During the batch mode experiment, aerated distilled water was used as cathodic electrolyte. Fresh distilled water was added for each feed cycle. The pH of cathodic solution increased with time, when the pH of the fresh distilled water was 6.8 ± 0.1 , the pH of cathode solution reached to the maximum value of about 8.3 ± 0.1 for both the MFCs. This indicates that the proton transport through the membrane is slower than its production rate in the anode chamber to support cathodic reaction. This finding is consistent with earlier reports of increase in pH of cathodic solution [13].

Carbonate alkalinity, bicarbonate alkalinity, hardness and TDS (total dissolved solids) of cathodic electrolyte were increased in both MFCs. Carbonate alkalinity, bicarbonate alkalinity, hardness and TDS (total dissolved solids) of cathodic electrolyte were 0-12 mg/l, 66-74mg/l, 28-48 mg/l and 60-102 mg/l, respectively for MFC-1 [Fig. 5]. Whereas carbonate alkalinity, bicarbonate alkalinity, hardness and TDS (total dissolved solids) of cathodic electrolyte were 0-16 mg/l, 64-78 mg/l, 28-52 mg/l and 54-100 mg/l, respectively for MFC-2 [Fig. 6]. This observation supports that alkalinity in cathode electrolyte is not due to hydroxyl ion but it is due to carbonates and bicarbonates of calcium, magnesium and sodium, and sometimes PEM works as a cation exchange membrane which allows transferring sodium, magnesium and calcium from anode chamber to cathode chamber. This finding is consistent with earlier reports of increase in pH of cathodic solution [13].

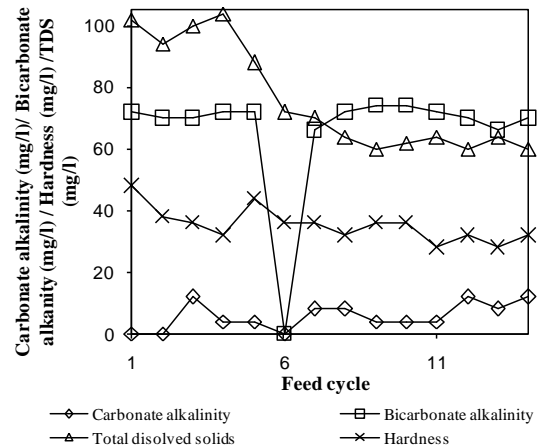


Figure 5. Variation of TDS, carbonate alkalinity, bicarbonate alkalinity and hardness of cathode electrolyte with time under batch operation in MFC-1.

3.4 Potential difference development in MFC

Open circuit voltage of both MFCs were measured using aerated distilled water and aerated distilled water with 10 gm/l NaCl as cathodic electrolyte. Open circuit voltages were 0.70 V and 0.32 V for MFC-1 using aerated distilled water and aerated distilled water with 10 gm/l NaCl as cathodic electrolyte, respectively; whereas open circuit voltages were 0.71 V and 0.325 V for MFC-2 using aerated distilled water and aerated distilled water with 10 gm/l NaCl as cathodic electrolyte respectively. The possible reaction in cathode chamber using oxygen as electron acceptor stated below [3, 9, 22]:



Observed potential difference in both MFCs is much lesser compare to theoretical Electromotive force. OCV was decreased from 0.70 V using aerated distilled water as cathodic electrolyte to 0.32 V using aerated distilled water with 10 gm/l NaCl as cathodic electrolyte for MFC-1, whereas it was decreased from 0.71 V using aerated distilled water as cathodic electrolyte to 0.325 V using aerated distilled water with 10 gm/l NaCl as cathodic electrolyte for MFC-2. The decrease in OCV for both MFCs might be due to sodium ion acting as an electron acceptor, which reduces electromotive force of microbial fuel cell. The possible reaction in cathode chamber using sodium ion as electron acceptor stated below

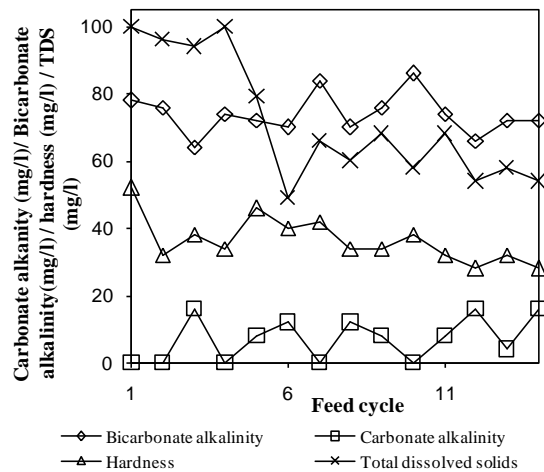
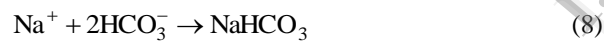
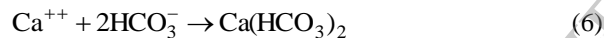
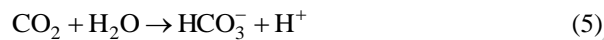


Figure 6. Variation of TDS, carbonate alkalinity, bicarbonate alkalinity and hardness of cathode electrolyte with time under batch operation in MFC-2.

Considering penetration of calcium, magnesium and sodium ions through PEM and possible reactions in cathode chamber which are responsible for increase in pH are as follows:



A bio-chemical reaction in the anode chamber of cell causes an increase in the number of electrons at the surface of one of the electrodes, making it negative, while reduction reaction at other electrode tends to remove electrons, thereby making it positive. The negative and positive electrode constitute an electrochemical cell. The electron flow from negative to the positive electrode through the external circuit, and in the process oxidation occurs at the negative electrode where electrons are given off and the reduction occurs at positive electrode. The overall cell reaction which is the sum of the two electrode reactions, which gives the emf of the cell.

Considering penetration of calcium, magnesium and sodium ions through PEM and possible reactions in cathode chamber which are responsible for decrease in potential difference of cell are shown in table. 1.

Table.1. Possible redox reactions and theoretical E_0 values [23].

Electrode Reaction	Standard reduction
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	potential, V
$\text{Ca}^{++} + 2e^- \leftrightarrow \text{Ca}$	-2.87
$\text{Na}^+ + e^- \leftrightarrow \text{Na}$	-2.714
$\text{Mg}^{++} + 2e^- \leftrightarrow \text{Mg}$	-2.37

In other words behaviour of MFC as whole system is complex and open circuit voltage developed depends upon the various cathodic reactions which act as an electron acceptor. As cations penetrate through the PEM which acts as a competitor to the oxygen to accept electron as a result potential difference developed is result of all reactions at cathode electrode.

4. Conclusion

Carbonate alkalinity, bicarbonate alkalinity, hardness, TDS (total dissolved solids) and pH of cathodic electrolyte were increased in MFCs. Carbonate and bicarbonate alkalinity increase might be due to carbonates and bicarbonates of sodium, magnesium and calcium. Sodium, magnesium and calcium ions are competitive to protons to penetrate through PEM. Observed potential difference in MFC is much less compared to theoretical open circuit voltage due to, cations penetrating through PEM and acting as an electron acceptor, which reduces potential difference of cell.

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6. References

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