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Performance of Microbial Fuel Cell with Clayware Wall Separation Subjected to Variation in Area of Separation, Permeability,Temperature

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***Abstract*- Microbial fuel cells (MFCs) are devices that can be used to convert chemical energy stored in biodegradable materials into electrical energy. Sustainable energy recovery from organic wastes is gaining a research interest from last few years. The microbial fuel cell will be cost-effective technology if replace costlier proton exchange membrane with the cheapest alternative. Hence, the performance of MFCs was evaluated using soil partition as an alternative to proton exchange membrane. Performance of six microbial fuel cells (MFCs) was investigated in terms of current, columbic efficiency and chemical oxygen demand removal efficiency under the batch mode of operation using aerated distilled water as a cathodic electrolyte. Effect of permeability, a surface area of partition, ambient temperature variation and substrate concentration were evaluated. It was observed that current and coulombic efficiency increases with increase in surface area and permeability of partition wall. It was observed that ambient temperature plays the vital role in energy harvesting and treatment efficiency.**

***Index Terms*— MFC, Current, Voltage, Bio-energy, Waste water treatment, Alternative to PEM.**

I. INTRODUCTION

Microbial fuel cell (MFC) provides new opportunity for the sustainable production of energy from waste, in the form of direct electricity from biodegradable compounds present in the wastewater, achieving simultaneous wastewater treatment. MFC is a device that converts chemical energy associated with biodegradable organic matter to electrical energy with the aid of the catalytic reaction of microorganisms (Allen and Bennetto, 1993). In a MFC, substrate (organic matter or biomass) is oxidized in the anode chamber producing carbon dioxide, protons and electrons (Rabaey and Verstraete, 2005). Microorganisms here fulfill the role of catalysts in analogs to chemical fuel cells. 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 [Angenent et al., 2004]. 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 [Jang et al., 2004; Pham et al., 2003; Oh et al., 2004].

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O \qquad E^\circ = 1.23\ V \qquad (1)$$

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 (Rabaey and Verstraete, 2005). 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 (Ringeisen et al., 2007), Geobacter sulfurreducens (Dumas et al., 2008), sedimentary bacterium (Zhang et al., 2006); spatial arrangement of effluent with respect to PEM (Jadhav and Ghangrekar, 2008); electrode distance (Ghangrekar and Shinde, 2007); cathode performance with different electron acceptor such as a permanganate, oxygen (Jadhav and Ghangrekar, 2008; You et al., 2006); and Hexacyanoferrate (You et al., 2006); cathode surface area and cathode mediator (Kim et al., 2007), etc. Most of the literature review supports performance of dual chamber MFC with proton exchange membrane partition. Microbial fuel cell will be cost effective technology, if replace costlier proton exchange membrane with cheapest alternative. The present study was aimed to investigate the effect of permeability of soil wall partition and surface area of partition on performance of MFC.

II. MATERIALS AND METHODS

2.1 Microbial fuel cells

Six dual-chambered MFCs were constructed using easily available plastic boxes. Total working volume of each anode and cathode chamber was 2400 ml. Soil wall partition of 2 mm thick was used to separate anode and cathode chamber. Soil plates were used as a cheaper replacement to the proton exchange membrane. Two different soil samples (sample-1 and sample-2) were used for the construction of partition wall. Soil wall constructed from soil sample-1 was used for MFC-1, MFC-2 and MFC-3; whereas Soil wall constructed from soil sample-2 was used for MFC-4, MFC-5 and MFC-6. Soil plates were used as a cheaper replacement to the proton exchange membrane. Surface area of partition wall (constructed from soil sample-1) used for MFC-1, MFC-2 and MFC-3 were 4 cm2, 8 cm2 and 12 cm2 respectively; whereas Surface area of partition wall (constructed from soil sample-2) used for MFC-4, MFC-5 and MFC-6 were 4 cm2, 8 cm2 and 12 cm2 respectively. Permeability of soil plates used for MFC-1, MFC-2 and MFC-3 was 6.77X 10-4 cm/min; whereas Permeability of soil plates used for MFC-4, MFC-5 and MFC-6 was 3.93 X 10-5 cm/min. Three graphite rods having total projected surface area of 150 cm2 were used as cathode as well as anode. Electrodes were connected externally with concealed copper wire through external load resistance.

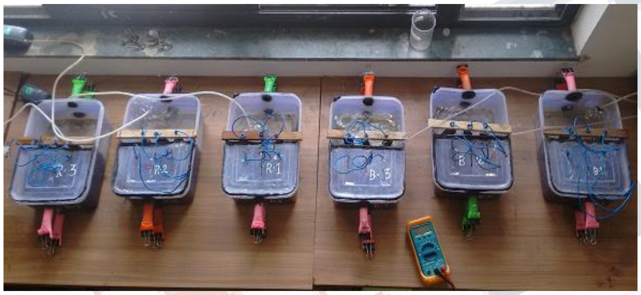

Fig. 1. Experimental setup

2.2 Wastewater

A synthetic wastewater containing sucrose as a carbon source was used throughout the study, as per the composition provided in Table 1 (Ghangrekar and Shinde, 2007). The operating chemical oxygen demand (COD) of synthetic wastewater was in the range of 1500-1600 mg/l. Influent pH in the MFC was in the range of 7.2 to 7.6 during the studies evaluating effect of temperature variation.

Component	Sucrose	$NaHCO_3$	NH_4Cl	K_2HPO_4	KH_2PO_4	$CaCl_2.2H_2O$	$MgSO_4.7H_2O$
mg/l	445	750	159	13.5	4.5	125	32

Table 3.1. The composition of the synthetic wastewater Component

Note: Trace metals were added as FeSO4.7H2O = 10 mg/l, NiSO4.6H2O = 0.526 mg/l, MnSO4.H2O = 0.526 mg/l, ZnSO4.7H2O = 0.106 mg/l, H3BO3 = 0.106 mg/l, CoCl2.6H2O = 52.6 □g/l, CuSO4.5H2O = 4.5 □g/l, and (NH4)6Mo7O24.4H2O = 52.6 □g/l.

2.3 MFC operation

These MFCs were inoculated with anaerobic sludge collected from septic tank bottom. The inoculum sludge was sieved through 1-mm sieve, preheated at 100 °C for 15 min to suppress the methanogens, cooled at room temperature and 750 ml of sludge was added to the anode chamber. This method was found effective to obtain an enriched culture of hydrogen producers (Ginkel et.al 2001). MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 were operated in fed batch mode for a total of 30 days at feed cycle time of 48 h, to study effect area of permeability of soil plates and partition area between anode and cathode chamber. Aerated distilled water was used as a cathodic electrolyte; whereas synthetic wastewater was used as a feed in anode chamber. All experiments were conducted at room temperature ranging from 22 to 41 °C, unless specifically mentioned. All the experiments were conducted with the external resistance of 50 Ω, unless specifically mentioned.

After 30 days of batch mode of operation, feed was not supplemented to the MFC for 25 days, to check the viability of MFC to sustain long duration of non feed conditions. After this shutdown period, during restart, the operation was started at feed cycle time of 12 h, with same feed composition in anode chamber and aerated distilled water as cathodic electrolyte. The effect of ambient temperature change on the performance of MFC was studied in terms of COD removal efficiency and energy harvesting.

2.4 Analyses and calculations

The influent and effluent COD and pH were monitored according to APHA standard methods (APHA et al., 1998). The potential and current were measured using a digital multimeter (RISH Multi 15S, 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 (Picoreanu et al., 2007). The coulombic efficiency (CE) was estimated by integrating the measured current relative to the theoretical current on the basis of consumed COD, CE = (CE/CT) x 100. The theoretical current production 'CT' was estimated as CT = (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 (Rabaey et al., 2003). The actual current production 'CE' was integrated as CE = I x t, where't' is time duration (sec). Theoretical current was estimated on the basis of complete conversion of sucrose, expressed as COD, in carbon dioxide and water. Permeability of earthen walls was measured by variable head method.

III. RESULTS AND DISCUSSIONS

3.1 Microbial fuel cell behavior after start up

The MFCs were started under batch mode of operation, at feed cycle time of 48 h, and it tooks start-up period of 8, 10, 8, 12, 10 and 10 days to reach stable conditions for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively. Aerated distilled water was used as cathode electrolyte. During the studies the ambient temperature range varied from 15 – 41 °C. After start-up, the current started increasing with duration of operation and the reached to the maximum value of 0.76 mA, 1.51 mA, 2.23 mA, 0.65 mA, 1.37 mA and 1.9 mA on the 6th, 8th, 8th, 8th, 8th and 8th day for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively. At peak current generation under batch mode of operation, chemical oxygen demand removal efficiency of these MFCs were more than 79%, 81%, 80%, 76%, 79% and 82 % for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively. And corresponding columbic efficiency were 1.2% , 2.35 %, 3.54 %, 1.123 %, 2.26%, and 2.97 % for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively

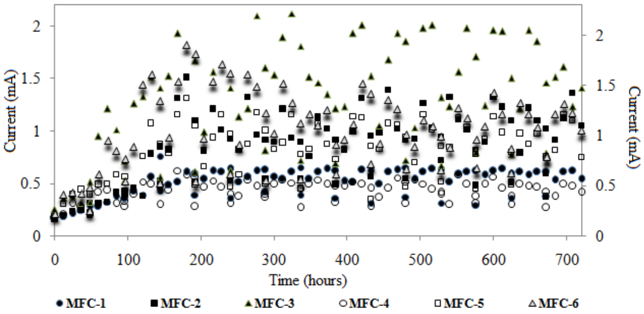

Fig.2. Variation of current with time under batch operation

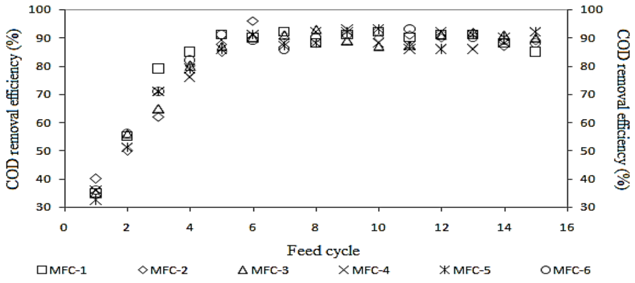

Fig.3. Variation of COD removal efficiency with time

Afterwards it got decreased to reach stable value of around 0.6 mA, 1.2 mA, 1.6 mA, 0.5, 1.1 and 1.5 mA for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively on 8th day onwards. Under stable conditions and batch mode of operation, chemical oxygen demand removal efficiency of these MFCs were more than 90%, 92%, 88%, 84%, 91% and 90% for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively.

The corresponding maximum current density, with respect to anode surface area, on 6th day was 50 mA/m2, 100.66 mA/m2, 148.66 mA/m2, 43.33 mA/m2, 91.33 mA/m2 and 126.66 mA/m2 for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively; which got decreased with further days of operation, and become stable around 40 mA/m2 80 mA/m2 106.66 mA/m2 33.33 mA/m2 , 73.33 mA/m2 and 100 mA/m2 for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively. Decrease in current, current density after peak might be due to reason that initially electrochemically active bacteria were more active than the methanogenic bacteria. Later favorable conditions promoted growth of methanogenic bacteria and resulted in decreasing current and increasing COD removal efficiency.

It was observed that at steady state conditions the COD removal efficiency for all MFCs was around 90% with corresponding coulombic efficiency of around 1.1 %, 1.9 %, 2.8%, 0.9 %, 1.8% and 2% for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively

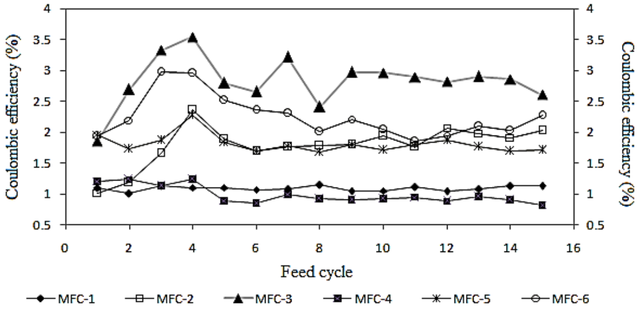

Fig.4. Variation on coulombic efficiency with time

This reduction in coulombic efficiency might be due to the increased concentration of sludge in anode chamber and hence increased activity of methanogens with time, contributing to enhance the COD removal. Favorable conditions promotes the growth of methanogenic bacteria faster than those of the electrochemically active bacteria in a mixed culture [Moon et al., 2006; Kim et al., 2004; Rabaey et al., 2003; Zhuwei Du 2007].

3.2 Effect of Surface Area of Partition on Current

Effect of surface area of partition on short current was evaluated with varying surface area of partition. Soil wall partition of 2 mm thick was used to separate anode and cathode chamber. Two different soil samples (sample-1 and sample-2) were used for the construction of partition wall. Soil wall constructed from soil sample-1 was used MFC-1, MFC-2 and MFC-3; whereas Soil wall constructed from soil sample-2 was used for MFC-4, MFC-5 and MFC-6. Soil plates were used as a cheaper replacement to the proton exchange membrane. Surface area of partition wall (constructed from soil sample-1) used for MFC-1, MFC-2 and MFC-3 were 4 cm2, 8 cm2 and 12 cm2 respectively; whereas Surface area of partition wall (constructed from soil sample-2) used for MFC-4, MFC-5 and MFC-6 were 4 cm2, 8 cm2 and 12 cm2 respectively. Permeability of soil plates used for MFC-1, MFC-2 and MFC-3 was 6.77X 10-4 cm/min; whereas Permeability of soil plates used for MFC-4, MFC-5 and MFC-6 was 3.93 X 10-5 cm/min.

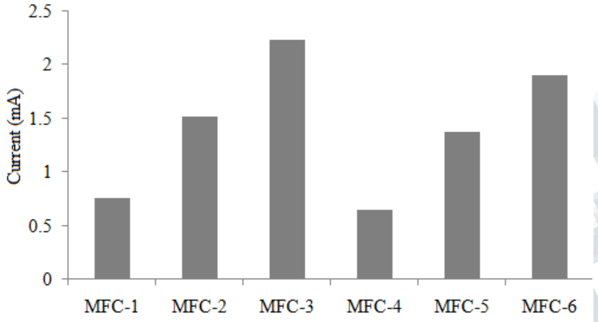

Fig. 5. Comparison of maximum currents showing effect of surface area of partition (MFC-1 and MFC-4 with 4 cm2 area; MFC-2 and MFC-5 with 8 cm2; MFC-3 and MFC-6 with 12 cm2)

Peak current for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 were 0.76 mA, 1.51 mA, 2.23 mA, 0.65 mA, 1.37 mA and 1.9 mA respectively. Afterwards short current got decreased to reach stable value of around 0.6 mA, 1.2 mA, 1.6 mA, 0.5, 1.1 and 1.5 mA for MFC-1, MFC-2, MFC-3, MFC-4, MFC-5 and MFC-6 respectively. It was observed that for both soil sample partitions short current increases with increase in surface area of partition this might be due to higher surface area of partition provides more opportunity to transfer protons from anode to cathode. Higher concentration of protons in anode chamber increases rate of reaction at cathode results in higher current.

3.3 Effect of permeability of partition on internal resistance

Performance of MFCs analyzed with reference to permeability of wall partition. Two soil samples having different permeability were used for the construction wall partition. Permeability of soil plates used for MFC-1, MFC-2 and MFC-3 was 6.77X 10-4 cm/min; whereas Permeability of soil plates used for MFC-4, MFC-5 and MFC-6 was 3.93 X 10-5 cm/min. Surface area of partition wall (constructed from soil sample-1) used for MFC-1, MFC-2 and MFC-3 were 4 cm2, 8 cm2 and 12 cm2 respectively; whereas Surface area of partition wall (constructed from soil sample-2) used for MFC-4, MFC-5 and MFC-6 were 4 cm2, 8 cm2 and 12 cm2 respectively.

Maximum current for MFC-1 and MFC-4 were 0.76 mA and 0.65 mA respectively; for MFC-2 and MFC-5 were 1.51 mA and 1.37 mA respectively and for MFC-5 and MFC-6 were 2.23 mA and 1.9 mA respectively. Coulombic efficiency for MFC-1 and MFC-4 were 1.2% and 1.12% respectively; for MFC-2 and MFC-5 were 2.35 % and 2.26 % respectively and for MFC-5 and MFC-6 were 3.54 % and 2.97 respectively.

It was observed that current and coulombic efficiency increases with increase in permeability of partition. This might be due to higher permeability of partition provides more opportunity to transfer protons from anode to cathode. Higher concentration of protons in anode chamber increases rate of reaction at cathode results in higher current.

3.4 Effect of Ambient Temperature Variation

In the later stage the MFC-3 and MFC-6 were operated at HRT of 12 h in the anode chamber to study the effect of day and night ambient temperature variation. Both MFCs were operated for 5 days. For both the reactors feed cycle was kept from 6 AM to 6 PM and 6 PM to 6 AM. For every day (6 AM to 6 PM) feed cycle temperature was increased from around 17-23 at 6 AM to around 31-36 at 1 PM and again decreased to 23 -27 at 6 PM. For every night (6 PM to 6 AM) feed cycle temperature was decreased from around 23-27 at 6 PM to around 12-15 at 4 AM and again increased to 17 -23 at 6 AM.

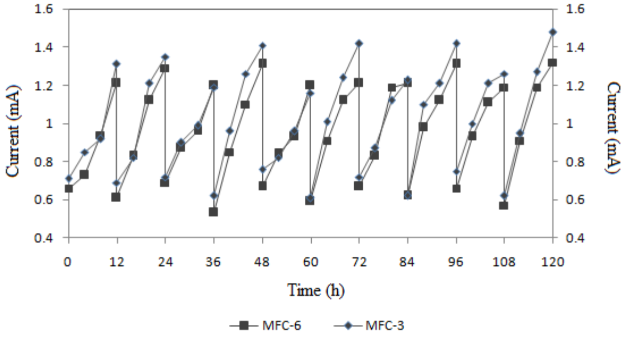

Fig.6. Variation of current during day and night time (temperature perspective) under batch operation

At the end of reaction cycle for each feed, the current was reaching to the maximum value of around1.4 mA for MFC-3 and 1.3 mA for MFC-6 at lower operating temperature (night time) and about 1.2 mA for both MFCs at higher operating temperature (day time) (Fig. 2). It was observed that at steady state conditions the COD removal efficiency for both MFCs were around 50% during night feed cycle; whereas 60 % during day feed cycle with corresponding coulombic efficiency of around 0.7 % and 0.8 %, for day feed cycle for MFC-3 and MFC-6 respectively; whereas coulombic efficiency of around 0.1 % and 0.9 %, for night feed cycle for MFC-3 and MFC-6 respectively. The decrease in COD removal efficiency during night feed cycle might be due to prevention of methanogens growth due to unfavorable lower temperature conditions, and as a result reducing the loss of charges and increasing the coulombic efficiency of MFC. However, this lower operating temperature proved that, the electrochemically active bacteria could remain active even at lower temperature. Capability of MFC converting substrate at lower temperature below 20 ^{0}C is reported earlier (Pham et al., 2006; Jadhav and Ghangrekar 2009). For each feed cycle (48 hours) initially increase in current followed by decrease after peak was reported by Jadhav and Ghangrekar 2009, but it is observed that for 12 hours feed cycle time current increases with time this might be due to less rate of proton transfer from anode chamber to cathode chamber and less rate of electron harvesting by cathode compare to electron and proton generation rate.

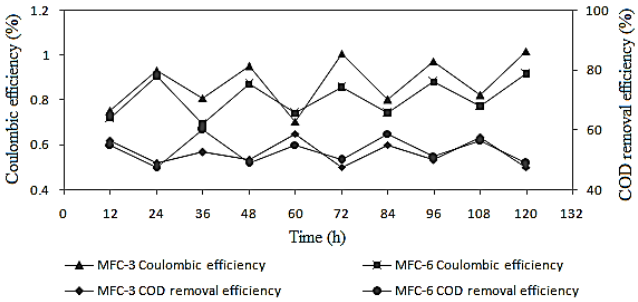

Fig.7. Comparison of COD removal efficiency and Columbic efficiency for MFC-3 and MFC-6 having same area of separation with different permeability

IV. CONCLUSION

From the present study, it was observed MFC could inoculate using easily available anaerobic inoculum which peaks the performance as a waste water treatment unit within 2 weeks, but later favorable conditions promotes the growth of methanogens. Microbial fuel cell can be made cost effective technology by replacing easily available soil partition as alternative to costlier proton exchange membrane. Performance of MFCs in terms of energy harvesting (current and coulombic efficiency) improves with increase in surface area of partition and its permeability. The ambient temperature plays vital role in energy harvesting and treatment efficiency. In mesosphilic temperature range, COD removal efficiency increases where as coulombic efficiency decreases with increase in temperature (Jadhav and Ghangrekar 2009).

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