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PERFORMANCE OF MICROBIAL FUEL CELL UNDER PSYCROPHILIC AND MESOPHILIC TEMPERATURE

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ABSTRACT

Good amount of research is going on to produce low cost microbial fuel cells (MFCs) and scale them up for field application. This current research is based on the objective of observing the functioning of a low cost MFC for generating energy along with simultaneous treatment of wastewater under two different operating temperature ranges namely psycrophilic (temperature less than 20 °C) and mesophilic (operating temperature of 30 °C) temperatures. Performance of three similar MFCs, fabricated using an earthen pot, was evaluated under these temperature ranges while treating synthetic wastewater. Maximum power densities of 14.2 mW/m^2 at resistance of 119 Ω, 20.62 mW/m^2 at resistance of 99 Ω, 21.65 mW/m^2 at resistance of 97 Ω were obtained for the three MFCs at mesophilic temperature; whereas operation at psychrophilic temperatures resulted in the power densities of 8.69 mW/m^2 at resistance of 317 Ω, 10.50 mW/m^2 at resistance of 151 Ω, 15.52 mW/m^2 at resistance of 99 Ω. Average COD removal of 30.12 ± 11.62 %, 80.66 ± 4.14 % and 74.12 ± 2.47 % were obtained in the three different operating conditions namely without temperature control (operating temperature of 11 - 13 ^{0}C) and non acclimatized inoculum, with temperature control (operating temperature of 30 ^{0}C) and then without temperature control (operating temperature of 15 - 17 ^{0}C) and acclimatized bacteria respectively. It is concluded that electrogenic bacterial growth is favored under mesophilic temperature; however, MFCs can be operated even at psychrophilic temperatures once the anodic biofilm is acclimatized at elevated temperature.

Keywords: Microbial fuel cell, Wastewater treatment, Psycrophilic, Mesophilic, Earthen pot, Power density

1. INTRODUCTION

Environmental pollution and depletion of non renewable sources of energy is cause of growing concern among people. Various researches are going on to find out alternative sources of energy. A best way that has come up in the past few decades to take care of the two major problems that humankind is now facing as mentioned earlier is generation of energy from waste [1]. Energy obtained from biomass, which is the biodegradable fraction of waste and residues from agriculture (vegetable and animal origin), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste is known as bioenergy [2]. One of the most convenient and cost effective approach to harvest energy from the waste is by using a microbial fuel cell (MFC). The MFC converts the energy stored in chemical bonds of organic compounds to electrical energy, through the catalytic reactions by microorganisms under anaerobic conditions while accomplishing the biodegradation of organic matters. It can be used in wastewater treatment facilities to break down organic matter and simultaneously generate electric power without a net carbon emission into the ecosystem. They have also been explored for applications as biosensors such as sensors for biological oxygen demand monitoring [3].

MFCs usually consist of anodic and cathodic chambers partitioned by a proton exchange membrane (PEM) [3]. Substrates containing oxidizable organic matter are added to the anodic chamber. Microbes oxidize the substrates in turn producing electron which moves through an external circuit to the cathode. Carbon dioxide is also produced as a product but there is no net carbon emission as the carbon dioxide in the substrate actually comes from the recently fixed carbon from the atmosphere by the biomass through the process of photosynthesis. Protons are also generated by the microbes in the anodic chamber which enter the cathodic chamber after crossing the PEM where they combine with oxygen to form water. Electric current generation is made possible by keeping microbes separated from oxygen or any other end terminal electron acceptor other than the anode and this requires an anaerobic anodic chamber. Microbes in the anodic chamber extract electrons and protons in the dissimilative process of oxidizing organic substrates [4].

Commercially available polymer membranes make a MFC very costly to be used for wastewater treatment.

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Membrane-less MFCs are being designed to reduce cost, obtain high power density and lower the internal resistance but they often suffer from low Coulombic Efficiency, oxygen intrusion into the anode and deactivation of cathode catalyst [5, 6, 7]. So researchers are trying to find out cheaper options for proton exchange membranes. Behera et al. [8] used an earthen pot as a membrane and obtained a maximum volumetric power density of 16.8 W/m^3. This MFC with manufacturing cost less than 1 US$ gave a quiet good performance compared to other MFCs prepared using expensive materials.

Liu et al. [9] operated two single chamber MFCs at different temperatures after successful startup they swapped the cell temperatures. They observed that if the reactor is started at a lower temperature then its performance did not change upon increasing the temperature but if it is started at a higher temperature then performance was found to improve at a lower temperature. Ahn et al. [10] used MFC to treat domestic wastewater at ambient temperature conditions and mesophilic conditions. They obtained a higher power density of 422 mW/m^2 at mesophilic temperature. Performance of MFC have been studies in different operating temperatures, but the behavioral difference of inoculum when transferred from one operating temperature to another using a low cost earthenware MFC have not yet been studied as far as our knowledge. The objective of this research was to evaluate the performance of the low cost MFC under two different operating temperatures. Three double chambered earthen pot MFCs were started at psychrophilic temperature, later they were shifted to mesophilic temperature and again back to psychrophilic temperature in a later stage. The MFCs were operated in batch mode using synthetic wastewater. The performance of these MFCs was evaluated in terms of COD removal and power production.

2. METHODS

2.1 MFC Construction

Three MFCs were made up of earthen pot anode chamber, each having a volume of 420 ml. The wall of the container was 4 mm thick which worked as the proton exchange membrane. The details of material properties of the earthen pot are already reported by Behera and Ghangrekar [8]. Stainless Steel mesh having a total surface area of 166 cm^2 was used as anode and two graphite plates of surface area 68.25 cm^2 each were used as cathode. The earthen pot anode chamber was placed in a plastic container working as a cathode chamber. Electrodes were connected externally through concealed copper wire through an external resistance of 100 Ω. Figure 1 shows the arrangement of the MFC experimental set-up. The three MFCs were operated at three different conditions as given in Table 1.

2.2 MFC Operation

These MFCs were inoculated initially with anaerobic sludge collected from a septic tank bottom. The inoculum sludge was given a heat pre-treatment (heated at 100 ^{0}C for 15 min) and 60 ml of sludge was added to the anode chamber. The sludge contained 26.5 gm/L of total solids and 7.5 gm/L of volatile solids. Initially these MFCs were operated under psychrophilic temperature of 11 to 13 ^{o}C. Since, after two weeks of operation the performance of these MFCs could not improve, the operating temperature was elevated to 30 ^{o}C using aquarium heater in the cathodic chamber. In the later phase of the experiment the MFCs were once again operated in the psychrophilic temperature range having acclimated biofilm on the anode, developed during earlier phase of operation. Feed solution containing sodium acetate as a source of carbon having chemical oxygen demand (COD) of 3000 mg/L was used. The acetate medium also contained (per gram of COD) $NaHCO_3$, 1500 mg; NH_4Cl, 318 mg; $CaCl_2.2H_2O$, 250 mg; $MgSO_4.7H_2O$, 64 mg; K_2HPO_4, 27 mg; and KH_2PO_4, 9 mg. Trace metals were added as $FeSO_4.6H_2O$, 10.00 mg/L; $MnSO_4$, 0.526 mg/L; $ZnSO_4.7H_2O$, 0.106 mg/L; H_3BO_3, 0.106 mg/L; and $CuSO_4.5H_2O$, 4.5 μg/L, $CoCl_2$, 105.2 μg/L, $(NH_4)6MO_7O_{24}.4H_2O$, 105.2 μg/L [8]. These MFCs were operated using aerated tap water as cathodic electrolyte. Initially these MFCs were operated at room temperature which was below 20 ^{0}C due to winter months. Fresh synthetic wastewater was fed to the reactors after fifth day and then after every 3rd day fresh feed was given after decanting 50 ml of the supernatant from the anode chamber. After 16 days the temperature of the reactors were increased to 30 ^{0}C. The MFCs were operated at this temperature for another 16 days and then heating was stopped and the MFCs were operated at normal room temperature.

Table 1: Operating Conditions of the different MFCs

Note: H – operation with heating; HS –heating stopped

MFC	Inoculum	Temperature (^{0}C)
MFC-1	Not acclimatized	12
MFC-2	Not acclimatized	12
MFC-3	Not acclimatized	12
MFC H-1	Not acclimatized	30
MFC H-2	Not acclimatized	30
MFC H-3	Not acclimatized	30
MFC HS-1	Acclimatized	16
MFC HS-2	Acclimatized	16
MFC HS-3	Acclimatized	16

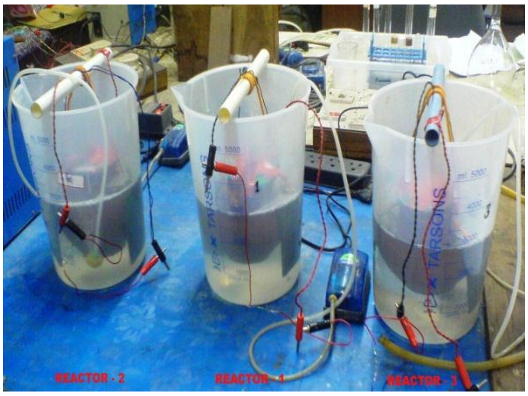

Fig.1. Arrangement of the MFCs

2.3 Analysis and Calculations

The potential and current were measured using a digital multimeter. Both open circuit voltage (OCV) and closed circuit voltages were measured. COD concentration was measured according to the Standard Methods. Temperature was recorded everyday by inserting thermometer in the cathodic chamber. Polarization studies were done on the MFCs by varying the external load resistance. Power was calculated from these data according to the formula $P = IV$, where P = Power in mW, I = Current in A and V = Voltage in mV. Power density was calculated by normalizing power to cathode surface area. Internal resistance of the MFCs was measured from the slope of the plot of voltage versus current [8, 11]. The anode and cathode potentials were measured using Ag/AgCl reference electrode. The Coulombic Efficiency (CE) of the MFC was calculated by integrating the measured current over time relative to the maximum current possible based on the observed COD removal. The CE evaluated over a period of time t, is calculated as given by [12]:

$$CE = MIt / FbV \Delta COD$$

Where M = 32, the molecular weight of oxygen, F is Faraday's constant, b = 4 is the number of electrons exchanged per mole of oxygen, V is the volume of liquid in the anode compartment, and Δ *COD* is the change in COD over time t.

3. RESULTS

3.1 Electricity generation

The variation of operating voltage and open circuit voltage (with 100 Ω external resistance) everyday is shown in Fig. 2 and 3, respectively. Although the reactors were started at psychrophilic condition but the bacteria could not get acclimatized even after 15 days resulting in very little COD removal (up to 30 %). The maximum operating voltages obtained were 16 mV, 32 mV and 14 mV in MFC-1, MFC-2 and MFC-3, respectively. After continuing the reactor for 16 days when no notable increase in performance was observed the temperature was increased to 30 ^{0}C by providing heaters so as to operate the reactors under mesophilic temperature condition.

Maximum operating voltages of 199 mV, 239 mV and 198 mV were obtained in MFC-H1, MFC-H2 and MFC-H3, respectively under elevated temperature conditions. Later when the bacteria got acclimatized the temperature was again reduced to ambient temperature of 16 ^{0}C. Maximum operating voltages of 188 mV, 212 mV and 189 mV were obtained in MFC-HS1, MFC-HS2 and MFC-HS3, respectively. It is evident from the Fig. 2 that there was not much difference in the performance of the MFCs in psychrophilic and mesophilic condition once the bacteria got acclimatized. In the psychrophilic temperature range MFCs could not pick up during two weeks of operation; however, once proper biofilm was developed on the anode under mesophilic temperature, subsequent drop in operating temperature resulted in very little drop in operating voltages for these MFCs. This emphasizes the utility of MFC for its working even at very low temperatures.

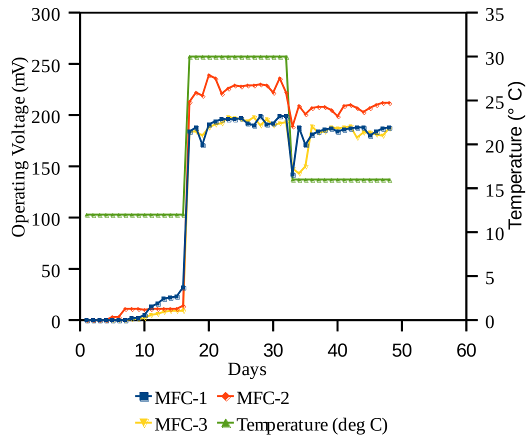

Figure 2: Operating Voltage of the MFCs

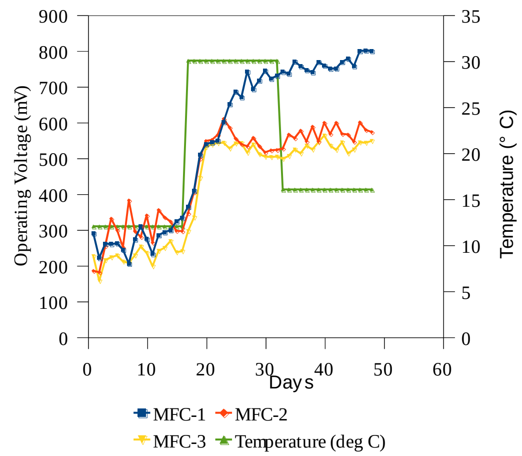

Figure 3: OCV of the MFCs

3.2 Wastewater Purification

COD of the effluent wastewater was recorded everyday starting from the 5th day. The supernatant from the anode chamber was collected and COD was measured.

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The average COD removal efficiencies were 30.12 ± 11.62 %, 80.66 ± 4.14 % and 74.12 ± 2.47 %, respectively, in the three different operating conditions such as without temperature control and non acclimatized inoculum, with temperature control and without temperature control and acclimatized bacteria, respectively (Fig. 4). From the results it is clear that the bacteria were not working properly at temperature below 20 ^{0}C when the reactors were freshly started. Once the operating temperature of the system was increased to 30 ^{0}C, a marked improvement in the performance of microbes was noticed. Although the performance decreased when the temperature was again reduced below 20 ^{0}C but the decrease was very small. The individual performance of all the MFCs is given in Table 2

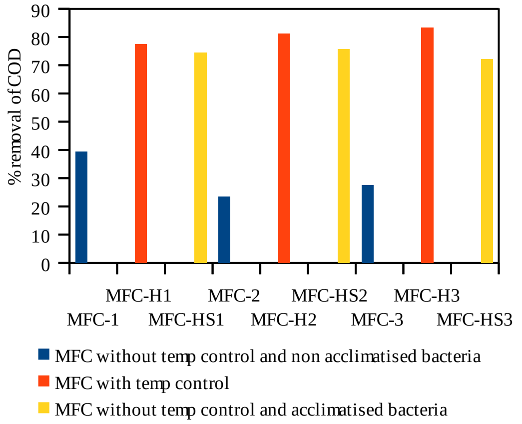

Figure 4: COD removal pattern of the MFCs

Table 2: Performance of the different MFCs

MFC	No. of days of operation	Max. Operating Voltage (mV)	Max. Open circuit potential (mV)	Max Power Density (mW/m^2)	Max. COD removal (%)	Internal resistance (Ω)
MFC-1	16	32	332		41.81	
MFC-2	16	14	381		23.97	
MFC-3	16	9	267		30.12	
MFC-H1	16	199	743	1419	78.44	239
MFC-H2	16	239	609	2062	80	122
MFC-H3	16	198	542	2165	83.34	122
MFC-HS1	16	188	800	869	74.74	306
MFC-HS2	16	212	599	1051	75.64	195
MFC-HS3	16	189	562	1552	74.55	140

3.3 Electrode Potentials

The anode and cathode potentials were measured separately vs Ag/AgCl standard electrode to determine how the electrodes are functioning individually. The average cathode potentials of MFC-H1, MFC-H2, MFC-H3, respectively were 122 mV, 107 mV, 160 mV and the average anode potentials were - 494 mV, - 416 mV, - 334 mV for the three MFCs, respectively. While the cathode potentials remained almost similar when heating was stopped later, anode potentials were found to have increased slightly. For MFC-HS1, MFC-HS2, MFC-HS3 the cathode potentials were 120 mV, 111 mV, 167 mV, respectively, and the respective anode potentials were – 547 mV, - 457 mV, - 362 mV. With reduction in operating temperature slight reduction in performance of both anode and cathode occurred.

3.4 Polarization

Polarization studies were done for the MFCs by varying the external resistance from 10440 Ω to less than 10 Ω under controlled temperature. After heating was stopped polarization studies were also carried out. During polarization current density was found to increase as the resistance was decreased which indicated the behavior of a typical fuel cell [13]. There was very little change in voltage at higher resistances but high voltage drop could be found with decreasing resistance because electrons can move more easily at a lower resistance thereby enhancing the oxidation of substrate. So a higher substrate degradation rate can be observed at lower resistances [8, 14]. Figure 5 shows the pattern of power density with current density and polarization curves for the MFCs. The internal resistances of these MFCs under elevated and reduced temperatures were respectively 239 Ω and 306 Ω for MFC-1, 122 Ω and 195 Ω for MFC-2, 122 Ω and 140 Ω for MFC-3. Maximum power densities under elevated and reduced temperatures were respectively of 14.19 mW/m^2 at resistance of 119 Ω and 8.69 mW/m^2 at resistance 317 Ω for MFC-1, 20.62 mW/m^2 at resistance 99 Ω and 10.50 mW/m^2 at resistance 151 Ω for MFC-2, 21.65 mW/m^2 at resistance 97 Ω and 15.52 mW/m^2 at resistance 99 Ω for MFC-3. As we can see that lesser power was generated once the MFC temperature was reduced. However, the MFC still performed at temperature lower than 20 ^{0}C to give appreciable COD removal and power production.

ISSN 2250-2459, *Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 244-249*

The established high rate anaerobic processes are not able to perform well at such low temperatures and face lot more operating difficulties.

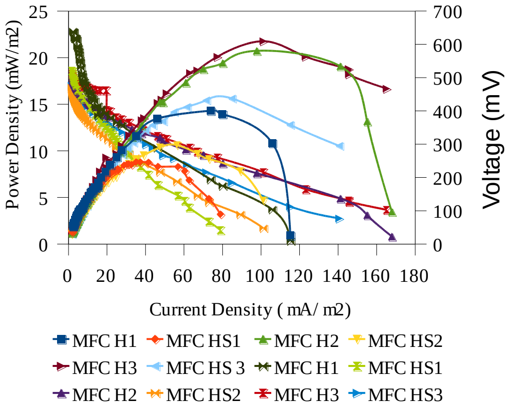

Figure 5: Polarization Curves

3.5 Coulombic Efficiency

The average Coulombic efficiencies obtained for MFC-H1, MFC-H2, MFC-H3, MFC-HS1, MFC-HS2, MFC-HS3 are 3.99 %, 5.04 %, 4.07 %, 4.02 %, 4.88 %, 4.49 %, respectively (Fig. 6). Such a low Coulombic efficiency indicates that the entire organic matter was not oxidized by electrogenic bacteria but by other groups of bacteria like methanogenic bacteria. Again anaerobicity might have been lost during COD sampling and feeding processes, thus causing oxygen to act as the electron acceptor and reducing the number of electrons transported through the external circuit. The trend of CE indicates that the lowering of operating temperature hardly had any effect and these MFCs continued to give similar CE even when the operating temperature was reduced to below 20 ^{0}C.

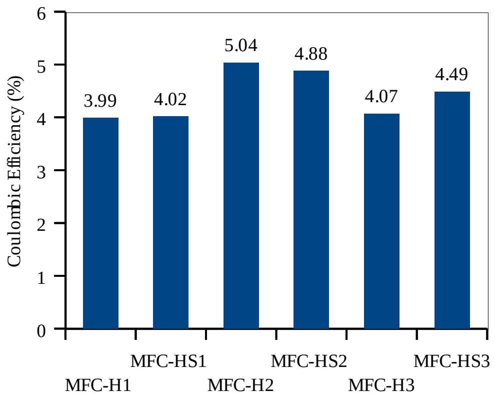

Figure 6: Coulombic efficiencies of the different MFCs

4 CONCLUSIONS

Effect of operating temperature was evaluated on low cost MFC made from earthen pot. The temperature of the MFC was well below 20 ^{0}C for the first phase of the experiment. As only psychrophilic bacteria grow in this temperature so bacterial action was very slow and MFCs could not be acclimated at this low temperature.

Later as the temperature was increased to 30 ^{0}C, the performance of MFC improved. In the last phase of the experiment when the heating was stopped and these MFCs were operated at lower temperature still the performance was good. This can be attributed to the fact that bacteria were already acclimatized in the last phase. The average operating voltage of the MFCs at mesophilic temperature was almost 10 % higher than that at psychrophilic range. The power densities were 1.5 times higher in the MFCs operated in mesophilic temperature than those at psychrophilic temperature. MFCs demonstrated similar Coulombic efficiency under psychrophilic and mesophilic temperature range of operation. Thus we may conclude that electrogenic bacterial growth is favored under mesophilic temperature conditions, however the MFCs can be operated even at psychrophilic temperatures successfully.

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ISSN 2250-2459*, Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 244-249*

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