INFLUENCE OF COD LOADING ON ELECTROCHEMICAL PROPERTIES
AND COD REMOVAL BY MICROBIAL FUEL CELL

Anu Chetalt* and Anubha Kaushik
Department of Environmental Science & Engineering, Guru Jambheshwar University of Science & Technology,
Hisar-125 001
*Corresponding Author

ABSTRACT
In the present study effect of substrate loading on power generation capacity and the COD removal efficiency of a two chamber Microbial Fuel Cell (MFC) was studied in batch mode using post methanation distillery effluent (PMDE). Greater COD loading led to more power generation and lesser internal resistance in the MFC. Removal of COD was however, more in the MFC fed with lower COD load (38%) than that with higher COD loading (29.7%). Open Circuit potential, anode potential and cathode potential at both the loading rates were decreased with the number of days.

INTRODUCTION
Fossil fuels have supported industrialization and economic growth during the past century but they cannot indefinitely sustain the global economy. Growing population is facing the basic challenges of adequate energy resources and management of waste. These requirements of energy and management of the waste can be fulfilled by microbial fuel cell (MFC), which is a bioreactor that can generate electricity coupled to the treatment of organic waste through microbial action. MFC systems have the advantage over traditional treatment processes of limiting both the energy input and the excess sludge production (Venkata Mohan et al. 2010). Wastewater treatment using MFC is considered to be a promising technology since this process converts major part of the chemical energy of the contaminants to electricity thereby reducing the generation of excess sludge (Kim et al. 2004). Thus it provides a sustainable source of energy.

There are several challenges to be addressed for the practical application of MFCs. Factors affecting the performance of MFCs include rate of substrate degradation, rate of electron transfer from bacteria to anode, circuit resistance, proton mass transfer in the liquid and performance of the cathode (Liu et al. 2005). In addition COD effects are of great importance in the practical application of MFCs because the COD profile of the wastewaters change in short term due to daily changes and in the long term due to seasonal changes (Johnson et al. 2009). However, a high COD concentration could also play a role in reducing the electrolyte resistance in MFCs (Logan et al. 2006), thus improving the power generation capacity of the reactor. The sludge characteristics produced by the MFC are governed by the organic loading rate (OLR) and sludge-loading rate (SLR) during start-up of the MFC (Ghangrekar et al. 2005). These two parameters, respectively, define the capacity of the reactor per unit volume and per unit mass of microorganisms to convert organic substrate.

Various types of wastewaters including pharmaceutical wastewater, paper mill effluent and food processing wastewater have been used as substrates in MFCs (Velvizhi & Mohan 2011, Huang et al. 2009, Oh and Logan 2005). Goldamerr (2008) emphasized that brewery wastewater is an important waste with high organic load that could be used as a substrate. However, distillery wastewater as a substrate for electricity production in MFC has not been systematically investigated. The quantum of the post methanation distillery effluent generated is the same as that of the original effluent but COD is lower than the untreated effluent. PMDE generated still has high COD in the range of 1800-2000 mg/L, which is much above the discharge limits of the effluent, and hence has to be treated further by processes like reverse osmosis that are cost intensive.

The present study was aimed to study the performance of a two chamber MFC, in terms of power generation and COD removal seeded with a mixed culture from cow-dung and fed with varying strength of postmethanation distillery effluent (PMDE). The COD strengths in the anode chamber were
adjusted to 650 and 1100 mg/L. The present study examined in long term studies the changes in electrochemical properties and the waste treatment efficiency of MFC under varying COD strengths of the feed solution.

**MATERIALS AND METHODS**

**MFC set up**

H shaped MFC design consisting of two borosilicate chambers separated by Nafion membrane (Sigma-Aldrich US). In the anode chamber semi-aerobic conditions prevailed. Nafion membrane was treated by first cleaning it with distilled water in a water bath at 80-90°C, followed by heating in 5% H\textsubscript{2}O\textsubscript{2} for one hour at 70-80°C to remove organic impurities. It was then heated in 0.5M H\textsubscript{2}SO\textsubscript{4} for 1 hour at 70-80°C then H\textsubscript{2}SO\textsubscript{4} was removed by repeated washing in boiled water. The membrane was stored in the dark overnight before assembling in reactor.

The electrodes consisted of graphite fiber brush (anode 13 cm / 6 cm dia and cathode 5 cm / 6 cm dia) and were kept in distilled water overnight. The membrane used to separate the chamber was of 2.5 cm diameter and external resistance used throughout the study was 1000 ohms except that during polarization experiments when external resistances were varied.

**MFC operation and experimental variations**

The MFC was started according to the procedure adopted by Kaushik and Chetal (2013). The PMD effluent was analyzed and was found to have pH 7.1-7.4, COD 1800-2000 mg/L, EC 2.85 mS/cm and TDS 1.42 ppt. The catholyte used in the MFC was 3g/L potassium ferricyanide solution adjusted to pH 2 which was found to be more suitable as a catholyte in our earlier study where effect of pH on power generation in MFC was tested. The pH of the anolyte were adjusted to 8 which was the optimized pH condition found in our earlier study.

Performance of the MFC was evaluated in terms of power generation and under different COD loads of 1100 mg/L and 650 mg/L. The experiment was carried out by first adding the anolyte with higher COD load in the MFC reactor containing ferricyanide solution as catholyte and monitoring the power generation as well as COD for ten days. After ten days anolyte of lower COD load replaced the anolyte effluent in the reactor to perform second experiment. The catholyte solution was also replaced for the new COD load. All other conditions of the MFCs were kept constant. The experiments were conducted for a period of 10 days and the power output and COD removal were regularly monitored. Physicochemical parameters of the effluent were estimated after 10 days in both the experiments, whereas electrochemical properties were studied on alternate days. Polarization experiments were carried out daily by varying the external resistances from 50 to 1000 ohms. The working volume in each of the chambers was 1L. The MFC was operated under 35 ±2°C temperature.

**ANALYSIS AND CALCULATIONS**

The potential (V) was measured with a digital multimeter at regular intervals of 24 hours and converted to power according to the equation: $P = I \times V$

Where, $P$= power, $I$=current, $V$= voltage

Power density was calculated by dividing the power by working volume of the anode chamber: $PD = P / V$ X 1000

Where $P$= Power, $V$, working volume of the anode chamber.

Similarly current density was calculated as: $CD = C / V$ X 1000

Where $C$= current, $V$, working volume of the anode chamber.

Internal resistance of the MFC was measured from the slope of the line from a plot of voltage and current. Effect of different external resistances on the performance of the MFC in terms of voltage was investigated at various conditions.

Performance of the MFC was studied in terms of COD removal and power generation. Removal of COD was calculated as:

$\text{Percentage Removal} = \frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}} \times 100$

COD was analyzed using standard methods (APHA 1998).

**RESULTS AND DISCUSSION**

**Removal of COD**

In MFC with COD Loading of 1100 mg/L there was 29.7% removal while that in case of 650 mg/L COD loading...
there was 38% removal in a period of 9 days. Change of COD in the MFC loaded at different concentration is shown in Fig 1.

The reduction in COD at both the loading rates was gradual. Removal of total COD from the PMD effluent was slow which might be due to the fact that the microorganisms already degraded the easily degradable substrate during biomethanation process and the PMDE was left with slow degradable complex substrate. The COD removal efficiencies in this study were lower than the range reported by previous researches of MFC (Gálvez et al. 2009, Kim et al. 2010). Gradual removal of COD may be due to the fact that, when COD stress is given to the microbes the microorganisms increase their enzymatic production to degrade as much COD as possible. It takes them some time to increase enzymatic production during which the degradation is less. However, after the degradation of the organic matter as the COD concentration declined substantially, the ability developed by the microorganisms to synthesize more enzymes persisted, for some time and then gradually decreased stabilizing the COD removal rates. Since many complex reactions occur in the wastewater containing intermediate fermentable organic matter, hence the accumulation of high concentration of such substances sometimes have a toxic effect on the microorganisms, thus deteriorating the removal efficiency (Behera and Ghangrekar 2009).

**Effect on electrode potentials**

![Graph showing change in anode and cathode potential with number of days](image)

**Fig. 2.** Change in Anode and Cathode Potential with number of days.

The electrode potentials of both anode and cathode were measured daily with respect to calomel electrode and are shown in Fig. 2.

The anode potential of the MFC with higher substrate loading shows a gradual change from -0.545 to -0.308 V and cathode potential changed from 0.325 to 0.200 V in ten days. In case of MFC with lower substrate load, there was an increase in cathode potential from 0.219 to 0.309 V and decrease in anode potential from -0.331 to -0.468 V in one day. After that it showed the same trend as that of the higher COD loading rate, up to 10 days showing a gradual decrease in cathode potential from 0.309 to 0.206 V and increase in anode potential from -0.469 to -0.358 V. The cathode potential at both the COD loading rates were almost similar since same catholyte was used in both the cases and it gradually decreased because of the consumption of ferricyanide and H+ ions with time.

The anode potential of the MFC with higher COD load of increased by 0.237 V but in the MFC with lower substrate load it increased by only 0.101 V, thus there was steep increase in anode potential with substrate load of 1100 mg/L than with loading rate of 650 mg/L. The difference in the anode potential of the MFC reactor may be due to the difference in the substrate load. Anode potential has been reported to depend on the substrate concentration as well as the biofilm formed on the brushes.

**Power generation**

The power output from the MFC with different COD loads at fixed external resistance of 1000 ohms during 10 days of operation is shown in Table 1.

In MFC with higher COD loading power generation was higher (0.48 W/m²) as compared to that of with lower COD loading (0.44 W/m²). Power output from both the MFCs decreased as the substrate degraded and COD was removed with time. In higher substrate loading power generation decreased by 16 times by 10th day but with lower loading rate it decreased by just 3.7 times. The decrease in power is attributed to both the exhaustion of substrate in the anode chamber as well as consumption of catholyte in the cathode chamber. Current density also followed the same trend of decrease with time at both the COD loads. Our results are
consistent with that of Wei et al. (2012) reporting increased power output from the MFC with increase in substrate concentration. Change of open circuit potential and closed circuit potential of both the reactors are shown in Fig 3.

The initial OCV of the reactor with loading rate of 1100 mg/L was 0.871 V, which decreased to 0.516 and 0.831 V in MFC with lower COD load, which then decreased to 0.595 V. Similar initial OCV of the MFC with different COD loadings has shown that change in substrate concentration beyond a certain limit does not affect the OCV of the reactor provided all other conditions are kept constant.

But it starts decreasing as the concentration of the substrate decreases, which may be due to observed decrease in the anode potential as well as the cathode potential of the MFC. Closed circuit potential measured at a resistance of 500 ohms, also declined with time in both the reactors. However, the decline was regular with higher substrate load but irregular trend was observed with lower loading rate. This decrease in potential is attributed to the decreased substrate concentration in the anode due to degradation by microbes.

Internal Resistance
Polarization was done in both the MFCs daily by varying the external resistance from 50 to 1000 ohms. It was observed that the voltage in both the MFCs increased with the increase in the external resistance of the MFC (Data not shown) following typical fuel cell behavior. Graph of voltage vs current was plotted and internal resistance was determined from the slope as already discussed (Kaushik & Chetal 2013). Changes in internal resistance at both the loading rates on every alternate day are shown Table 2.

In the MFC at higher COD load (1100 mg/L), the internal resistance of the system continued to increase, concomitant with decreasing substrate concentration in the anode except a slight decrease during the second day. However, in case of lower COD load (650 mg/L) oscillations in internal resistance were observed. Internal resistance of the MFC with lower COD load is higher due to lower amount of substrate available in anode chamber.

CONCLUSION
Integrated bio-electro treatment system in MFC showed that it is possible to use real wastewater of post methanation distillery effluent for both power generation and organic pollution removal at different substrate loading rates as is necessary for practical application of the MFC. Increasing organic load decreased internal resistance of the MFC and enhanced power generation.

Table 2. Temporal variations in Power & Current density of MFCs loaded with varying COD concentrations.

<table>
<thead>
<tr>
<th>Days</th>
<th>Initial COD Conc. (1100 mg/L)</th>
<th>Initial COD Conc. (650 mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Internal Resistance (ohms)</td>
<td>Peak Power Density (W/m²)</td>
</tr>
<tr>
<td>1</td>
<td>382.9</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>372.8</td>
<td>0.47</td>
</tr>
<tr>
<td>5</td>
<td>648.3</td>
<td>0.14</td>
</tr>
<tr>
<td>7</td>
<td>845.3</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>1210.4</td>
<td>0.03</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS
Financial assistance to one of the authors (A.C.) in the form of Sir C. V. Raman Fellowship from Haryana Technical Education Society, Chandigarh, India is gratefully acknowledged.

REFERENCES


