Performance of a Dual Chamber Microbial Fuel Cell using Sodium Chloride as Catholyte

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ABSTRACT: Microbial fuel cell represents an emerging technology to attain electrical energy from wastewater. There are several alternative methods available for wastewater treatment; Microbial fuel cell is one of them, which generates green energy from wastewater for making a contribution to renewable sources of energy. This study states the performance of microbial fuel cell with different parameters i.e., catholyte, electrodes, and initial COD concentration. Sodium chloride was used as catholyte and graphite rods were used as both electrodes. The sodium chloride concentrations in the cathode and initial chemical oxygen demand have also been optimized. The optimum sodium chloride of 70 mM in the cathode solution generates the maximum power density of 408.98μW/m². As the sodium chloride concentration increases in catholyte, the capacity for power production also increases. The voltage output of Microbial fuel cell increases when the initial concentration of chemical oxygen demand increases to a peak value of 1500 mg/l and if the value exceeds this limit, the performance of Microbial fuel cell (in terms of voltage) starts decreasing. The chemical oxygen demand removal efficiency of a microbial fuel cell with simple graphite electrode and graphite electrodes with coated iron were 79% and 90% respectively.

KEYWORDS: COD Removal; Electricity generation; Catholyte; Wastewater treatment; MFC.

INTRODUCTION

As the population of the world is growing fast, residential and commercial energy demands are increasing day by day. As per International Energy Agency (IEA), by 2035 the power requirement is predicted to rise from 12 billion metric ton oil equivalent (current requirement) to 18 billion metric ton oil equivalent (Chu & Majumdar, 2012; Li et al., 2018). Due to increasing energy requirement per year and huge consumption of non-renewable sources of energy, the need of the hour is to find and use of new cost-effective renewable sources of energy (Ye et al., 2019; Li & Chen, 2017). In India, there is no proper utilization of renewable energy sources and non-renewable sources are used extensively at higher rates (Chaturvedi & Verma, 2016; Kumar et al., 2015). One of the renewable and green energy sources for the production of electricity is fuel cells (FC) (Rahimnejad et al., 2011; Catal et al., 2019). Fuel cells directly convert the chemical energy of fuels into electricity without considering the inefficiencies of internal combustion engines based on the Carnot cycle (Li & Chen, 2018; Iranpour et al., 1999). Recently, microbial fuel cells (MFCs) have been studied to convert organic matter
into electrical energy by using the diversity of bacterial catalytic abilities (Santoro et al., 2017; Slate et al., 2019; Angenent et al., 2004; Liu & Logan, 2004). Wastewater is mainly comprised of domestic and industrial wastes as it contains organic and inorganic impurities which act as a substrate for the microbial growth and its biochemical reaction which corresponds to the generation of electricity (Danial et al., 2009; Kumar et al., 2017; Bhowmick et al., 2019). The very first idea was evolved by British Scientist Potter in 1911 by obtaining electrical energy using bacteria that oxidize organic matter (Larminie et al., 2003; Pandey et al., 2011). Microbial fuel cells are a special type of Fuel Cells that has a dual advantage. The microbes added are responsible for the conversion of organic compounds into electricity and at the same time, they perform purification of wastewater, thereby reducing the operating costs of wastewater treatment plant (WWTP) (Lu et al., 2009; Oji et al., 2012; Wang et al., 2013). The microbial fuel cell (MFC) is a new technology devised for obtaining renewable energy that can produce electricity from wastewater (Barua & Deka, 2010). Microbial fuel cell (MFC) is emerging biotechnology being capable of converting organic substrates (e.g. domestic wastewater, swine wastewater, leachate, and urine) to electrical energy (Goswami & Mishra, 2018; Santoro et al., 2013; Ieropoulos et al., 2017). MFC consists of two chambers- anodic and cathodic chamber, both are separated by an ion-exchange membrane (Proton/cation). The micro-organisms biofilm produced at anode chamber acts as a catalyst to convert the chemical energy of the organic products into electrons while the oxygen produces water (H₂O) at cathode chamber (Zhou et al., 2013). For better performance of MFCs in terms of bacterial growth, electron transfer and electrochemical efficiency, the selection of suitable electrode material is a very important factor to be considered. There have been many practices to enhance energy production by using different types of carbon-based materials such as carbon felt (Lv et al., 2012; Deng et al., 2010), carbon paper (Yuan & Kim, 2008), carbon fiber and carbon nanotube-based composites (Zhang et al., 2012; Xie et al., 2012). The material of the anode plays a very significant role in the formation of biofilm and the transfer of electrons between the microorganisms and the electron acceptors. The various materials required in an MFC include carbon rods, carbon fiber, stainless steel mesh (Dumas et al., 2007; Das & Ghangrekar, 2019), carbon cloth (Cheng & Logan, 2007). The main disadvantage of the microbial fuel cell is that it works on a small scale and has higher fabrication cost yet.

Catholyte plays an important role in the performance of a microbial fuel cell. Different researchers used sodium hypochlorite, aerated water (Jadhav et al., 2014; Zhang et al., 2010), saline water (Neethu et al., 2019), potassium permanganate (Pardhan & Ghangrekar, 2019) but no research has been conducted using the different concentration of sodium chloride as catholyte. In this study, 5 MFCs were fabricated with a salt bridge. Different concentration of sodium chloride was used as catholyte to analysis the behavior of microbial fuel cell. Electrodes material was also examined to check better efficiency in terms of COD removal. This study was carried out in environmental engineering laboratory at the National Institute of Technology (NIT) Hamirpur (H.P.).

MATERIALS AND METHODS
Five batch scale MFCs were implemented to carry out the experiment. Each MFC was made with two bottles of plastic having a capacity of 800ml each, which were connected to each other via a salt bridge as shown in Figure 1. The salt bridge was fabricated using a plastic tube having internal diameter and length of 2.5 cm and 5 cm respectively. It was made using 10% agar-agar technical (Merck) and 3M sodium chloride (NaCl) solution.
Graphite rods were used as both electrodes with a surface area of 13.18 cm$^2$. The electrode spacing was 11 cm c/c from each electrode for all setups. The circuit was completed using copper wire to transfer the electrons and measurement of open-circuit voltage (OCV). 5 setups were fabricated and named as MFC-1, MFC-2, MFC-3, MFC-4, and MFC-5 respectively. Sodium chloride concentrations i.e., 30mM, 40mM, 50mM, 60mM and 70mM were used as catholyte in MFC-1 to MFC-5 respectively.

The electrodes were connected to the circuit with the help of copper wires. A 10-ohm external resistance was connected to it and a digital multi-meter (CHY DT-9205 A+) was used to measure the current developed in the circuit. An Aquarium pump with a constant airflow of 4 L/min and pressure of 0.197atm (SB-348A, SOBO aquarium air pump) was provided in the cathodic chamber for the aeration. To have control over the characteristics of wastewater, Synthetic wastewater was used in one of the experimental setup processes and controlled COD was varied between 500-2500mg/l. The composition constituents of synthetic wastewater used are shown in Table 1.

The closed reflux method has been used for the COD determination by using Hach DRB 200. The pH value and the conductivity have been measured by using pH meter (Model: HI96107) and the conductivity meter (aquapro digital water tester) respectively. The research laboratory-scale water has been prepared by using distillery apparatus and the double-distilled water (DDW) has been used to prepare the solutions. All the experimentations have been performed at ambient temperature and normal pressure conditions. The various reagents used for the determination of COD were such as ferrous ammonium sulfate (FAS), ferroin indicator, potassium dichromate, and sulphuric acid reagent.

The experimental setup has been put on in the form of the batch by pouring wastewater in the anaerobic anodic chamber. In the case where synthetic wastewater is used, 100 ml sludge collected from Sewage Treatment Plant (STP), NIT Hamirpur, has been added as inoculums after pre-treatment where the artificial wastewater is poured into the anodic chamber. The pH and electrical conductivity
(EC) of the wastewater have been measured. The primary COD of wastewater has been calculated with closed reflux methodology (Hach digester) and is followed by titration. The Biochemical Oxygen Demand (BOD) of wastewater and initial dissolved oxygen (DO) content has also been measured. The NaCl solution and buffer solution (pH=7) has been taken in the cathode chamber. An aquarium pump has been installed to deliver air in cathodic compartment. After a couple of hours of this process, MFC starts generating electrical energy as the outcome. The digital multimeter measures both the voltage and current. The readings have been observed and noted down thrice in a single day and finally, the average of reading has been calculated. After this procedural operation, the concluding value of COD has been recorded.

RESULTS AND DISCUSSION
Effects of NaCl concentration in cathode solution: The concentration of NaCl in cathode based solution affects the energy generation and COD removal efficiency of MFC. The NaCl solution having different concentrations along with buffer solution has been taken in different MFCs. For example, NaCl has the concentration value of 30mM in MFC1, 40mM in MFC2 and similar order in other MFCs as shown in Table 2.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Conductivity (μS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>5473</td>
</tr>
<tr>
<td>60</td>
<td>4939</td>
</tr>
<tr>
<td>50</td>
<td>4389</td>
</tr>
<tr>
<td>40</td>
<td>3669</td>
</tr>
<tr>
<td>30</td>
<td>2975</td>
</tr>
</tbody>
</table>

Electricity generation in MFC1 to MFC5: After the nine consecutive operating days since MFC1 started operating, the COD removal efficiency has gone up to 74%. The observations show the hike in both the voltage and current production, reaching a peak value and started decreasing during the further operation of MFC. The maximum readings of voltage and current produced were 5.2 mV and 47 μA respectively in MFC1 on the fourth day of operation as shown below in Figure 2 and Figure 3. The maximum power density and the maximum current density obtained with respect to electrode surface area were 185.45 μW/m² and 35.66 mA/m², respectively as in Figure 4 and Figure 5.

After the nine consecutive days since MFC2 started operating, the COD removal efficiency has gone up to 76%. Initially and final COD was analyzed to check the removal efficiency of different MFC setups. Initially MFC5 has higher values of all electrical parameters due to higher alkaline (70mM NaCl) behavior of cathodic chamber. MFC4 showed higher performance in terms of electricity generation while MFC3 showed in terms of COD removal. The observations show the hike in both the voltage and current production, reaching a peak value and started decreasing during the further operation of MFC2. The maximum readings of voltage and current produced were 6.4 mV and 58 μA respectively for MFC2 on the fourth day since it started operating. The maximum readings regarding power and current density were recorded as 281.66 μW/m² and 44.01 mA/m² respectively.
Fig. 2. Current (μA) versus Time (days) Graph for MFC-1 to MFC-5

Fig. 3. Voltage (mV) versus Time (days) Graph for MFC-1 to MFC-5

Fig. 4. Current density (mA/m²) versus Time (days) Graph for MFC-1 to MFC-5

Fig. 5. Power density (μW/m²) versus Time (days) Graph for MFC-1 to MFC-5
After the nine consecutive days since MFC3 started operating, the COD removal efficiency has gone up to 79%. The observations show the hike in both the voltage and current production, reaching a peak value and started decreasing during the further operation of MFC. The maximum readings of voltage and current produced were 6.6 mV and 60 μA respectively for MFC3 on the fourth day of operation. The maximum power density and the maximum current density obtained were 300.48 μW/m² and 45.53 mA/m², respectively. After the nine consecutive days since MFC4 started operating, the COD removal efficiency has gone up to 72%. The observations show the hike in both the voltage and current production, reaching a peak value and started decreasing during the further operation of MFC. The maximum readings of voltage and current were recorded as 6.2 mV and 56 μA for MFC-4 on the fourth day of operation. The maximum power density and the maximum current density obtained were 263.45 μW/m² and 42.49 mA/m² respectively. Finally, after the nine consecutive days since MFC4 started operating, the COD removal efficiency has gone up to 83%. It has been observable that there is an increment in both the voltage and current production, reaching to the maxima and then further decreasing during MFC5 operation. The maximum readings of voltage and current recorded were 7.7 mV and 70μA respectively for MFC5 on the fourth day during operation of MFC. The maximum power density and the maximum current density were recorded as 408.98 μW/m² and 53.11 mA/m² respectively.

CONCLUSION
The current study highlights the various parameters affecting the performing ability of MFC, in terms of both productions of electricity and COD removing efficiency. On the basis of the results obtained, the optimum sodium chloride of 70mM in the cathode solution catalyzes the maximum power density of MFC at 408.98μW/m². As the NaCl concentration increases in cathode solution, the capacity of power production also increases. The voltage output of MFC increases with increase in the initial concentration of COD to an optimum peak value of 1500 mg/l and if the value exceeds this limit, the performance of MFC (in terms of voltage) starts falling; this is due to low organic matter (domestic wastewater) into the anodic chamber. At the initial concentration of COD of 1500 mg/L the power density when produced, found to be maximum with the value of 95.45 μW/m². The power density produced in MFC with simple graphite electrode was 300.48 mW/m² and with graphite electrodes with iron was 170.67mW/m². The COD removal efficiency of MFC with simple graphite electrode and MFC with graphite electrodes with iron were 79% and 90% respectively.

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CONFLICT OF INTEREST
The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

ABBREVIATIONS
μA Micro-ampere
μS Micro-siemens
μW/m² Micro-watt per metre square
BOD Biochemical oxygen demand
Cm Centimetre
COD Chemical oxygen demand
DDW Double distilled water
DO Dissolved oxygen
EC Electrical conductivity
FAS Ferrous ammonium sulfate
FC Fuel cell
IEA International energy agency
L/min  Litre per minute
M    Mole
mA/m²  Milli-ampere per metre square
MFC  Microbial fuel cell
MFC1-MFC5  5 Setup of microbial fuel cell
Mg/l  Milligram per litre
Ml    Millilitre
mM  Mili-mole
mV  Millivolt
NaCl  Sodium chloride
pH  Potential of hydrogen
STP  Sewerage treatment plant
WWTP  Wastewater treatment plant

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LIFE SCIENCE REPORTING
No life science threat was practiced in this research.

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