Bioelectricity generation from agro-industrial waste water using dual-chambered microbial fuel cell

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Abstract - Bioelectricity production from wastewater beside treatment is the main goal offered by microbial fuel cells (MFCs) technology. This study was demonstrated to evaluating the electricity generated by the double-chamber air-cathodic MFC while reducing pollutants from sugar industry wastewater (SIW). A simple double-chamber MFC was configured with Nafion 117 membrane, and operated without adding any chemical mediators. SIW used as an electron donor and was fed in batch-mode into the MFC for three consecutive operational cycles. While the maximum MFC output voltage in open circuit (OCV) mode was 890 mV after 24 operational days, the closed circuit voltage (CCV) was 340 mV when 550 ohm as external load was applied. From the polarization curve, the maximum power density of 160.16 mW/m^2 as power output was observed at a current density of 320.9 mA/m^2. The efficiency of the MFC was measured based on columbic efficiency (CE) and chemical oxygen demand (COD) removal rate. While the CE was 46%, the COD removal efficiency reached 85.4%. The anodic biofilm was observed through scanning electron microscopy (SEM). The current study results indicated that SIW microbial communities in the anodic biofilm have the ability to produce bioelectricity using MFC in parallel with the SIW substrate treatment.

Keywords - Microbial fuel cell, microbial community, biofilm, current density and power density.

I. INTRODUCTION

The waste water generated during the sugar manufacturing process of sugarcane contain lots of organic compound in the form of carbohydrates like glucose, sucrose etc. This can be treated as well as used as substrate for the generation of power in Microbial fuel cell[1]. For the treatment of waste water, we design Microbial fuel cells (MFCs). In Microbial fuel cells (MFCs) there are two chambers which are anode and cathode and separated by polymeric proton exchange membrane [2].

To utilize the substrate and convert it into electricity we introduce bacteria in anode chamber. Most MCFs contain aqueous cathode in which dissolved oxygen can be provided to electrode by mean of water bubbled with air[3, 4]. To make MFCs more economical and energy efficient, we investigate the power generation in an air-cathode MFC having carbon electrode during the absence and presence of the polymeric proton exchange membrane (PEM)[2, 5]. The waste water and glucose were used as substrate and the biocatalyst were the bacteria which are in the domestic waste water[6]. The power density is much higher than that of the normally reported aqueous cathode MFCs, using a maximum of 262 ± 10 mW / m^2 (6.6 ± 0.3 mW / L, liquid volume)[7]. The maximum power density “494 ± 21 mW / m^2 " (12.5 ± 0.5 mW / L) is achieved by eliminating PEM. The Coulomb efficiency is 40-55% of PEM, and the efficiency of removing PEM is 9-12%, which indicates that in the absence of PEM, the oxygen in the anode compartment diffuses in large amounts [7].

The chemical energy of the substrate in waste water is converted into electrical energy by utilization of bacteria in Microbial fuel cells (MFCs). In this cell electron are being transfer by the bacteria to the electrode rather than directly to an electron acceptor [8]. Its technical feasibility has recently been tested, and the scientific community has great enthusiasm for MFC’s ability to generate “green power” sources by using household and industrial waste to generate energy[9].

Acetate, lactate, and glucose are used as the feed stocks for MFCs. By using the Microbial fuel cell, we can generate the electricity from the domestic waste water and at the same the biological treatment of waste water has also been done such as removal of chemical oxygen demand; COD[10]. These tests are carried out in the single chamber microbial fuel cell (SCMFC) with eight graphite electrodes (anodes) and a single air cathode.
Primary clarified effluent which is taken from the local wastewater treatment plant was used in the system at continuous flow conditions. The waste water COD removed up to 80% while generating the electricity (maximum of 26 mW m−2) in the prototype SCMFC reactor. Power generated was proportional to the hydraulic retention time (3–33 hour) and to the influent wastewater strength (50–220 mg/dm³ of COD)[11]. Fuel cell and voltammetry were utilized for understanding the mechanism of electron transfer with the addition of Shewanella putrefaciens. The bacterium’s electrochemical activity without any electrochemical mediators were determined by the both methods. By the studies of cyclic voltammetric, electrochemical activities were showed by the Shewanella putrefaciens anaerobically, but for another condition regarding aerobically there was not enough. The activates measured regarding electrochemical system is nothing but the related closely with electric potential and current generation[12].

From the various operating condition, a mediator-less microbial fuel cell was optimized. pH, resistance, electrolyte used, and dissolved oxygen concentration in the cathode compartment are the several factors on which current generation depends. In neutral solution (pH=7) generation of current was maximum. The proton transfers and dissolved oxygen supply limited the cathode reaction at lower resistance than 500 Ω. Under the operating condition, the rate determining factor was resistance at over 500 Ω[13]. Up to some extent proton limitation were reduced by high strength buffer solution. At the DO (dissolve oxygen limited condition the concentration of DO was around 6 mg l−1 The fact that oxygen limitation was observed at high DO concentration is believed to be due to the poor oxygen reducing activity of the electrode used, graphite [14].Some of bacterial culture use glucose as carbon source to identify the power generation with respect to glucose utilization. With the utilization of glucose dose 0.5–3 g l−1 d−1 the power output about 3.6 W m−2 and 89% electron recovery in terms of electricity reported by Lab-scale double chamber MFC was used for power generation.

Electric current was produced from the sewage organics using the Saccharomyces cerevisiae sp. as a mediator and potassium ferricyanide as an oxidizing agent. The anodic and cathodic solutions were introduced in batch and dissolved oxygen supply limited the cathode reaction at lower resistance than 500 Ω. Under the operating condition, the rate determining factor was resistance at over 500 Ω[13]. Up to some extent proton limitation were reduced by high strength buffer solution. At the DO (dissolve oxygen limited condition the concentration of DO was around 6 mg l−1 The fact that oxygen limitation was observed at high DO concentration is believed to be due to the poor oxygen reducing activity of the electrode used, graphite [14].Some of bacterial culture use glucose as carbon source to identify the power generation with respect to glucose utilization. With the utilization of glucose dose 0.5–3 g l−1 d−1 the power output about 3.6 W m−2 and 89% electron recovery in terms of electricity reported by Lab-scale double chamber MFC was used for power generation.

Protection and perseverance of our environment and energy crises are the two major problems that have played havoc with our lives. The conversion methods of other renewable energy contain transitional conversion into mechanical power but Microbial fuel cell (MFC) offers an advantage that transmit chemical energy directly into the electrical energy. In this context, the sewage sludge which is the sources of major environmental pollution but also contains high levels of organic compounds is utilize to generate power in the MFC[18]. By using the microbial fuel cell, we converted the chemical energy from the substrate of sewage sludge into the electricity by using mediator which is methylene blue and biocatalyst which is Saccharomyces cerevisiae sp. By varying the agarose’s concentration in the salt bridge of MFC we can examined the efficiency of MFC. Concentration of agarose salt which range from 7% to 12% was utilized for analyzes of the best possible concentration was noticed being 10% because it exhibited maximum voltage generation of 0.97V[19].

The utilization of the fossil fuels and pollutant producer must be reduced to make the world more feasible and conventional for living. These types of problems can be solved by treating the waste in an appropriate manner, such as sewage sludge. As we know that the sewage sludge is full of organic compound so it can be used as a perfect substrate for the power generation. According to the study it was found that dual compartment MFC with the bio cathode was used to generate the voltage from the sewage sludge (2L)[20]. An internal resistance of 36–46 ohm were developed by the bio cathode to obtained maximum voltage (2.5 V) Saccharomyces cerevisiae sp. was used as biocatalyst. Methylene blue (10 ml) was used a mediator and potassium ferricyanide (350 ml) was used as an oxidizing agent for the conversion of sewage sludge into voltage generation [21].

The results show that although the substrate has a high impedance, all the general parameters on the 5th day prove to be the maximum, and then the trend is observed after 6 days. The corresponding maximum values of the
generated parameters are 0.825 V, 0.0113 μA, 0.009223 μW and 0.000000947 mW/m², respectively. It has also been found that the obtained voltage, current, power and power density have similar patterns. This work is related with the potential use of sugar mill waste water for electricity generation using microbial fuel cell[22].

II. EXPERIMENTAL METHODS

1. MFC configuration and operation
A mediator-less air-cathode double-chamber (H type MFC), MFC was used as a bioreactor for bioelectricity production as well as bio-incubator of SIW substrate. Fig. 1 illustrate the diagrammatic design of fabricated double-chamber MFC. The MFC made-up from Perspex material (Homemade, Assiut University, Assiut, Egypt) with a total inner volume of 60 ml. The MFC design allows the cathode external surface directly contacted with air through small holes while keeping the anode zone within the anaerobic condition[23]. The MFC electrodes have the same size, made from carbon cloth.

The intra-distance between the electrodes is 1 cm separating membrane and the electrodes surface-active area is 25 cm². All tests completed at room temperature of about 30°C, which considered the optimum temperature for the bacteria to be active[24]. The MFC was operated in both, the open circuit mode (without external load) and the closed mode using external resistance (550 Ω) as mentioned in previous literature[25]. The performance analysis of MFCs conducted according to the mathematical calculation of the system bioelectricity outputs records as mentioned in latature[26].

2. Bacterial growth stimulation
The MFC was configured, sterilized, and fueled with SIW as mixed bacterial and carbon source. SIW samples obtained from the industrial wastewater effluent of Abu Qurqas Sugar Factory (Minya, Egypt). The chemical properties of SIW samples was determined according to the association of official analytical chemists (AOAC)[27](Table.1). The MFC was operated and the outputs data was recorded continuously during three consecutive cycles of fed-batch operational mode[28].

![Diagram of MFC](image)

Fig.1. Illustres the diagrammati scheme of opertaed double- chamber MFC.

3. Sugar industry waste water (SIW)
SIW used in this study was kindly provided Via Abu-Qurqas Co. Ltd. (Egypt).

4. Analysis and calculation
The MFC current (ampere) and the MFC power were calculated from the following equations[29].

\[ I = \frac{V_{MFC}}{R_{ext}} \] (1)

Where \( V_{MFC} \) is MFC voltage, \( R_{ext} \) is the external resistance.

The Current density (mA m⁻²) was calculated from the followed equation[30]:

\[ C.D = \frac{I}{A} \]

Where \( I \) is the current per mA and \( A \) is the active area of the anode (m²).

The Power density (PD, mW/m²) calculated from the followed equation[31]:

\[ P.D = \frac{V_{MFC} \times C.D}{A} \]

The Columbic efficiency (CE), describes the efficiency of the MFC in facilitating the electrochemical reactions for charge (electrons) transmission, i.e. the Current represented in the recovered fraction electrons versus the complete of oxidation of the substrate. The CE was calculated by the followed equations[32]:

\[ CE = \frac{C_P}{C_T \times 100\%} \]

\[ C_T = \frac{(F \times n \times \Delta c \times V)}{M} \]

Where the CP is actual current production collected by the anode during one batch cycle was integrated as \( CP = \int x \, dt \) and the CT is the theoretically available amount of produced coulombs depending on the COD removed in the MFC from the fully oxidation of substrate organic content into CO2 and water. It was estimated as in formula no.5, where \( F = \) faraday’s constant (96485 C/mol), \( n = \) no. of electrons per mole of substrate (= 4 electrons), \( \Delta c \) is the daily COD removed, \( V \) is the inner reactor volume per liter, \( M \) = molecular weight of O2 (= 32 g/mole).

COD removal efficiency calculated as the following equation[33]:

\[ \text{COD removal efficiency} = \frac{[\text{COD}]_{\text{inlet}} - [\text{COD}]_{\text{outlet}}}{[\text{COD}]_{\text{inlet}}} \times 100 \% \]

While CODinlet refers to the initial COD concentration (mg/l), CODoutlet represents COD concentration (mg/l) at the end of full operational cycle.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Characteristic value</th>
</tr>
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<tbody>
<tr>
<td>Color</td>
<td>Blackish grey</td>
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<tr>
<td>pH</td>
<td>7-7.2</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>2300</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD)</td>
<td>1400</td>
</tr>
<tr>
<td>Dissolved solids</td>
<td>1350</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>318</td>
</tr>
</tbody>
</table>

Table I: Chemical properties of SIW samples.
5. Scanning electron microscopy
The surface of the anode electrode was characterized (after 46 days from the incubation with the microbial culture in the MFC system) using scanning electron microscope SEM (JEOL, JXA-840A) to determine the microbial-electrode attachment, possibility of biofilm formation on the anode electrode surface. Technically, the electrode was fixed with 2.5% glutaraldehyde (Sigma-Aldrich) for 4 hrs at 40°C. The samples were then washed three times with water and dehydrated by successive immersion in a series of ethanol solutions of increasing concentration (30%, 50%, 70%, 80%, 90%, and absolute ethanol) for 10 min. Then the specimens were dried, mounted onto specimen stubs using graphite paste, and then the specimens were coated with gold.[34].

III. RESULTS & DISCUSSION

1. Microbial fuel cell performance
The MFC was operated in a fed-batch mode to encourage the growth of electro-active bacteria to reach the maximum performance. Figure 2 shows the MFC performance over three consecutive cycles under fed-batch manner at OCV mode. It observed that the maximum voltage output may contribute to decreasing cell life, so the voltage generated from the MFC expected to decrease overtime. Through the OCV mode, there are Consecutive increase in voltage, which was reached to about 700 mV after 100 hours of the first operational cycle, after that, the voltage was stapled for 100 hours before decreased sequentially. Due to the microbial activity and an increase in substrate consumption, the voltage dropped to less than 100 mV at the end of the 10th day of operation.

Based on fed batch operational mode the reactor was re-fed with SIW substrate to start the second operational cycle, as a result, the voltage values increased again and the highest value was 890 mV at 20th to 25th day of the MFC operation then began to decrease again. The Voltage value reached to maximum steady value 890 mV within 24 days under OCV mode of the third operational cycle (Fig. 2). The MFC operated in OCV mode for three consecutive rounds, and at the end of each cycle, SIW was added to reactivate the anodic electrode with active microorganisms and anodic biofilm development [35].

In this study, the MFC was inoculated with SIW as a bacterial cultures source and showed an increase in the bioreactor output voltage over the time. The voltage values are not reported at the start of bioreactor operation on OCV mode because no biofilm has been formed when the bacterial consumption of the substrate started the voltage values was increased in the first OCV operating cycle After that, the cell potential dropped gradually with time. On the other hand, the MFC was operated in closed-circuit voltage mode (CCV) through applying 550 Ω as external resistance. The reactor was operated for three consecutive cycles in fed-batch mechanism as the previous OCV operation.

The highest CCV voltage value in the third cycle of operation reached 340 mV (Fig. 3). During all three operational cycles in both OCV and CCV operational modes, the recorded voltage results may be attributed to the anodic biofilm formation, furthermore the ability of bacterial content to release and transfer the electrons to the anode surface directly. The current study results showed that the ability of SIW bacterial content to catalyzing bioelectricity production through the MFCs. In a previous research by Kumar et al. [36], they used the aerobic mixed bacterial culture from sugar mill effluent and their the reactor maximum voltage was 318 mV (1000Ω) with power density 140 mW/m2 (1000Ω, 50 mA/m2).

1. Polarization characteristics
Polarization curves were constructed for examining and analyzing the changes in MFCs potential from balance condition based on a streaming current [37]. The polarization curve properties were determined when the voltage reached a stable state in OCV mode and various external loads have been applied. Fig. 4 shows the polarization curve of current and power density against MFC voltage. The maximum obtained MFC power density and current density 160.16 mW/m2 and 320.9 mA/m2 respectively. The MFC eternal resistance was obtained from the slope of the plotted voltage versus current as mentioned elsewhere[38] and it was 225 Ω.
Parasad et al. [39] reported that the maximum power density obtained from polarization curves of MFC fed with sugar industry effluents was of 5.62 W m−3 at current density reached 6.8 W m−3. The variability in behavior of polarization curves and results may be due to many factors such as electrode composition, bacterial activity as well as internal resistance generated [39]. The polarization curve indicated the power harvested by the reactor, which was considered the principal objective of MFCs. In addition, the polarization curves demonstrate the relation between SIW as a carbon source for the bacteria activity and produced power.

2. Substrate degradation and COD removal
The COD removal rate of the operated MFC was increased continuously overtime. Fig. 5 clarifies the degradation of SIW substrate (COD values) over time. The operated SIW fed-batch MFC was started with initial COD 2300 mg.L−1. The graph cleared that there is a correlation between the substrate consumption and the bioelectricity production, where the voltage value on the CCV MFC operational fifth day was 360 mV and COD efficiency percentage was about 70 %. While the maximum removal efficiency was reached by the end of the cycle duty and recorded 80.4%.

These results are in line with previously recorded results of Patil et al. [40], they revealed that the percentage of COD removal of sugar industrial effluent was more than 85.4% at the end of the MFC operation time. The coulombic efficiency (CE) referred to the full charge proportion transmitted into the anode over the highest extractable charge after complete oxidation of the substrate [41]. The calculated coulombic efficiency was 46%; this result verified the inverse relationship between coulombic efficiencies and substrate concentration. The CE ratio recorded in this study falls within the CE measurements range of Kumar et al. [36] which reached 72%.

IV. CONCLUSION
The bioelectrical performance of mediator-less double-chamber MFC fed with SIW as a microbial source and substrate was determined after three consecutive operational cycles during 33 days. According to the MFC COD removal efficiency analysis, the study was indicated that the SIW was oxidized completely, which translated into a direct transmission of the electrons to the anode. The COD removal efficiency of SIW at maximum voltage yield was 85.4% with a coulombic efficiency of 46% was achieved within the operational cycle. The maximum reported open-circuit voltage (OCV) is 890 mV in addition to the system successfully revealed a maximum power density of 160.16 mW/m2 at a stable current density of 320.9 mA/m2.

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