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MICROBIAL FUEL CELLS USING DIFFERENT TYPES OF WASTEWATER FOR ELECTRICITY GENERATION AND SIMULTANEOUSLY REMOVED POLLUTANT

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Abstract

Microbial fuel cells (MFCs) are a device that converts chemical energy to electrical energy during substrate oxidation with the aid of microorganisms that act as biocatalysts. The energy contained in organic matter is converted to useful electrical power. An MFC operates as electrons from the microorganisms transfer from a reduced electron donor to an electron acceptor at a higher electrochemical potential. The aims of the study are to determine the most efficient wastewater source that can generate the highest rate of electricity production by using MFCs and to determine the removal rate of carbon and nitrogen in wastewater by using MFCs. The three different wastewater samples used were activated sludge, palm oil mill effluent (POME) and leachate from food waste. The highest rate of voltage generation is achieved when the MFC was operated with leachate (0.455 V), followed by POME (0.444 V) and activated sludge (0.396 V). However, based on the study of the graph pattern generated, activated sludge provided the most consistent record in terms of electricity generation. The highest efficiency of COD removal is achieved by activated sludge (37.5 %), followed by leachate (6.11 %). The activated sludge has also shown the highest efficiency in terms of nitrogen removal (65.28 %), followed by POME (48.12 %) and leachate (25.15 %).

Keywords: MFC, Electricity generation, Activated sludge, POME, Leachate.

1. Introduction

Microbial fuel cells (MFCs) are an emerging technology that directly converts the chemical energy stored in organic matter to electricity. Driven by the increasing concern over the energy–climate crisis and environment pollution, MFCs have been developed rapidly in the past decade. This is because MFCs are not only an alternative approach for electric generation; but they can also be used to treat wastewater. MFCs can generate bio-energy from the organic matter while simultaneously removing carbon and nitrogen [1-5].

In the first step of the MFC, an anode respiring bacterium digests the organic waste to carbon dioxide and transfers the electrons released to the anode. There are several possible mechanisms for electron transfer from the microorganism to the anode, which involve direct electron transfer via outer membrane cytochromes, mediators and nanowires. Next, the electrons travel from the anode through an external circuit to generate electrical energy. Finally, the electrons complete the circuit by traveling to the cathode, where they are taken up by oxygen and hydrogen ions to form water.

Analyses of wastewater typically concentrate on the water quality parameters that affect the receiving stream. For instance, if the receiving stream for wastewater discharge is a lake, the nutrients, nitrogen and phosphorous in the wastewater may be the primary concern. Nutrients discharged to a lake or river can cause eutrophication, a degraded water quality condition. If the receiving stream is a high-quality river, the primary concern may be the oxygen-consuming organics in the wastewater. The chemical oxygen demand, COD test and ammonia nitrogen and organic nitrogen tests are the methods that measure the oxygen-consuming organics and the nitrogen level in the wastewater sample. There are also few parameters that govern the MFC when generating electricity, such as substrate oxidation, internal resistance, electron transfer and cathode reactions.

Although there are many types of MFC reactors and many research teams throughout the world, all reactors have the same operating principles. All MFCs have a pair of battery-like terminals: anode and cathode electrodes. The electrodes are connected by an external circuit, and an electrolyte solution helps conduct the electricity. The difference in voltage between the anode and cathode, along with the electron flow in the circuit, generates electrical power. In a microbial fuel cell, the substrate (organic matter or biomass) is oxidized at the anode, producing carbon dioxide and protons and electrons, which are transferred to the electrode. Microorganisms act as the biocatalysts in an analogy to chemical fuel cells. The electrons and the protons produced in the anode end up in the cathode via the external electrical circuit for electrons and the exchange membrane for protons. At the cathode, an oxidant (normally oxygen) is being reduced [6]. The equations below illustrate the basic process occurring in MFCs for the case of a glucose-fed system.

Anode: $$C_6H_{12}O_6 + 6\,H_2O \rightarrow 6\,CO_2 + 24\,H^+ + 24e^- \quad (1)$$

Cathode: $$24\,H^+ + 24\,e^- + 6\,O_2 \rightarrow 12\,H_2O \quad (2)$$

2. Material and Methods

The MFC reactor (Fig. 1) was designed and fabricated from acrylic material. It consisted of two chambers (1 liter each) for the anode and cathode compartment, which were separated by a NafionTM membrane (*D* =3.6 cm). The cathode chamber of MFC was filled with phosphate buffer (50 mM, pH 7.5) as a catholyte. The anode chamber was filled with the wastewater samples. The cathode and anode electrodes that were used were composed of carbon paper. The cathode and the anode are connected with an external circuit by using connecting wires. Both sides of the anodic chamber and cathodic chamber are capped tightly to avoid the addition of unwanted material throughout the entire MFC process (as long as 96 hours). A computerized digital voltmeter is connected to a resistor in a parallel circuit to measure and record the open electric voltage produced by the electric flow in the MFC throughout the process. Chemical Oxygen Demand (COD) and Total Kjedahl Nitrogen (TKN) were measured before and after the MFC operation to determine the rate of carbon and nitrogen removal in wastewater. The pH value of the wastewater is observed to identify suitable pH conditions for bacterial growth during MFC operation. The MFC operation is conducted by testing on three types of wastewater samples: activated sludge, palm oil mill effluent (POME) and leachate from food waste.

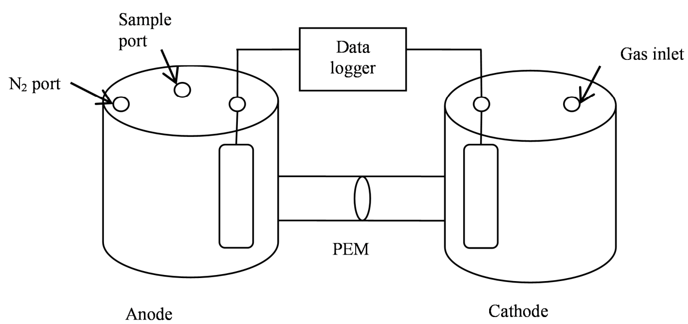

Fig. 1. Schematic Diagram of MFC.

3. Results and Discussion

3.1. Activated sludge

Based on Fig. 2, the open-circuit voltage recorded at the beginning of the study is only 0.079 V. According to the pattern of the graph shown, the voltage generation starts to stabilize 10 hours after the MFC is operated, which means that the formation of a biofilm on the surface of the electrodes took place in the first 10 hours of the MFC operation. The increasing voltage produced is due to the higher rate required for the microorganism to form the biofilm on the surface of the electrode. After the formation of the biofilm on the surface of the electrode, the rate of electric voltage decreases because the competition occurs between the microorganisms to obtain their food from the organic matter and nutrients in the activated sludge. This phenomenon affects the rate of electric voltage production by the microorganisms [7]. Thus, the rate of electric voltage produced becomes lower compared with the beginning of the MFC operation in which the formation of biofilm occurs. The graph pattern shown by the operation of the MFC using activated sludge is consistent due to the efficiency of the reaction at the cathode.

Another factor that influences the consistency of the electric voltage production is the efficient rate of proton transfer through the Nafion to the cathode, which helps in completing the electrical circuit. The increase in the rate of electric voltage production continues until the 96th hour of MFC operation, and the highest voltage recorded is 0.396 V.

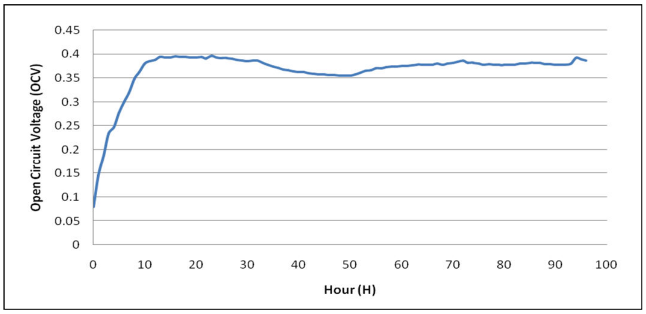

Fig. 2. The Open-Circuit Voltage Produced by the MFC when Using Activated Sludge as the Anolyte.

3.2. Palm oil mill effluent (POME)

The initial voltage recorded by an MFC that ran with the POME is 0.053 V, as shown in Fig. 3. The rate of electric voltage production experiences a rapid increase at the beginning from the first to the sixth hour. This is because the exoelectrogens in the wastewater are capable of forming a biofilm for electron transfer to the surface of the electrode at a more efficient rate. As observed from Fig. 3, the electric voltage reading experiences sudden drops at the 7th, 19th, 31st, 47th and 72nd hour. The factor that can explain to the sudden drops in the voltage reading in the stated hours is the thickness of the biofilm formed on the electrode surface. The biofilm can produce more current when the biofilm thickness is at an intermediate level, not too thick or thin. If the biofilm is too thick, the electrons will have to travel too far to get to the anode. In contrast, if the biofilm is too thin, it has too few bacteria to extract the electrons rapidly from the fuel. Other than that, the decrease in electric voltage may also occur due to inactive microorganisms and low electron transfer from the microorganisms to the electrode. However, the electric voltage shows an increase in the reading after each of the drops in the reading, most likely because there is a lower level of competition between the living and active microorganisms to obtain their source of food [8]. From the graph pattern, we can see that at a certain point, the voltage dropped to zero. It is can be deduced that at that point, the biofilm that is formed on the surface of the electrode completely detached from the electrode. A new biofilm is formed to replace the previous degraded one, which explains the increasing voltage after the sudden drop. It is also noticeable that the range of the new biofilm build up for each interval is approximately 2 to 3 hours. The highest voltage recorded by the POME-running MFC is 0.444 V. This simultaneous increase and decrease in the electric voltage reading is predicted to continue until all the microorganisms in the wastewater are dead and no electric voltage can be generated at the end.

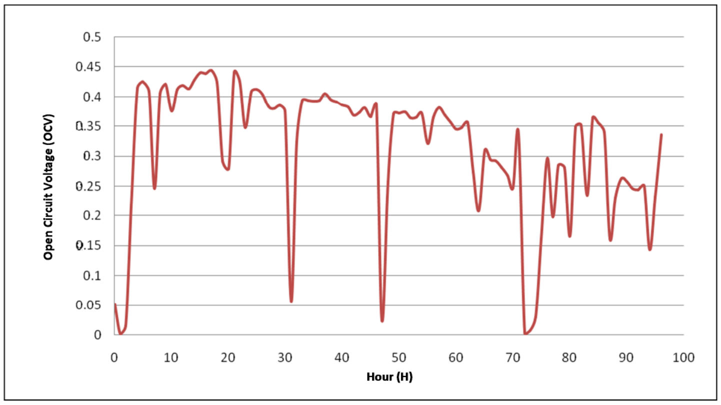

Fig. 3. The Open-Circuit Voltage Produced by the MFC by Using Palm Oil Mill Effluent (POME) as the Anolyte.

3.3. Leachate

Referring to Fig. 4, the rate of voltage production by the MFC when using the leachate as an anolyte is much lower compared with when the MFC is operated with activated sludge and POME. The initial voltage recorded is 0.02 V. The low rate of voltage production occurs due to the lower rate of biofilm formation. The formation of biofilm on the electrode surface occurs in the first 19 hours, whereas after that, the open-circuit voltage shows a rapid increase in the graph pattern, which signifies a high rate of voltage production. However, from the 19th to 48th hour, there are two rapid drops at the 34th and 47th hour. This may occur because of the death of microorganisms, which causes less formation of biofilm and less electron transfer to the anode surface. This is further proven with the observation of the graph pattern after the 48th hour, in which the rate of voltage production is observed to be increasing. The graph pattern shown in Fig. 4 is rather dispersed and inconsistent due to the inconsistent rate of electron transfer, which causes the rate of voltage production to be less stable. The highest voltage recorded by the experiment, however, is the highest voltage ever recorded from running the MFC on the three wastewater sample (0.455 V).

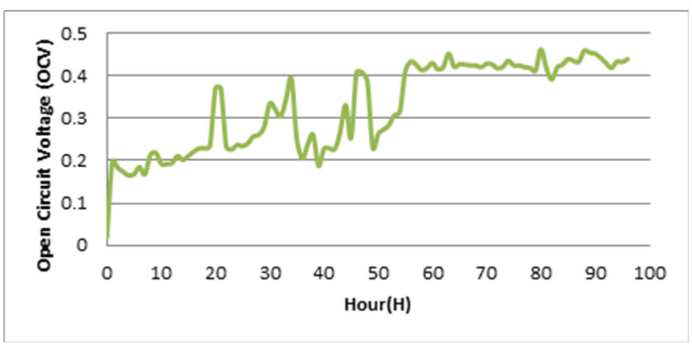

Fig. 4. The Open-Circuit Voltage Produced by the MFC by Using Leachate as the Anolyte.

3.4. Comparison of the three wastewater samples used in the MFCs

After each of the samples is run in the MFC for 96 hours each, the results of the open-circuit voltage (OCV) recorded are studied and compared, as shown in Fig. 5. Based on the graph pattern for the comparison between the result of the electric voltage shown by the three samples in Fig. 5, different substrates and microorganisms that exist in each of the samples affect the value of the electric voltage produced from the beginning of the study. For the MFC that has been operated with the activated sludge, the range of electric voltage produced is between 0.079 V to 0.396 V. Next, the use of POME in the MFC gives values for the electric voltage in the range of 0.053 V to 0.444 V. Finally, the electric voltage production when using leachate is in the range between 0.198 V and 0.455 V.

The study shows that among the three results shown, leachate produces the highest voltage recorded. However, by observing the graph pattern, we can conclude that the rate of electric voltage production by using activated sludge is the most consistent comparing to POME and leachate, which show inconsistency in their rate of voltage production. The difference in the consistency of the rate of voltage production may be due to the formation of different types of microorganisms that exist in the sample and the rate of electron transfer. The results from a previous study on identification of the electricity-producing bacteria in activated sludge [9] have shown that the combination of *β-Comamonas sp*, *γ-Enterobacter sp*, *Bacillus cereus sp* and *Clostridium sp* produced a consistent power density with the highest of 67.57 mW/m^2. Further studies on the fundamental understanding of the microorganisms are needed in order to optimize the MFC process for different types of wastewater.

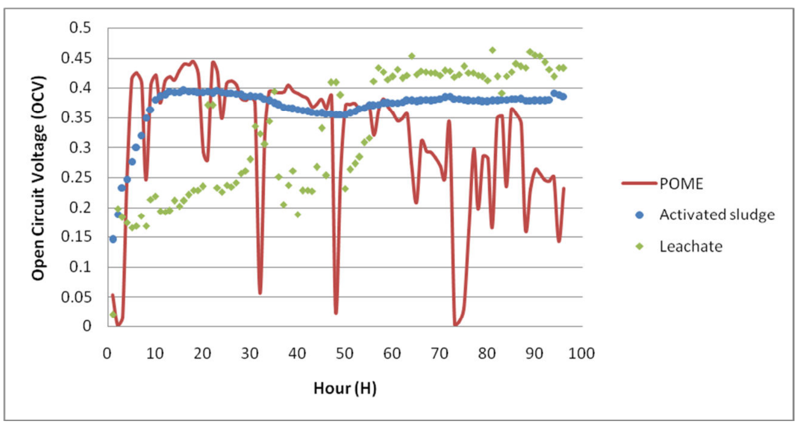

Fig. 5. Comparison between the Open-Circuit Voltage Results when Using Activated Sludge, POME and Leachate.

Microorganisms are able to transfer electrons outside of their cell to an electron acceptor to generate electricity in either mixed culture or pure cultures. *Escherichia coli* and *Saccharomyces* are among the very first microorganisms discovered by Potter in the year of 1911 when he used platinum as electrode in MFC [10]. MFC occupied by bacteria with different genetic groups which range from *β-Proteobacteria* such as *Rhodoferax* [11], *γ-Protobacteria* such as *Shewanella* and *Pseudomonas* [12-14], *δ-Protobacteria* such as *Aeromonas*, *Geobacter*, *Geopsychrobacter* and *Desulfobulbus* [15-17], *Firmicutes* such as *Clostridium* [18], and also *Acidobacteria* such as *Geothrix* [19].

3.5. Chemical oxygen demand (COD)

The initial COD value recorded before the MFC process for the activated sludge was 1128 mg/L, for POME was 589 mg/L and for leachate was 540 mg/L. Based on the COD removal after the MFC process, the highest carbon removal efficiency was demonstrated by the activated sludge, which had a value of 37.5%, followed by the leachate sample, which shows a carbon removal efficiency of 6.11%. However, the COD value for the POME recorded 0% removal after running with the MFC process.

3.6. Nitrogen

3.6.1. Activated sludge

The nitrogen concentration in the activated sludge before the MFC process was 112 mg/L for ammonia nitrogen, 16.67 mg/L for organic nitrogen and 128.67 mg/L for TKN (Table 1). The result shows that the removal rate for ammonia nitrogen is 75 %, which is the highest removal percentage among the three samples of wastewater used. The value of organic nitrogen does not show any change after the MFC process. Meanwhile, the percentage of TKN removal is 65.28 %, which is also the highest.

Table 1. Nitrogen Concentration in Activated Sludge before and after the MFC Process.

	Ammonia Nitrogen, $N\text{-}NH_3$ (mg/L)	Organic Nitrogen (mg/L)	TKN (mg/L)
Before MFC	112	16.67	128.67
After MFC	28	16.67	44.67

3.6.2. POME

The results for the ammonia nitrogen, organic nitrogen and TKN before the MFC process and after the MFC process are shown in Table 2. After 96 hours, the percentage removal of ammonia nitrogen is 66.67 %, for organic nitrogen is 16.67% and for TKN is 48.12 %.

Table 2. Nitrogen Concentration in POME before and after the MFC Process.

	Ammonia Nitrogen, $N\text{-}NH_3$ (mg/L)	Organic Nitrogen (mg/L)	TKN (mg/L)
Before MFC	56	33	89
After MFC	18.67	27.5	46.17

3.6.3. Leachate

For leachate, the test results for the ammonia nitrogen, organic nitrogen and TKN analysis are shown in Table 3. The rate of removal for ammonia nitrogen after the 96th hour of MFC operation is 22.23 %, the value for organic nitrogen is 34.38%, and TKN is reduced by 25.15%. The value of nitrogen removal shown by the leachate is the lowest compared with activated sludge and POME. The value of nitrogen removal for activated sludge, for instance, is as much as twice the nitrogen removal for leachate.

Table 3. Nitrogen Concentration in Leachate before and after the MFC Process.

	Ammonia Nitrogen, $N\text{-}NH_3$ (mg/L)	Organic Nitrogen (mg/L)	TKN (mg/L)
Before MFC	84	26.67	110.67
After MFC	65.33	17.5	82.13

3.7. pH

The results for the pH value for each of the samples after the MFC process is shown in Table 4. There is no apparent change in the pH value for the samples after the MFC operation. For all the samples, the result shows a pH decrease after the MFC operation.

Table 4. pH Value before and after the MFC Process.

	pH value	
	Before MFC	After MFC
Activated sludge	6.99	6.75
POME	3.72	3.64
Leachate	8.68	8.42

The difference in the pH value for each of the samples is also affected by the rate of electric voltage production for each of the samples. This is because many analyses state that the pH value at the anode, which is close to the pH value of 7, is the most suitable condition for the growth of microorganisms. This explains the consistency in the rate of electric production in activated sludge; the initial and final pH values for activated sludge are 6.99 and 6.75, which are near a neutral pH value. However, a study has also shown that for the type of MFC reactor that allows open aeration at the cathode with a pH value of 8 to 10 (alkaline) at the anode, the rate of electricity production is also high [20]. Compared with the almost neutral value of the pH for the activated sludge, the pH value for POME is acidic, and it is slightly alkaline for leachate.

4. Conclusions

An MFC has the ability to generate electricity from the wastewater while simultaneously removing carbon and nitrogen. The highest rate of voltage generation is achieved when the MFC is operated with leachate (0.455 V), followed by POME (0.444 V) and activated sludge (0.396 V). However, based on a study of the graph pattern generated, activated sludge provides the most consistent record for the electricity generation. The highest efficiency of COD removal is achieved by activated sludge (37.5 %), followed by leachate (6.11 %). The activated sludge also showed the highest efficiency for nitrogen removal (65.28 %), followed by POME (48.12 %) and leachate (25.15 %). The electricity voltage generation and the rate of the carbon and nitrogen removal for the activated sludge have been shown to be the most efficient among the three types of samples.

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