Microbial Fuel Cells for Simultaneous Electricity Generation and Organic Degradation from Slaughterhouse Wastewater

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ABSTRACT: Microbial fuel cell (MFC) has gained much attention in recent years due to its capability in simultaneous organic decomposition and electricity generation. Here, self-fabricated MFCs system were used to generate electricity and to reduce organic pollutant contained in slaughterhouse wastewater. In order to investigate the MFC configuration for process optimization, the experiments were conducted by employing different types of electrode materials, electrode size, and substrate-rumen microbes’ ratio. Results shows that configuration of MFC with graphite-copper electrode 31.4 cm² (active surface), and substrate-rumen microbes ratio 1:10 shows the best result by producing 318 mA m⁻² of current density, potential of 2.4 V, and achieve maximum power density up to 700 mW m⁻². In addition, self-fabricated MFC also shows its ability in reducing organic component by decreasing the chemical oxygen demand (COD) of the slaughterhouse wastewater to 67.9% and increasing the system pH from 5.9 to 7.5 which emphasize that MFC (operating at ambient condition 29°C) can be used as an alternative green-technology for slaughterhouse wastewater treatment.

Keywords: microbial fuel cells, slaughterhouse wastewater, electricity generation, chemical oxygen demand, maximum power density

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1. Introduction

Microbial fuel cell (MFC) is a bio-electrochemical devices that use microbe as catalyst to convert organic and inorganic substrates into electrical current (Hubenova and Mitov, 2015; Prasad et al, 2007; Min and Logan, 2004; Babanova et al, 2011). The core principle of MFC is the metabolism process of microbe which consist of two steps. The first step requires the removal of electrons from organic matter degradation (oxidation), and the second step consists of giving those electrons to something that will accept them (reduction), such as oxygen or nitrate.

Microbe grown under anaerobic conditions (without the presence of oxygen) can transfer electrons to electrode (anode), which further generate the current and voltage to produce electricity. The system basically consists of substrate as organic source, microorganism as biocatalyst, proton exchange membrane and electrochemical device to collect the electron generated by the system. Although the achieved power and current densities generated by MFC are still very low, this technology is worth for further development as it can produce a sustainable energy from organic source such as waste.

Wastewater from petroleum industry, municipal, and agricultural have been successfully employed as a source for MFC substrate (Karthikeyan et al., 2016; Ge et al., 2015; Guo et al., 2016; Abbasi et al., 2016).
addition, Heilmann and Logan (2006) also confirmed the possibility of using rich protein meat packing wastewater (MPW) as substrate and successfully reduce chemical oxygen demand (COD) and biological oxygen demand (BOD) value and at the same time generate electricity through MFC system. Slaughterhouse wastewater also possible to be used as MFC substrate as it contained various and high amounts of organic matter (e.g., proteins, blood, fat and lard) (Bazrafshan et al., 2012). COD and total organic carbon (TOC) values of slaughterhouse wastewater are up to 15900 ppm and 1200 ppm respectively (Bustillo-Lecompte et al., 2015). Several works have been introduced in terms of employing MFC for slaughterhouse wastewater treatment by using different types of microbe, for instance Katuri et al. (2012) applied MFC using granular anaerobic sludge as microbe source. On the other hand, Elanthamilan et al. (2014) and Ghanapriya et al., (2012) employed MFC with wild anaerobic bacteria. Rumen microbe normally collected from ruminant animal which consists of mixture of bacteria, fungi, archaea, viruses, and protozoa with predominantly is anaerobic microbe (40–60%) and they can live at pH 5.5–6.5 (Dijkstra et al., 2005; Hobson and Stewart). This type of biocatalyst may be beneficial for improving the performance of MFC. So far, research on rumen microbe utilization for slaughterhouse wastewater treatment via MFC is rarely performed.

Generally, parameters that influence the process performance of MFC include electrochemical device configuration such as size and shape of electrodes, solutes in both chambers, arrangements of electrodes and proton exchange membrane available area for transporting solutes between anode and cathode, surface chemical properties of electrodes, electrode materials (Wang et al., 2011). Type of electrode material is one of the parameters that can affect with performance and productivity of the MFC. Physical and chemical stability which include resistance to corrosion, the formation of oxide or hydride particular, the rate and selectivity of the product to be formed, electrical conductivity, and the electrode resistance is a factor to consider in selecting electrode. According to Logan, the terms of good anode are high conductivity, non-corrosive, high specific surface area (area per volume), high porosity, not pollute, inexpensive, easy to use and can be used in large scale (Logan, 2008).

In this study, we investigated the effect of material type and size of electrode MFCs performance, COD and pH values of slaughterhouse wastewater before and after the degradation process via MFC by using rumen microbe as biocatalyst. We emphasize that in spite of our extensive inquiry, the slaughterhouse wastewater treatment by using rumen microbe as MFC fuel has hardly reported. Based on that, we anticipate that our study will be a cornerstone to establish a baseline protocol of MFC.

2. Materials and Methods

2.1 Materials

Slaughterhouse wastewater (the primary clarifier overflow) and multicultural rumen microbe were collected from a local slaughterhouse factory (Semarang, Indonesia) without any filtration. The slaughterhouse wastewater characteristic and composition can be shown in Table 1. The average pH; total dissolve solids (TDS); and chemical oxygen demand (COD) in raw wastewater were 5.9; 983 ppm and 9858 ppm, respectively. KMnO₄ and H₂SO₄ were purchased from Sigma Aldrich (St Louise, USA). K₂Cr₂O₇ was purchased from Merck (Massachusetts, USA).

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>pH</td>
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<td></td>
</tr>
<tr>
<td>TDS</td>
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<td>ppm</td>
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<tr>
<td>DO</td>
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<td>ppm as O₂</td>
</tr>
<tr>
<td>COD</td>
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<tr>
<td>Alkalinity</td>
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<td>ppm</td>
</tr>
</tbody>
</table>

2.2 Rumen Microbe Incubation and Electrolyte Preparation

Rumen microbes were used as biocatalyst in anodic chamber. Slaughterhouse wastewater which act as a substrate was mixed with rumen microbes ratio 1:10; 10:1; and 1:1 v/v. Incubation was conducted for 120 hours at 28-30°C. Incubated slaughterhouse wastewater and rumen microbes were placed in anode chamber and 1L of 1 M KMnO₄ was placed in cathode chamber as electrolyte.

Fig. 1 Construction of Microbial Biofuel Cell by using Multicultural Rumen Microbes.
2.3 Bioreactor Construction

Self-fabricated dual chamber MFC reactor was used in this experiment (Figure 1). It has 150 mm length, 150 mm width, and 150 mm height and it was operated under ambient temperature and pressure.

Both anode and cathode plate were placed on each chamber (1L volume). Salt bridge was used as proton exchange system between two chambers, anodic and cathodic chamber. It was prepared by mixing saturated NaCl and agar, and then fed in the pipe that connecting the anodic and cathodic chamber. Good sealing is necessary to prevent any leaked in the joint connection between chamber and salt bridge.

Several types of electrode materials (Zinc, graphite, and Copper) were used as cathodes with only graphite as anode material. This electrode has various sizes; 7.8, 15.7, and 31.4 cm². Prior experiment, graphite electrode, was treated to remove impurity inside graphite electrode (Deepika et al., 2015). Graphite electrode was soaked with 1M HCl and 1M NaOH overnight before and after experiment, and then washed with H2O. Multimeter (SUNWA YX-1000A) was connected to each electrode to measure current and voltage. The MFC was operated for 120 hours, enough for anolyte containing multicultural rumen microbes produce the electron, and then followed by current and potential measurement. The anolyte was used without any replacing fresh substrate.

2.4 Chemical and Electrochemical Measurements

Acidity measurements were performed at the beginning and end of batch experiment for each variable by using a pH meter (HM TDS-3, USA). Organic content of anolyte was analysed at the same time via chemical oxygen demand (COD) measurement using spectrophotometer (Optima SP-300, Japan) followed colorimetric method (LaPara et al., 2000). Currents and potential generated from the process were measured using a multimeter (SUNWA YX-1000A, Japan). Power density analysis was calculated by Potential and Current Density \( P = V \times I \) with the resistance was set around 1 KΩ. Data was collected every 6 hours for 120 hours incubation process.

3. Results and Discussion

3.1 Electricity generation

Copper, graphite, and zinc were used as cathodes with only graphite as anode material. Electrode material is important that determine the performance of MFC as different material generated different electrical energy and potential. Figure 2a-b shows the graphite-copper electrode combination produce highest current density 236 mA m⁻² and potential 1.2 V compare to other materials (zinc-graphite was 191 mA m⁻², 0.7 V and graphite-graphite was 203 mA m⁻², 0.9 V). Cu has potential standard (E°) value higher than Zn with +0.337 V and -0.763 V respectively. It means that Cu can accept more electron than Zn, as it favored electron transfer from anode to cathode and produce higher power density. Zn was susceptible to corrosion that causes impurities in the electrode. These impurities might cover the surface of Zn and inhibit cathode to accept electron from anode which lead to low power density production. Copper also proved as an outstanding cathode material in other research conducted by Deepika et al., which shows highest output voltage and current compared with other five different materials of anode (Deepika et al., 2015).

Fig. 2 Comparison (a) Potential and (b) current density of different materials used as cathode graphite, zinc, and copper

Surface area or electrode size is also an important parameter in determining the MFC configuration of certain system. By increasing the electrode size means providing larger surface area for microbe to transfer the electrons and by then can increase the power density produced from the MFC system. Figure 3a-b shows the trend line of potential and current density produced.
during the observed process at 120 hours in different size of electrodes. As expected, electrode with highest surface area 31.4 cm$^2$ produced highest current density with value was 270 mA m$^{-2}$ and potential with value 1.42 V. Size of electrode 15.7 cm$^2$ generated 236 mA m$^{-2}$, 1.2 V while the smallest one 7.8 cm$^2$ generated 205 mA m$^{-2}$, 0.4 V. As mentioned previously, surface area is important part of electron transfer in MFC system. Higher surface area provides larger contacting surface that favored the electron transfer from microbe to the electrochemical device. As already reported in other research, the higher size of electrode could produce the higher current density and potential (Qian and Morse, 2011).

![Graphs showing comparison of potential and current density for different electrode sizes.](image1)

The phenomena that take place in a MFCs are complex as many biological, physical-chemical and electro-chemical processes are involved. Biological process, including the metabolism and the growth of microbe. Preliminary observation was finding out the optimum ratio of the substrate and microbe as biocatalyst. For the test, mixed substrate-rumen microbes with ratios 1:10, 10:1, and 1:1 were used with optimum electrode configuration 31.4 cm$^2$ of graphite-copper. Figure 4a-b depict substrate- rumen microbes with ratio 1:10 produce highest power density compared to other ratio. Substrate- rumen microbes with ratio 10:1, 1:1, and 1:10 generate current density value 172, 270, 318 mA m$^{-2}$ and potential value 0.75, 1.42, 2.4 V respectively. Microbes need sufficient food to growth, and in this particular system (slaughtered wastewater: rumen microbes with) the ratio of substrate 1 to 10 rumen microbes with produced highest power density. Excessive substrate may not beneficial for the process, as putting equal ratio in the process only give less potential that lead to lower power density generation. In addition, putting huge amount of substrate (10:1) may not beneficial as it could inhibit the electron transfer from microbes system to the electrode surface.

![Graphs showing comparison of potential and current density for different substrate-rumen microbes ratios.](image2)

3.2 Organic degradation

From the previous section, it can be stated that for this particular system and particular research framework the maximum power density that can be generated is 700 mW m$^{-2}$ (Figure 5). It is higher than other MFC research, for instance COD removal by using single chamber MFC reactor with graphite electrode was 26 mW m$^{-2}$ (Liu et al., 2004), utilization of olive mill wastewater by using single chamber MFC reactor with platina electrode was 124.6 mW m$^{-2}$ (Sciarria et al,
2013), and utilization of alcohol distillery wastewater by using anaerobic fluidized bed MFC reactor with carbon fiber paper was 124.03 mW m$^{-2}$ (Huang et al., 2011).

The steep trend line of potential and current density observed from 0 to 80 hours is due to rumen microbe’s growth along the time by following growth mechanism which need to be investigate further. Extracting from the graph it can also be observed that the growth reached it maximum value from 80-120 hours which might be due to no more substrate that could be degrade to generate electricity.

Lack of substrate at the end of the process means that organic degradation did happened. To prove that, the measurement of COD value was conducted. We investigated the performance of rumen bacteria to remove COD inside slaughterhouse wastewater. For the test, we used the optimum parameter with 31.4 cm$^2$ graphite-copper electrode and substrate-microbes ration 1:10 that can reduce COD value and neutralize pH of system.

Beside COD, pH of the system before and after the process was also investigated. The acidity of mixture solution increased from 5.9 to 7.5. In MFC mechanism, electrons were captured by anode and transferred to the cathode via external circuit, while protons that are generated from oxidation of substrates should be transferred to cathode via salt bridge to cathode. We indicate that the rate of proton transferred to cathodes is faster than proton generation in anode. The fast consumption of protons leads the increasing pH of wastewater. This is opposite from research that was conducted by Karthikeyan et al., (2016) where the protons generation rate faster than the protons consumption in the cathode, so that the pH decreases.

### 3.3 Simple modelling of power density

Modeling is a powerful tool for the in-depth study and optimization of MFC. A model is basically aimed at describing MFC performance based on certain laws and equations. The complexity of any model depends on different factors such as the dimension selected, the assumptions made and the level of detail used in describing the processes involved. Study of the phenomena that take place in an MFC covers a wide range of processes, from mass transport through the cell, the phases of matter considered and the boundary conditions, to microbial growth, the anode and cathode reaction kinetics and the electrochemical behavior of the system. The robustness of a model will be judged by its predictive capacity and the balance between the computation time needed and the precision of the results (Ortiz-Martinez et al., 2015).

Generated from the data observed, the only modelling that can be draw is the power density modelling. As power density of the experimental data can be calculated using $P = V \times I$ and $V = I \times R$, where $P$ is power density (mWm$^{-2}$), $V$ is the potential (V) and $I$ is current density (mA$m^{-2}$). While modelling data of power density can be calculated using $P = I^2 \times R$ where $P$ is power density (mWm$^{-2}$), $R$ is the resistance and $I$ is current density (mA$m^{-2}$), with assumption the resistance in experimental and modelling is constant. The comparison between experimental data and model can be observed in Figure 6. The experimental data is nearly fit into equation model $y = 0.00736x^2$ ($R^2 = 0.96$).
4. Conclusion

Slaughterhouse wastewater treatment via MFC by employing rumen microbes with as biocatalyst has been successfully conducted with electricity as by product. Configuration of MFC with graphite-copper electrode 31.4 cm² in size, and substrate-rumen microbes with ratio 1:10 shows the optimum result with current density of 318 mA m⁻², potential 2.4 V, and maximum power density up to 700 mW m⁻². In addition, self-fabricated MFC operating at ambient condition (29°C and pH 7.5) also shows its ability in reducing organic component by measuring the chemical oxygen demand (COD) up to 67.9% followed by increasing pH from 5.9 to 7.5. The correlation between current density and power density in experimental is nearly fit with equation model \( y = 0.00736x² \) (R²=0.96). It all emphasize as a green-technology for slaughterhouse wastewater treatment with further improvement in process efficiency.

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References


