Microbial fuel cell based biocatalyst from traditional market waste water for energy production

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Abstract. Microbial Fuel Cell (MFC) based on bacteria from Cikurubuk Traditional market waste water has been applied for energy production. We have been observed that there were some potential of microorganisms could be applied as a renewable source of energy in term of electricity production. A traditional market plays a major role in socio-economics and constitutes a significant aspect of Indonesian culture. One of the major contributors to domestic pollution is a pollution from wastewater traditional market which is containing organic substance and nutrients. This conditions if not properly solved can causes seriously harm the human health and environment. The objective of this study is to develop the waste water treatment technology without energy supply by using the potential activities of microorganism through microbial fuel cell system. We have been determined some biocatalysts from biofilm at the surface of anode. To provide the results some characterizations have been conducted using Chronoamperometry. The optimization of anode conditions have been also studied to maintenance the long performance of MFC. Results confirmed that the biocatalyst activities could be a promising renewable source for energy production and very suitable as an alternative technology based green chemistry technology.

1. Introduction
Nowadays, energy demand is still increasing. We need energy for our everyday lives to sustain us. They play the most significant role in the modern world. We were totally dependent on their existence as a source of energy. We have been applying a conventional source of energy, including coal and oil, for quite a long time, and these conditions will cause their availability to be limited in the world. Today’s, many researcher and studied have been resulted for maintenance the capacity to supply fossil fuels can be reduced someday due to limited production capacity and lack of infrastructure. According to data, 80% of the world energy market is supplied by major global energy sources, such as fossil fuels, liquid fuels (oil/petroleum), coal and natural gas [1].

As we know that the demand of energy supply for human life is very high. It could be predicted that 9.4 billion of human will present in the world in 2050. In the meantime, fossil fuel cells have helped countries' economic and industrialization development over the past century, but they will not sustain the global economy forever. The growth will change not only our lifestyle, but the infrastructure as well. The amount of electricity supply will be affected by this situation. The cost of energy and the use of resources that we use will control our way of life and our economy in the coming decade [2].

However, the present of fossil fuel cell may have a negative environmental impact, and this is one of the drawbacks of fossil fuels. The climate change and global warming is the harmful effect, since the
Combustion affects the atmospheric greenhouse 
CO₂ gas that causes them and could cause average global temperatures to rise, as well as human activities and natural disasters [2], [3].

For years, the global warming trend and the issue of the diminishing availability of fossil fuels have been addressed as a global problem. This situation has motivated many researchers to learn more about renewable energy sources. As a result, there are many sources of renewable energy that have power to be used, such as hydrogen, geothermal hydropower, wind, solar, or biomass energy [4], [5].

One of the prospective renewable energy sources is Biomassa. The key benefits are that renewable energy production, such as biomass, is critical for reducing global CO₂ emissions and creating sustainable energy production. Instead of energy production from organic materials, it is now known that from Microbial Fuel Cell (MFC), the electricity can be produced directly from organic matter degradation. The biological fuel cell could contribute to solving the global environmental problems and this method is one of the most promising discoveries. The advantages of using a biofuel cell are a highly efficient and pollution-free way of producing energy that transforms a chemical reaction into electrical energy directly and emits a small harmful gas. Bio-electrochemistry, i.e. electrophysical concepts applied in biology, can be used and chosen as an alternative technology to solve the problem of ecosystem preservation. MFCs technologies provides the newest application for electricity-bioelectricity generation from biomass using microorganisms [6], [7].

The MFC idea of the use of microorganisms as catalysts in fuel cells was first observed in 1970, and a proposal for the treatment of domestic waste water was submitted in 1991. However, an improved power output from MFC has been developed for practical applications to provide future opportunities in wider applications. MFCs have many advantages as a promising system, such as having a high degree of performance, being simple to operate (room temperature), needing no energy supply, and can be applied to a variety of places with insufficient electrical infrastructure [6]. They use substrates from sustainable sources during the process, do not pollute the environment, and this section offers the most benefits from MFC. The production of these devices was developed with an attention-scale approach and studied as alternatives to traditional wastewater treatment for sustainable generation of electricity [8], [9].

The development of MFC has recently been examined, most of them for improving the performance of the MFC [10]–[13]. Many research laboratories and industries have generated a significant portion of waste water. In some countries, several waste management methods have also been explored, and they have been concerned with finding the right approach to solve this key issue. Waste from conventional markets is one of the main sources of significant amounts of waste. A traditional market can produce a significant amount of daily waste. If this condition is not treated appropriately, it may lead to a severe environmental issue.

For this reason, in this research, MFCs were carried out as biocatalyst media from traditional market waste water in order to generate electricity and to achieve efficiency in processes that are highly effective in treatment at low cost. This source of opportunity could be implemented in biofuel cells as a renewable substrates to reduce global CO₂ emissions and establish sustainable energy production. Therefore, the introduction of efficient technologies for the treatment of organic pollutants in waste water plays a fundamental role. Therefore, this experiment focuses on the bacteria activities in process of organic degradation by integration of alternative energy sources such as MFC.

2. Material and method

2.1. Procedure
The preparation of electrode has been conducted, Graphite Carbon (GC) has been used as anode material. This electrode has been cleaned using a 1M HCl solution continued with ultra pure water. This electrode was then immersed in an ethanol-water mixture of 1:1 (volume ratio) for a few minutes to clean water from the waste material, followed by sonification in ultrapure water. The surface of the GC was electrochemically triggered prior to use by implementing a potential interval between -0.5 V and 1.5 V vs. Saturated Calomel Electrode (SCE) at a scan rate of 50 mV/s in a 1M H₂SO₄ solution until
a stable voltammogram was obtained. The dual fuel cell chambers have been prepared as illustrated in Figure 1.

Figure 1. The design of MFC

The dual MFC chamber was prepared for the application of fuel cells, each with a volume of 100 mL (2*100) mL. A Proton Exchange Membrane (PEM) (A Nafion 117 PEM from DuPont USA) was mounted to separate the two chambers where the membrane was maintained via a coupling between the chambers. In this phase, each experiment was conducted with a new membrane to prevent any contamination and/or interference from previous experiments. A graphite carbon (GC) plate with dimensions 1.5 x 1 x 7 cm purchased from ERG (Oakland, CA) as anode and a nickel plate (7 cm x 1.5 cm) as cathode were used. Meanwhile, to measure pH variations during experiment a digital pH meter (Sensorex, PHMA transmitter and pH probe) was used. The anolyte solution is consist of artificial waste water of traditional market and a traditional market waste as well. Meanwhile, as catholyte a K$_3$Fe(CN)$_6$ (PF) has been applied as catholyte solution. Figure 1 displays the MFC design and to avoid loss of solutions through evaporation, each chamber was hermetically closed when operating.

All the substrates i.e., microorganisms from traditional market waste water have been prepared using artificial and real waste water as well in phosphate buffer (PB) pH 7. D-glucose (Sigma Aldrich) has been also soluted in PB pH 7. The concentration of both D-glucose and PF solutions were 0.1M and 0.5 M, respectively.

Artificial waste water, compose of E. Coli:Salmonella sp:Proteus sp (E:S:P) 1:2:3, has been prepared as anode solution, 4.08 g Na$_2$HPO$_4$ (Sigma Aldrich, France) and 3.28 g NaH$_2$PO$_4$ (Sigma Aldrich, France) have been set for PB pH 7 solution, and all the substances were dissolved in 1L ultrapure water. Meanwhile, the cathode compartment was filled with a PF solution in PB pH 7 as catholyte and explained in a previous study [9], [14].

The MFC procedure was performed at 25 ± 1°C. The simple mechanism was performed during MFC, where the electrons produced at the anode by glucose oxidation promote the reduction of potassium ferricyanide at the cathode into ferrocyanide. Thereafter the oxygen present in the cathodic chamber will re-oxidized ferrocyanide to ferricyanide allowing thus the MFC work. The voltage, E, (V) delivered was recorded using a digital multimeter Voltcraft (model VC 850) then the current, I, (A) was calculated from the equation of I = E/R. R (Ω), being the resistance of the system where the value has been varied from 100 Ω to 3 kΩ to define the maximal power output as previously presented [10], [14].

3. Result and discussion

The anode condition should be maintained and suitable for growth compartment. The Chamber sets out all the conditions required for the development of a sustainable microorganism. The chamber is filled with organism, growth media, and an electrode that acts as the anode of MFC. The metabolic reaction will generates protons and electrons during the bacterial growth. Meanwhile, The recombination
compartment for protons, electrons and oxygen molecules is the cathode chamber. However, ferricyanide as an electron acceptor has already existed in cathode chamber and being a cation exchanger serves as a portioning to complete the reaction between anode and cathode chamber. The most widely used cation exchanger acting as a proton exchange membrane (PEM) is the Nafton™ membrane.

The characterization of Bacteria has been reported that *E.Coli, Salmonella sp* and *Proteus sp.* presented in traditional market waste water. This bacteria has identified using media of nutrient agar (Nutrient agar), TSB (Triptic Soya Broth), BA (Blood agar), MC (Mc Concey), MSA (Manitol Salt Agar) and biochemistry test such as MSA, TSIA (Trip tic Soya Iron Agar), SC (Simon citrate), SIM (Sulfur Indol Motility). They were found in the traditional market waste which are the composition of amount of colony were 1:2:3. As a consequence, they expand on the anode, then oxidize organic matter and release electrons. The cathode is connected to air to provide dissolved oxygen for the completion of the circuit and the resulting power from the reaction of electrons, protons and oxygen at the cathode.

In our current work, the electrons have been extracted from the microbial oxidation of the substrates and transferred to the anode. Through this process, there are three probable mechanisms such as (1) direct electron transfer (DET) from soround bacteria, (2) mediator of bacterial origin or exogenous mediator (3) highly conductive nanowires delivered as a long distance transfer by specific bacteria. The transfer mechanisms as seen in figure 2.

![Figure 2. Schematic of three extracellular electron transfer mechanisms [15].](image-url)

*Aeromonas hydrophilia, Shewanella putrefaciens, Rhadroferrax ferrireducens Geobacter metallireducens*, and others are bacteria known to pass electrons into their outer membranes through cytochromes [16], [17]. Physical contact between the bacteria and the electrode for oxidation and reduction of (redox) membrane-associated proteins is needed for the DET mechanism. In the meantime, electrochemical-conducting pili, called nanowires that allow *Geobacter* and *Shewanella* families to join distant solid electron acceptors and that is not in direct solid electron acceptors [18]. Figure 3. shows the current density deliver from MFC after 14 days operation compose of bacterias composition of E:S:P is 1:2:3 in anode compartment.
This result verified that, during the MFC process, the current density was created from the anode compartment for 14 days with the addition of 5 mL glucose of 0.1 M every 3rd day of operation. The glucose addition will serve as a source of nutrition and fuel to generate an electron for organic oxidation and then continue to be captured by anode. The maximum density of the current could reach up to 5.29 A.m\(^{-2}\). It has been verified by this artificial waste solution that this biocatalyst will oxidize organic matter and generate electricity. Meanwhile, protons will also be formed as one of the products of organic compound oxidation. The evolution of the pH value reveals that the oxidation mechanism is carried out by bacteria.

**Figure 3.** Current density and pH generates from 14 days of MFC operation based anode compartment of artificial waste water consist of E:S:P composition of 1:2:3, respectively.

**Figure 4.** Current density and pH generates from 7 days of MFC operation based anode compartment of artificial waste consist of E:S:P composition of 1:2:3, respectively.
Figure 4 shows that the current density derived from MFC for 7 days without the addition of glucose during the next day is significantly different. Up to the seventh days of MFC service, the currents were decreased day by day. It is also believed that the addition of glucose has made a major contribution to the oxidizing process carried out by biocatalyst operations. Meanwhile, the MFC operation based waste water traditional market has been observed for 14 days and 7 days operation, respectively. The result shows in Figure 5.

![Figure 5](image.png)

**Figure 5.** Current density generates from 7 days and 14 days of MFC operation based anode compartment of traditional market waste

The efficiency of the MFC process could depend on the time of operation, verified in Figure 5. The 5 mL of glucose 0.1M only applied on the first day in 7 days, then the next days we did not have glucose addition. In the meantime, we maintain the anode solution with the addition of glucose every 3 days from the 14 days of MFC perform until the end of the MFC. The overall current density produced from this process was 3.33 out of 7 days, compared with 5.23 out of 14 days of operation. MFC’s perform time reduction efficiency could reach up to 37%. It implies that without maintenance of glucose addition, MFC could be run with shorter time and the effectiveness of the MFC process still carried out in a good efficiency. This is why, besides the availability of glucose, there are so many forms of organic matter as a source of fuel in conventional market waste. However, this condition could be considered, that MFC could be carried out without having the addition of glucose or any kind of organic matter sources by using traditional market waste as organic rich media. The results also report that the pH produced during MFC process has not a different significant value confirmed from artificial or traditional market waste as well.

In our present research, PF was used as a catholyte and many were used as an electron acceptor in the two-chambered MFC [9], [14], [19]. Oh and Logan [20], Oh and Logan found that power increased up to 1.5-1.8 times by replacing the aqueous cathode with ferricyanide and oxygen, although the high internal resistance of the system can cause the power densities produced in this system to be low.

As an electron acceptor, the characteristics of MFC electricity generation using PF catholyte flowing with air have been studied. The findings indicate that there is no comparison between the output of MFC with aerated catholyte PF and catholyte PF. Therefore, a two-chambered electron acceptor as desired does not know which one is the best selected for MFC. In addition, in order to perfectly increase MFC power generation, it is necessary to select an appropriate concentration, due to the kinetics of redox reaction and Nernst equation, changes in the electron acceptor concentration can affect their efficiency.
Meanwhile, to maintain an aerobic state in the anode chamber, the biofuel cell system was calibrated. However, for the operation of the entire biofuel cell, the presence of oxygen in the anode compartment is not profitable because it will interfere with the flow of electrons through the external circuit. The MFC study confirms that oxygen can play a role as a terminal electron acceptor.

4. Conclusion
In conclusion, the study provides information on the potential of traditional market biocatalyst waste to be used as a sustainable source of MFC for energy production. MFCs have many advantages as a promising system, such as providing a high degree of performance, being simple to operate (room temperature), needing no energy supply, and can be applied to a variety of places with insufficient electrical infrastructure. This study confirmed that MFC could be one of the alternative technologies in terms of waste management, in particular created by the traditional market and very suitable for implementation in Indonesia.

5. Acknowledgment
This project is part of the Grant reseach founding by Ministry of Department Higher of Research and Technology Indonesia (KemenristekDIKTI) in term of Basic Research Grant.

References

[1] Singal S 2007 Renew. Sustain. Energy Rev. 11 1607–15.
[2] Singh B R and Singh O 2012 Fossil fuel and Env. Global Trends of Fossil Fuel Reserves and Climate Change in the 21st Century ed Khan S chapter 8 pp 167-192
[3] Steinberg M 1999 Int. J. Hydrogen Energy 24 771–7.
[4] Jacobson M Z and Delucchi M A 2011 Energy Policy 39 1154–69.
[5] Salameh M G 2003 Appl. Energy 75 33–42.
[6] Rabac K and Verstraete W 2005 Trends Biotechnol. 23 291–8.
[7] Logan B E and Regan J M 2006 Trends Microbiol. 14 512–8.
[8] Champavert J, Mardiana U and C. Innocent C 2017 Current Org. Chem. 21 1702–12.
[9] Mardiana U, Innocent C, Cretin M, Buchari, Gandasasmita S 2016 IOP conferences series: material science and engineering 107 2-14.
[10] Mardiana U, Innocent C, Cretin M, Buchari, Setiyanto H, Nurpalah R and Kusmiati M 2019 Russ. J. Electrochem. 55 78–87.
[11] Mardiana U, Innocent C, Jarrar H, Cretin M, Buchari Gandasasmita S 2015 Int. J. Electrochem.Sci 10 8886–98.
[12] Jarrar H, Rolland M, Downard A J, and Cretin M 2011 Sens. Lett. 9 2368–70.
[13] Wei J, Liang P and Huang X 2011 Bioresour. Technol. 102 9335–44.
[14] Gunawardena A, Fernando S and To F 2008 Int J. Mol. Sci. 9 1893–1907.
[15] Schröder U 2007 Phys. Chem. 9 2619–29.
[16] Yi H, Nevin K P, Kim B C, Franks A E, Klimes A, Tender L M, Lovely D R 2009 Biosens. Bioelectron. 24 3498–503.
[17] Pandit S, Khilar S, Roy S, Pradhan D and Das D 2014 Bioresour. Technol. 166 451–7.
[18] Malvankar N S and Lovley D R 2014 Curr. Opin. Biotechnol. 27 88–95.
[19] Mardiana U, Innocent C, Cretin M 2020 AIP Conference Proceedings 2229 1-9.
[20] Oh S-E and Logan B E 2006 Appl. Microbiol. Biotechnol. 70 162–9.