Performance Of Sediment Microbial Fuel Cells In Generating Electricity Using Fish Wastewater And Shrimp Wastewater As A Nutrient And Their Effect On Waste Quality

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Abstract.
Sediment Microbial Fuel Cell (MFC) is a technology that can convert chemical energy into electrical energy through the process of nutrient degradation by microbes. Sediment taken from the bottom of shrimp ponds was added as a source of microbes, while fish and shrimp wastewater were used as a source of nutrients for microbes. This study aims to measure the performance of the SMFC system on fish effluent and shrimp effluent to produce bio-electricity while reducing the waste load. The research method was experimental laboratories. The treatment given was the different types of electrodes, namely zinc-copper and aluminum-copper. In addition, 0.2 M $KMnO_4$ electrolyte solution was used. This study consisted of four stages: the manufacture of nutrients from fish and shrimp wastewater, the manufacture of a dual chamber MFC bioreactor, the measurement of electrical values, and the analysis of waste quality. Experiments were carried out for 30 days by measuring electricity every 24 hours. The average value of electricity generated in the nutrients of fish wastewater with Zn/Cu electrodes was 0.705 V and Al/Cu was 0.472 V. Meanwhile, the average value of electricity in shrimp wastewater nutrients with Zn/Cu electrodes was 0.630 V and Al/Cu was 0.625 V. The number of colonies after adding sediment in the shrimp wastewater sample were 8.9 x 10^6 CFU/mL, the fish wastewater sample was 9.5 x 10^6 CFU/mL. It indicates the presence of microorganisms that play a role in the SMFC system.

Keywords: *Electrical energy, fish wastewater, microbial fuel cell, and shrimp wastewater*

I. INTRODUCTION

One of the basic needs of human life is the availability of electrical energy. The increase in human growth has led to an increase in the need for electrical energy, the supply of electrical energy, and the supply of electrical energy to date is decreasing. In 2019 the availability of petroleum is the main energy source, which is estimated to be only 31% of the world's total oil [1]. This energy crisis urges to development of alternative energy sources to replace fossil fuels. The choice of the form of energy itself can depend on the amount of energy and environmental conditions. Sediment Microbial Fuel Cell (MFC) is one of the alternative technologies developed as a backup energy because this technology converts chemical energy into electrical energy through reactions using microorganisms present in the sediment. MFC represents a variety of green energy conversion technologies that combine wastewater and energy discovery from the metabolic processes of microorganisms [2].Fish and shrimp waste is a type of waste that causes many problems for the environment. One of them is in the Mawasangka District, Central Buton Regency. This area is designated as a fishery and shrimp aquaculture sector area because of the large coastal area and the availability of sufficient water resources. Waste from fisheries and shrimp ponds is disposed of directly by the community into public waters without first causing environmental pollution, such as bad smells and heavy pollution in water if the disposal is not handled properly. Improper handling of waste in the environment results in a high content of wastewater, such as oil, fish flakes, fish scales, shrimp heads, and leftover shrimp feed carried along the waste stream.

This waste can be utilized in the SMFC system to avoid environmental pollution. According to Riyanto et al. (2012) reported that the MFC system using shrimp pond waste can be applied to generate electrical energy of 0.39 V [3]. Ibrahim et al. (2017) have also shown the potential for using fish to generate electricity using electrode variants. High electricity is generated by using a 0.34 V aluminum-carbon electrode [4]. Therefore, fish and shrimp wastewater can be utilized in an MFC system to generate electricity.Organic compounds found in fish and shrimp waste are potential that can be used in MFC systems. The involvement of electricity-producing (electrogenic) microbes is an important part of the MFC system in breaking down organic components in waste into electrical energy. These electricity-producing microorganisms include *Geobacter sp*, *Shewanella sp*, and *Escherichia coli* which are commonly found in sediments or mud bottoms [5].In general, the working principle of MFC is that the waste substrate is oxidized by microbes, then produces electrons and protons at the anode. Electrons are transferred through an external circuit, whereas protons are diffused through a proton transfer membrane or salt bridge to the cathode. Protons and electrons at the cathode will then react with oxygen to produce air. These ions produce an electric potential difference so that energy can be generated [2]. Some results from previous studies, the electrical energy produced tends to be smaller. Therefore, through this research, it is necessary to make efforts to increase the production of electrons and protons by treating various types of electrodes. In addition, the shrimp pond sediment as a source of microbes and fish and shrimp wastewater as a substrate used to generate electrical energy. The purpose of this study was to determine the potential of fish and shrimp waste as an electricity-producing SMFC nutrient and to determine the effect of different electrodes and observations on SMFC performance.

II. METHODS

Materials and Equipment

The microbes used in this study were sourced from shrimp pond sediments with fish wastewater and shrimp wastewater as substrates. The chemicals needed are ethanol, potassium permanganate ($KMnO_4$), sodium hydroxide (NaOH), hydrochloric acid (HCl), zinc plate electrode, aluminum plate electrode, copper plate electrode, salt bridge; potassium chloride (KCl) and agar, distilled water.Research tools used in this study were hotplate stirrer, analytical balance, thermometer, pH meter, digital multimeter, connecting cable, copper wire, crocodile clip, electric stove, blender, a set of MFC bioreactors and glassware others available in the laboratory.

Research procedure

There were four stages in this research procedure: the manufacture of artificial wastewater, the manufacture of MFC bioreactors, measuring the electrical value, and analyze the waste quality

Manufacture of Artificial Wastewater

The first stage was the manufacture of artificial wastewater which refers to Safitri et al., (2020) by treating the use of solid waste and water with a ratio of 1:2. Each fish and shrimp waste was mashed using a blender then added water and boiled for 10 minutes. After boiling, it is filtered and the filtrate is taken. The filtrate called fish wastewater dan shrimp wastewater then used as a substrate in the MFC system [6]

Manufacturing of SMFC Bioreactor

The bioreactor used was a dual chamber bioreactor model, which is a model of two separate compartments. The cathode compartment was filled with 0.2 M $KMnO_4$ electrolyte solution, and the anode compartment was filled with 400 ml of sediment and 250 ml of wastewater. The two were then connected via a KCl salt bridge [7]. The type of electrode used were a combination of Zn/Cu plate electrodes and Al/Cu plate electrodes. Each electrode in the chamber was connected using a copper wire to the multimeter

Electrical value measurement

The measurement of waste electrical energy referring to Holmes et al., (2004). The performance of the MFC system was measured using a digital multimeter every 24 hours during 30 day through a variable current (I) and a variable voltage (V). Furthermore, the value of power density or power per unit area (mW/m^2) can be determined through these two variables through the formula [8]

$$Power\ density\ \left(mWm^{-2}\right) = \frac{I \times V}{A}$$

where I is the current (mA); V is the voltage (V); and A is the surface area (m^2).

Waste Quality Analysis

The last stage is to analyze the quality of the wastewater which consists of the analysis of temperature, pH, chemical oxygen demand (COD), and Biological Oxygen Demand (BOD). COD and BOD evaluation was carried out before and after the addition of microorganisms to the mud sediment

III. RESULT AND DISCUSSION

Artificial Wastewater

Fish waste samples were taken from fishery activities in the form of bones, fish heads, fins, skin, scales, and entrails. Meanwhile, samples of shrimp waste were in the form of shells, legs, and tails of shrimp. The waste samples were then prepared to be made as fish wastewater and shrimp wastewater. Treatment of the use of solid waste and water is carried out with a ratio of 1:2. Each fish and shrimp waste was mashed using a blender then added with water and boiled for 10 minutes. The purpose of the boiling process is to dissolve the organic and inorganic compounds contained in the waste. After boiling, it is filtered and the filtrate is taken. The artificial results of this wastewater were used by microbes in breaking down organic compounds by utilizing dissolved oxygen in the water.

SMFC Bioreactor

The Sediment Microbial Fuel Cell system used in this study consists of two compartments, namely anode, and cathode with separate models. Each room has been installed with various electrodes of copper plate (Cu), aluminum plate (Al), and zinc plate (Zn) with a size of 10 x 4 cm^2. The anode and cathode compartments are separated by a KCl salt bridge.

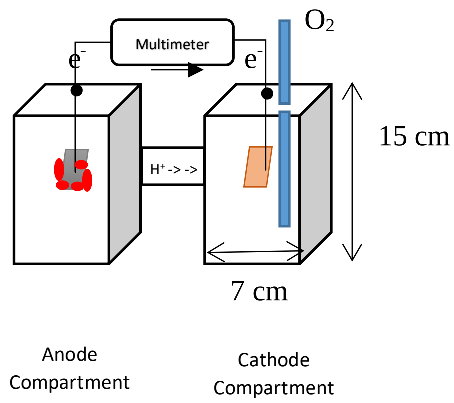


Fig 1. Dual chamber MFC circuit model

The substrate used is fish and shrimp wastewater obtained from market activities. Then given the addition of sediment by utilizing the microorganisms in it. Microbes then break down organic compounds contained in fish and shrimp waste into a source of energy, water, and carbon dioxide [9]. The substrate and microorganisms were incubated for 24 hours in the anode room so that the microbes could adapt to the new environment. During incubation, bacteria in the anode room metabolize and produce energy in the form of CO_2, protons (H^+), and electrons. Electrons generated from metabolic processes are then transferred to electrodes through the outer plasma membrane of microbes called cytochromes. The electrons are then released from the anode and then transferred to the cathode via an external circuit. The protons produced from the metabolic process are transferred from the anode to the cathode via a salt bridge. KCl salt is the type of salt bridge used. The use of KCl salt facilitates the diffusion of protons (H^+) because the radius of K^+ is larger than the radius of H^+. Protons and electrons generated from the anode are used to reduce Mn^{7+} ions to Mn^{4+} at the cathode when using $KMnO_4$ electrolyte solution [10]. The electrons and protons that flow from the anode to the cathode are then converted into electrical energy in the form of voltage and current by the SMFC bioreactor.

Electrical value measurement results

The results of measuring the electrical value of the fish and shrimp wastewater substrate every 24 hours during 30 day can be seen in the following graph.

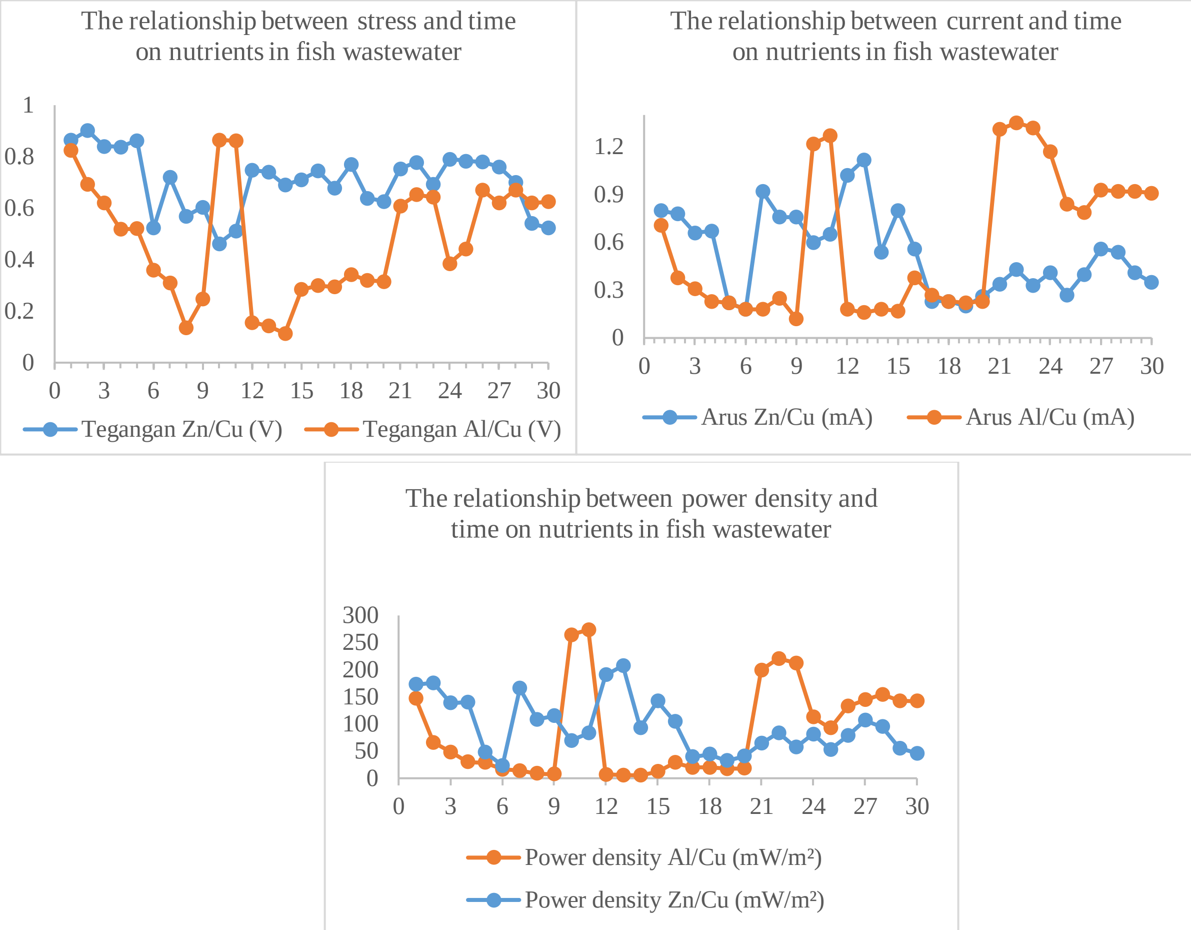
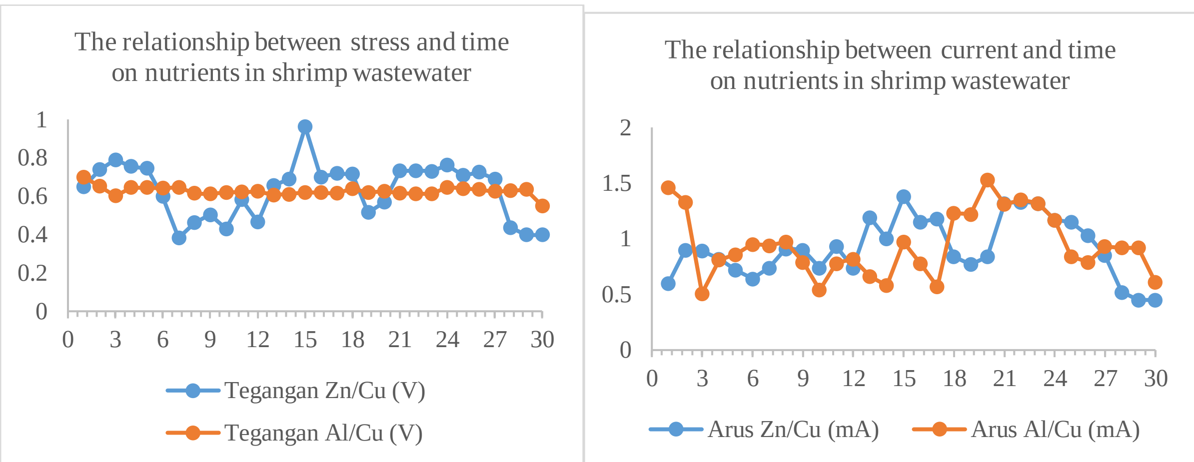


Fig 2. Graph of the relationship between SMFC operating time on voltage, current, and power density with the addition of 0.2 M $KMnO_4$ electrolyte solution on fish wastewater substrate

Figure 2 shows the relationship between the operating time of the SMFC and the electrical value of the fish wastewater substrate. The value of the electricity produced in all types of electrode treatments has a fluctuating values. The SMFC system on fish wastewater substrate with Zn/Cu electrode produced the highest value with a voltage of 0.902 V, a current of 1.12 mA, and a power density of 207.48 mW/m². The lowest values obtained are voltage 0.463 V, current 0.18 mA, and power density 23.53 mW/m². The Al/Cu electrode produces the highest value with a voltage of 0.866 V, a current of 1.35 mA, and a power density of 237.68 mW/m². The lowest values obtained are voltage 0.114 V, current 0.12 mA, and power density 5.13 mW/m². The results of the average electrical value from all observations showed the highest results in the fish waste substrate SMFC system with Zn/Cu electrodes (0.705 V and 0.533 mA) followed by Al/Cu (0.472 V and 0.585 mA). The results of the measurement of the electrical value of the fish and shrimp wastewater substrate can be seen in the following graph.



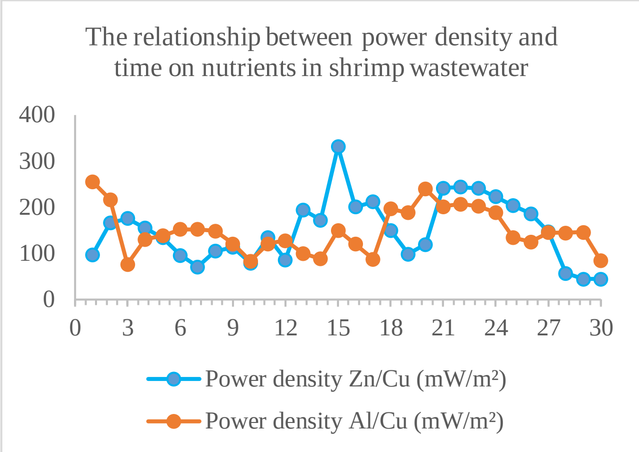


Fig 3. Graph of the relationship between MFC operating time on voltage, current, and power density with the addition of 0.2 M $KMnO_4$ electrolyte solution on shrimp wastewater substrate

Figure 3 shows the relationship between the operating time of the SMFC and the electrical value of the shrimp wastewater substrate. The SMFC system on shrimp wastewater substrate with Zn/Cu electrode produced the highest value with a voltage of 0.961 V, a current of 1.38 mA, and a power density of 331.55 mW/m^2. The lowest values obtained are voltage 0.382 V, current 0.45 mA, and power density 44.75 mW/m^2. The Al/Cu electrode produces the highest value with a voltage of 0.700 V, a current of 1.53 mA, and a power density of 149.17 mW/m^2. The lowest value obtained is a voltage of 0.550 V, a current of 0.51 mA, and a power density of 76.75 mW/m^2. From the overall observations, the highest average value of electricity was in the shrimp waste substrate SMFC system with Zn/Cu electrodes (0.630 V and 0.915 mA) followed by Al/Cu (0.625 V and 0.94 mA).The electrical energy measured in this study comes from the ability of MFCs to change the organic content of waste through microbial metabolic activity [11]. The content of organic matter present in fish and shrimp wastewater was degraded to produce electrons that can bind to oxygen, nitrate, nitrite, and sulfate known as Terminal Electron Acceptor which diffuses through the cell. The electrons were captured by the anode and protons were captured by the cathode which causes a potential difference to generate bioelectricity [12].According to Ibrahim et al. (2014) when microbes carry out metabolic processes by breaking down simple substrates, at that time there may also be an increase in electrical energy measured by a multimeter [9]. While the decrease in electricity that occurs was probably caused by microbes that are still adapted to break down more complex substrates into simpler ones. The high and low value of the electrical energy produced shows the dynamics of the system because it is driven by living things.

Research Safitri et al. (2020) also experienced the same thing. According to him, the fluctuating increase and decrease in electricity were caused by the competitive interaction between bacteria in the medium in breaking down the substrate. According to Ibrahim et al. (2017), the increase and decrease in the generated electricity were also related to the number of free electrons produced by microbes [7]. In addition, as the day goes on, the electrical value decreases at the end of the measurement because the nutrients in the substrate decrease due to the longer bacterial metabolic activity, so the electrons and protons produced are reduced, which can affect the decrease in electrical energy.Based on the average value of electricity generated on fish waste substrates in all types of electrode treatments, SMFC with the combination treatment of zinc-copper electrodes was the treatment that produces the highest average electricity compared to the combination of aluminum-copper electrodes. The value of electricity generated in this research study tends to increase. The difference in reactivity properties and the value of the standard potential of each type of electrode used causes the power density value to be quite high. Aluminum is a group IIIA element that has a standard potential value of -1.66. Zinc is an element of group IIB with a standard potential value of -0.76, while Copper is an element of group IB with a standard potential value of 0.34. Based on the difference in standard potential values, aluminum and zinc have higher reactivity than copper, so that aluminum and zinc are on the left of the voltaic series. The further to the left of the position of a metal in the voltaic series, the more reactive the metal is, so it was easier to oxidize in releasing electrons.

Therefore, the use of zinc and aluminum electrodes was placed in the anode compartment and copper electrodes in the cathode compartment. The reactivity of each electrode greatly affects the microbial activity in transferring electrons to the electrodes and affects the electrical energy produced.Based on observations of the results of previous studies regarding the SMFC system, the results of measuring the value of voltage and current in this study tend to increase. Research conducted by Kalzoum et al. (2018) by utilizing tofu wastewater as an electricity producer by using a dual-chamber model zinc-copper combination electrode provides the highest voltage and current values of 0.78 V and 0.29 mA [7]. While Putra et al. (2018) also used a combination of zinc-copper electrodes in utilizing wastewater resulting in the highest voltage value of 0.920 mA [13]. The nutrients contained in the substrate become one of the important factors in producing efficient electricity. The nutrients used range from simple organic materials to complex mixtures such as in wastewater [14]. In another study that has the same nutrients as this study, Ibrahim et al. (2017) analyzed the performance of MFC based on differences in electrodes in the wastewater of the fishing industry. The highest electricity value was obtained at the 0.34 V aluminum-carbon graphite combination electrode [4]. Riyanto et al. (2012) have also utilized shrimp pond sediment in the MFC system to produce the largest electric current production of 161.99 mA/m^2 and a voltage of 0.39 V [3]. Safitri et al. (2020) has also reported the performance of MFCs with the addition of sediment as microbes and fish fillet waste as nutrients with electricity production of 0.55 V and 0.217 mA [6].

Waste Quality Analysis

Analysis of the quality of wastewater consisting of analysis of temperature, pH, chemical oxygen demand (COD), Biological Oxygen Demand (BOD), and the calculation of the number of bacteria. The average value of pH during the measurement of electrical energy in the fish waste substrate was 5.0 and in shrimp wastewater was 5.3. The average temperature produced in both was 30 ^oC. COD evaluation was carried out using a spectrophotometer testing method and BOD evaluation was carried out using a BOD meter. The evaluation was carried out before and after the addition of microorganisms to the mud sediment.

Table 1. COD and BOD values in samples

Sample	Chemical Oxygen Demand (COD) (mg/l)	Biological Oxygen Demand (BOD) (mg/l)
Fish Wastewater Nutrients	575.10	210.70
Shrimp Wastewater Nutrients	680.60	239.20
Fish Wastewater Nutrients + sediment	980.90	310
Shrimp Wastewater Nutrients + sediment	1180	420

These results indicate that the addition of microorganisms present in the sludge does not provide significant results on the quality of the wastewater. This could be due to the improper composition of the sediment and nutrients in the wastewater. But besides that, this research can be able to decompose organic compounds contained in the waste as evidenced by the presence of large currents and voltages.The number of bacteria was measured by the TPC (Total Plate Count) method. This method is done by growing microorganisms on nutrient agar media. So that after incubation for 24 hours colonies were growing on the surface of the media that could be counted directly. The average number of colonies contained in the shrimp waste sample was 8.9 x 106 CFU/ml and the fish waste sample was 9.5 x 106 CFU/ml. These results indicate the presence of microorganisms that play a role in the SMFC bioreactor system in producing electrical energy.

IV. CONCLUSION

From the results of the measurement of the electrical value, it shows that the best electrode that is able to produce the highest average on fish waste and shrimp liquid waste substrates is a combination of zinc-copper electrodes with a voltage of 0.705 V and 0.630 V and a current of 0.53 mA and 0.91 mA, respectively. The average value of pH during the measurement of electrical energy in fish wastewater substrate is 5.0 and in shrimp wastewater is 5.3. The average temperature produced in both is 30 ^oC. Evaluation of COD and BOD did not give significant results on the quality of the waste. Therefore, suggestions for further research are to be able to study further the composition of sediment and nutrients used in wastewater.

V. ACKNOWLEDGMENTS

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REFERENCES

[1] [KESDM] Ministry of Energy and Mineral Resources, ***The strategic plan of the ministry of energy and mineral resources for 2020-2024***. Jakarta (ID): Ministry of Energy and Mineral Resources, 2020

[2] Nawaz, A. Hafeez, S. Z. Abbas, I. Haq, H. Mukhtar, & M. Rafatullah, A state of the art review on electron transfer mechanisms, characteristics, applications and recent advancements in microbial fuel cells technology. ***Green Chemistry Letters and Reviews***, 13(4), 2020, p. 365–381.

[3] Riyanto, A. Maddu, & Y. Firmansyah, Degradation of Organic Materials and Utilization of Electric Current in Traditional Shrimp Pond Sediments through SMFC***, Indonesian Journal of Fishery Products Processing***, 15(3), 2012, p.183-193

[4] Ibrahim, P. Suptijah, & Z. N. Adjani, Performance of Microbial Fuel Cell to Generate Bioelectricity Uses Different Kinds of Electrode in the Fish Processing Wastewater, ***Indonesian Journal of Fishery Products Processing***, 20(2), 2017, p. 296.

[5] R. Januarita, & A. Azizah, Preparation of wastewater and electricity. Artikel Ilmiah Universitas Diponegoro, ***e-Journal,*** 2016, hlm 1-6

[6] U. N. Safitri, A. D. Anggo, & A. S. Fahmi, Performance of Sediment Microbial Fuel Cell to Generate Electricity with Nutrients of Fish Filet Industrial Waste. ***Journal of Fisheries Science and Technology*** 2(1), 2020, p.20-28

[7] N. Kalzoum, M. R. Kirom, &, A. Qurthobi, Utilization of Tofu Wastewater as a Generator of Electrical Energy Using the MFC System, ***e-Proceeding of Engineering***, 5(3), 2018, p. 5724

[8] D. E. Holmes, D. R., O, Neil, R. A., Reimers, C. E., Tender, L. R., & Lovley, D. R, Microbial Communities Associated with Electrodes Harvesting Electricity from a Variety of Aquatic Sediments, ***Microbial Ecology***, 48(2), 2004, pp. 178–190

[9] B. Ibrahim, P. Suptijah, & S. Rosmalawati, Performance of the Microbial Fuel Cell System Series as a Bioelectric Generator from Fishery Liquid Waste, ***Journal of Indonesian Fishery Products Processing***,17(1), 2014

[10] Muftiana, L. Suyati, D.S. Widodo, The Effect of $KMnO_4$ and $K_3[Fe(CN)_6]$ Concentrations on Electrical Production in Fuel Cell Microbial System with Lactobacillus bulgaricus Bacteria in a Tofu Whey Substart. ***Journal of Science Chemistry and Applications,*** 2018, 21(1), p. 49-53

[11] D. Pant, G. Van Bogaert, L. Diels, & K. Vanbroekhoven, A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. ***Bioresource Technology,*** *101*(6), 2010, p.1533–1543.

[12] B.E. Logan, ***Microbial Fuel Cells***, United States of America: A John Wiley & Sons Inc, 2008

[13] F. A. Putra, Analysis of Electrical Energy Production from Microbial Fuel Cells with Wastewater Treatment, ***e-proceeding of engineering,*** 5(3), 2018, p.5610-517

[14] E. Kristin, Electrical Energy Production through Microbial Fuel Cell using Tempe Industrial Waste, ***Thesis.*** Faculty of Engineering, University of Indonesia, Jakarta, 2012, 63 p.