Utilization of Montmorillonite-Modified Earthenware from Bentonite-Ca as a Microbial Fuel Cell (MFC) Membrane Based on Tempe Liquid Waste as a Substrate

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Abstract

Modifications of the Microbial Fuel Cell (MFC) membrane need to be carried out to increase its electric potential energy. This research aims to determine the effect of montmorillonite from bentonite-Ca as a composite in modified earthenware (GT), which is then used as a membrane of the MFC-based on tempe wastewater as substrate. The results obtained were compared to MFC that used pure earthenware membrane (GM). The ratio of bentonite-Ca and clay in GT was 50:50, while GM used 100% of clay. Characterizations of GT dan GM were performed using FTIR, XRD, and SAA. MFC testing was carried out for 24 hours, where every 2 hours, measurements of potential difference (V), current (A), and power density (W/cm²) were carried out. FTIR and XRD data showed an increase in montmorillonite content in GT, while SAA data showed a decrease in pore volume in GT. The decrease in pore volume GT occurs due to an increase in the number of trivalent cations (Al³⁺, Fe³⁺) and bivalent (Mg²⁺). These cations help transfer protons from the anode to the cathode, which causes a decrease in the potential difference and an increase in the current and the MFC-GT power density. The average difference between the decrease in potential difference from MFC-GM to MFC-GT is 0.043 V, while the increase in current is 0.022 mA, and the increase in power density is 0.163 mW/cm².

1. Introduction

Microbial Fuel Cell (MFC) is an alternative energy system that utilizes organic matter with microorganisms to produce electrical energy [1]. Various studies have been conducted to improve the performance of MFC. The research was conducted on the electrode, reactor design, type of bacteria, membrane, and substrate used [2].

For the type of membrane used, one that has been successfully developed and produced on an industrial scale is the Proton Exchange Membrane (PEM) such as Nafion 117, Nafion 424, and Nafion 551WX. However, water in the anode vessel makes PEM use less efficient and easily damaged because water can directly deliver protons to the cathode, resulting in a reduction in electrical energy. Besides, the costs required for the production of this membrane are relatively expensive [3].

To overcome this problem, alternative MFC membranes that can be used are clay membranes, such as ceramics or earthenware. Winfield et al. [4] state that ceramics are more stable in proton transfer and provide a safer environment for microorganisms’ metabolism. Ceramics in MFC technology can be used as waste containers, ion exchange media, and MFC electrodes.

In another research, Winfield et al. [5] using earthenware as an ion exchange media. The waste used is synthetic waste in a single chamber reactor. The results obtained indicate a high-power density of 3660 mW/m². The weakness of using pure earthenware in this study is its relatively short operating time, which is only six weeks.
The use of pottery as an MFC membrane has also been carried out by Andika and Sudarlin [6], which uses tempe liquid waste as a substrate. The results obtained show a reasonably high-power density of 2197.343 mW/m². The disadvantage is the same as in the study of Winfield et al. [4, 5], in which the relatively short operational time at which a decrease in power density occurs at the 14th hour [6].

Different things are found if the earthenware used is montmorillonite ceramics. Research of Ghadge et al. [7], which uses montmorillonite as a membrane in the dual-chamber MFC, can achieve an operating time of up to 8 weeks with a higher power density of 7550 mW/m². In other studies, the more montmorillonite content used, the higher the density of power produced [8]. However, the use of montmorillonite is inefficient for the MFC system because the operating temperature is quite high, which is 32°C higher than pure earthenware, whose operating temperature is only 24°C. If it reaches a high temperature, waste in the MFC system must be recycled because microorganisms cannot last long.

The weaknesses of pure clay earthenware and pure montmorillonite ceramics can be overcome using a composite method between pure earthenware and montmorillonite. Therefore, the earthenware produced is montmorillonite modified earthenware. Uddin [9] reported that clay could be compiled with montmorillonite to nano size. Similar research results were also published by Li and Peng [10], who made composites from MoSe₂ soil types with montmorillonite for the decomposition of rhodamine dye waste. These two studies show that pure clay and montmorillonite can produce stable earthenware composites in the moist environment of the MFC system.

Related to the waste that can be used, the tempe industry is one source of waste in the form of tempe liquid waste. Water is widely used in the process of soaking and boiling soybeans. As a result, the contents of carbohydrates, proteins, fats, and acids will be dissolved in the wastewater. The wastewater is generally disposed of in rivers or waterways. Waste in waterways causes environmental problems such as foul odor and reduction of oxygen levels in sewer water.

The utilization of tempe liquid waste as a substrate in the MFC system has been conducted by Luthfiyah and Artsanti [11] using a dual-chamber MFC with a cation exchanger in the form of a salt bridge and graphite carbon electrodes. Tempe liquid waste substrate in the system is capable of producing a power density of 6296 mW/m² in control waste, 5719 mW/m² in waste with 2% glucose addition, and 4% glucose obtained the highest value of 5856 mW/m². The COD value in the controlled waste decreased by 1.52%, in the substrate with the addition of glucose 2% and 4% decreased by 9.76% and 9.64%, respectively.

The ability of earthenware as an ion exchange media based on the results of research by Winfield et al. [5] and its chance to be modified as a composite with montmorillonite based on the results of Ghadge et al. [7] and Li and Peng [10] as well as increasing the MFC power density using tempe liquid waste and decreasing the COD content of waste based on the results of the Luthfiyah and Artsanti [11] can be combined to improve the efficiency of MFC as the objective of this study. In this study, the membrane used is a composite in the form of montmorillonite modified earthenware (GT) and compared with pure earthenware from brown clay (GM). Montmorillonite used is montmorillonite as the main mineral in Ca-bentonite. The parameters studied in this study are the effectiveness of proton transfer between GT and GM in the form of potential difference (V), current (A), and power density (mW/m²).

2. Methodology

The research process includes designing the device (MFC chamber), manufacturing earthenware, electrode preparation, substrate preparation, and running the MFC. The details of the tools and materials needed and the stages of the research are detailed as follows:

2.1. Tools and Materials

The instrument used in this study is the dual-chamber MFC reactor with anode and cathode chamber separated by a membrane in the form of earthenware, as presented in Figure 1. Other tools used include glassware, volumetric pipettes, cuvettes, claws, cables, waste containers, sterile plastic bottles, turntables, refrigerators, Aditeg A-830 digital multimeters, Shimadzu Prestige-21 Fourier Transform–Infra Red (FTIR), Shimadzu 6000–Elmer X-Ray Diffractometer (XRD), and Quantachrome Surface Area Analyzer (SAA).

![Figure 1. Schematic design of a double chamber MFC using an earthenware membrane](image)

The material used in this research was tempe liquid waste from Hj Tukiran Tempe Industry JL. Pandean Yogyakarta, brown clay loam from Kasongan Bantul, bentonite–Ca from Pacitan, graphite carbon rod size 29.5 cm², 1 M HCl solution (Merck), practical grade (PA), 1 M NaOH solution (Merck) p.a, distilled water, alcohol 70% technical grade, and KMnO₄ 0.1 M Merck solution p.a.

2.2. Manufacturing Earthenware

Earthenware was made from brown clay using a throwing technique. Modified earthenware (GT) was added by bentonite–Ca at a ratio of 50:50, while pure earthenware (GM) used 100% clay. Earthenware was in
the form of 10 x 10 x 1 cm³ plates, and two plates each were made. One plate was used for MFC membranes, and the rest was used for XRD, FTIR, and SAA characterization.

2.3. Electrode Preparation

The electrodes used were graphite carbon bars with a surface area of 29.5 cm². Before use, the electrodes were first cleaned and activated. Graphite sticks were immersed in 1 M HCl solution and 1 M NaOH each for 24 hours. After that, the electrodes were stored in containers containing distilled water until they were used.

2.4. Waste Substrate Preparation

Tempe liquid waste was obtained directly from the Hj. Tukiran Tempe Industrial waste Jl. Pandean Yogyakarta. Waste was put into sterile 1 L plastic bottles. Previously, plastic bottles were sterilized using 70% alcohol. Waste was taken by dipping a sterile plastic bottle directly into a waste collection container. Before being analyzed, the waste sample was stored in a refrigerator at 4 °C.

2.5. Running MFC

Anode vessel was filled with tempe liquid waste substrate as much as 900 mL. Meanwhile, the cathode vessel was filled with 900 mL of KMnO₄ 0.1 M electrolyte solution. The two graphite carbon electrodes were connected to a digital multimeter. MFC reactors run for 24 hours. Measurement of current and the potential difference was conducted every 2 hours using a digital multimeter.

3. Results and Discussion

3.1. Earthenware Characterization

The results of X-Ray Diffraction (XRD) characterization are presented in Figure 2 in the form of pure earthenware (GM) diffractogram and modified earthenware (GT). The results show a value of 2θ at 26.9° (d = 3.31Å), following JCPDS standards No.13-0259, i.e.,

\[ d = 3.34 Å \]

is a montmorillonite mineral. The increase in basal spacing from 2θ = 26.6° in GM to 2θ = 26.9° in GT indicates an increase in montmorillonite content. This increase is linear, with an increase in Ca-bentonite quartz intensity due to an increase in the number of SI-O-Si bonds [12].

The increased montmorillonite presence in GT is also shown by 2θ = 5.2° (d = 16.85 Å), according to JCPDS No.13-0135, i.e.,

\[ d_{001} = 15.00 Å \]

is a montmorillonite mineral. Other minerals are indicated by peaks of 2θ = 22.2° (d = 4.01 Å), according to JCPDS No.11-0695, i.e.,

\[ d_{001} = 4.05 Å \]

which is a cristobalite mineral [13]. High intensity indicates higher levels of cristobalite in GT.

Peak 2θ = 20.3° (d = 4.37 Å) in accordance with JCPDS No. 05-0490, i.e.,

\[ d_{001} = 4.26 Å \]

is a quartz mineral. This mineral is a mineral contained in GT but not in GM. Other minerals found in both earthenware are illit which is shown at three different peaks, i.e., 2θ = 23.9°, 27.9°, and 36.6° for GT, and 2θ = 24.5°, 27.8°, and 35.6° for GM. The data is in accordance with JCPDS No.24-0495 and JCPDS No.26-0911. The difference in the value of 2θ between GT and GM is due to differences in the metamorphic epizone mineral illit properties in both [14].

The high content of montmorillonite and cristobalite in GT can enhance the earthenware cation exchangeability as an MFC membrane [15]. The increase in montmorillonite content was confirmed by FTIR characterization, as presented in Figure 3. Increased absorption intensity at 1056.9 cm⁻¹ indicates an increase in montmorillonite intensity in GT. The absorption and absorption of 1064.7 cm⁻¹ in GM are the buckling vibrations of Si-O. The absorption of Si-O-Si buckling strengthens the presence of Si-O groups at 470.6 cm⁻¹ [16]. The sharper absorption of GT shows that the Si-O-Si environment is increasingly homogeneous, supported by a peak shift from 1064.7 cm⁻¹ in GM and to 1056.9 cm⁻¹ in GT [12].

![Figure 2. XRD diffractogram of pure earthenware (GM) and modified earthenware (GT)](image)

Figure 3. FTIR spectra of pure earthenware (GM) and modified earthenware (GT)

The absorption at 3749.6 and 3448.7 cm⁻¹ shows the stretching vibrations of OH (hydroxyl groups bound to Al in the octahedral layer Al-Al-OH or Mg-OH-Al). The absorption band reinforces this at wave number 1635.6 cm⁻¹, which shows the bending vibration of H-O-H water adsorbed on Ca-bentonite. Another group observed was Fe³⁺–OH–Mg at wave number 794.7 cm⁻¹ with low intensity. This data shows that modified earthenware (GT) is rich in trivalent ions (Al³⁺, Fe³⁺) and bivalent (Mg²⁺) [17].

Overall the FTIR characterization results showed an increase in montmorillonite content in GT. Also, there was absorption in the fingerprint area at 370 cm⁻¹, a characteristic of montmorillonite smectite dioctahedral
absorption. This absorption shows the high content of $\text{Al}^3+$ and $\text{Mg}^2+$ ions in GT [18].

The increase in montmorillonite material in GT is supported by an area based on SAA (Surface Area Analyzer) data, as presented in Table 1. The SAA results using the BET method both single point and multipoint indicate that the GT area is wider than the GM area. In contrast, GM pore volume is higher than the GT pore volume. This proves that the GT pore has been filled with trivalent cations ($\text{Al}^3+$, $\text{Fe}^{3+}$) and bivalent ($\text{Mg}^{2+}$), ready to be exchanged with MFC protons.

| Table 1. Area and pore volume of pure earthenware (GM) and modified earthenware (GT) |
|-----------------------------------------------|-------------------|-------------------|
| Parameter                     | Method       | Pure earthenware | Modified earthenware |
| Surface area (m$^2$/g)         | Single Point BET | 39.55            | 44.88              |
|                               | MultiPoint BET   | 40.69            | 46.34              |
| Pore volume (cm$^3$/g)         | BJH           | 0.173            | 0.165              |

3.2. Electric Potential

A comparison of the potential difference (V) and current (I) of MFC based on pure earthenware (MFC-GM) and modified earthenware (MFC-GT) is presented in Figures 4 and 5. The results obtained indicate that the potential difference in MFC-GM is higher than MFC-GT. This is due to the transfer of protons in the form of $\text{H}_2\text{O}^+$ from the anode to the cathode on MFC-GT aided by the exchange of montmorillonite cations.

The presence of trivalent cations ($\text{Al}^3+$, $\text{Fe}^{3+}$) and bivalent ($\text{Mg}^{2+}$) of montmorillonite, which is more in GT, helps the proton exchange; hence it diffuses faster to the cathode and does not accumulate at the anode. The cation exchange involves the interaction of OH groups in montmorillonite with $\text{H}_2\text{O}^+$ ions [19]. If the protons accumulate at the anode, the potential difference in the system will increase. Conversely, the rapid transfer of protons from the anode to the cathode will reduce the potential difference between the anode and the cathode [7]. This happens because a large number of protons in the cathode will accelerate the reduction of $\text{MnO}_4^-$ according to the reaction $\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$. As a result, the concentration of $\text{MnO}_4^-$ at the cathode gets smaller, so the potential at the cathode gets bigger according to the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{[\text{MnO}_2]}{[\text{MnO}_4^-]} \right]$$

The higher the cathode potential reduces the potential difference between the anode and the cathode [20]. The average difference in the decrease in potential difference from MFC-GM to MFC-GT in this study is 0.043 V.

The faster reduction reaction at the cathode causes the flow of electrons through the external circuit to accelerate; thus, the current system increases [7]. Another factor that increases currents is montmorillonite’s ability to prevent oxygen diffusion from the cathode to the anode making the reduction reaction at the cathode occurs more fully [8]. As presented in Figure 5, the current data shows that MFC-GT currents are higher than MFC-GM, with an average increase of 0.022 mA.

Related to operational time, which is 24 hours, the potential difference produced by MFC-GM and MFC-GT starts to be constant at the 6th hour, which is in the range of 1.2-1.3 V. This corresponds to the stationary phase of the bacteria [20]. This phase causes proton transfer from the anode to the static cathode so that there is no change in the potential difference. However, this research still needs to be continued until the time variations indicate the phase of bacterial death to decrease each MFC’s potential difference.

Meanwhile, the time variation on the current measurement shows stable data after the 14th hour, where the current MFC-GT is consistently higher than the current MFC-GM. Current before the 14th hour shows unstable data, although on average, MFC-GT current is still higher, at 0.044 mA compared to 0.022 mA. This shows that many factors influence the transfer of electrons from bacteria to the anode, external circuits,
the cathode, and finally, to the catholyte in the MFC system.

One of the influencing factors is the type of electrode used. The use of graphite bars as electrodes at the anode triggers the formation of *E. coli* biofilms on the surface of the graphite [21]. As a result, graphite electrodes will be covered by *E. coli* biofilms so that the electron transfer only comes from *E. coli* by direct transfer [22]. This condition prevents the transfer of electrons from other bacteria so that the strong current of the MFC system begins to stabilize at the 14th hour, where the MFC-GT current is higher than the MFC-GM current. That is, the current of the MFC system is only influenced by the type of membrane used. The current is no longer affected by the competition of bacterial electron transfer to the electrode, which causes the current to be inconsistent before the 14th hour. Bacteria that can grow in tempeh and tofu waste are *Escherichia coli*, *Saccharomyces fibuligera* [23], *Bacteroides*, *Bifidobacterium*, *Clostridium*, *Lactobacillus*, and *Streptococcus* [24].

The conclusions generated based on the above data show that the addition of bentonite rich in montmorillonite to GT can increase the cation in earthenware pores. The existence of these cations helps proton diffusion so that the transfer of protons from the anode to the cathode becomes faster. The proton transfer rate is proportional to the current produced. Thus, the use of a montmorillonite modified earthenware membrane from Ca-bentonite is quite efficient in increasing the MFC’s electrical potential. The increase is based on the power density (mW/cm²) produced, as presented in Figure 6, i.e., the average MFC-GT power is consistently higher, especially after the 14th hour with an average increase of 0.163 mW/cm². The power density curve pattern is the same as the current curve described earlier.

**Figure 6.** Comparison of power density in pure earthenware-based MFCs (MFC-GM) and modified earthenware (MFC-GT)

In addition to biofilm formation factors on graphite electrodes at the anode, current and power density as the data in Figures 5 and 6 are also influenced by the formation of MnO₂ layers on the surface of graphite electrodes at the cathode [25]. In MFC-GM, the formation of the MnO₂ layer is so significant that the surface of the graphite electrode at the cathode is closed. As a result, the current and power density dropped significantly at the 14th hour. Meanwhile, in the MFC-GT, the formation of the MnO₂ layer is still in the initiation stage so that the current and power density produced remains high. This research needs to be continued for a longer time variation, to show a decrease in current and power density on the MFC-GT.

Bacterial growth at the anode is also a factor that influences the current and power density of the MFC. Rapid bacterial growth will increase the density of bacteria at the anode, thereby inhibiting electron transfer to the anode [26]. As a result, electrons passing through the external circuit are reduced to decrease the MFC’s current and power density. These conditions occur in this study. Based on the data in Figures 5 and 6, there is a similar pattern of data due to the formation of the MnO₂ layer as previously described. Based on existing data patterns, GT’s use as an MFC membrane can reduce the influence of the MnO₂ layer and increase bacterial density so that current and power density remain high.

4. Conclusions

The results of FTIR and XRD characteristics showed an increase in montmorillonite content in GT. SAA characterization shows that the pore volume of GT is smaller because it is filled with trivalent cations (AP⁺, Fe³⁺) and bivalent (Mg²⁺). These cations help the transfer of protons from the anode to the cathode, which causes a decrease in the potential difference and an increase in the current and power density of the MFC-GT. The average difference between the decrease in potential difference from MFC-GM to MFC-GT is 0.043 V, while the increase in current is 0.022 mA, and the increase in power density is 0.163 mW/cm².

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