Membrane-less microbial fuel cell: effect of pH on the electricity generation powered by municipal food waste

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Abstract. Fossil fuels have supported the industrialization and economic growth of countries during the past centuries and it is clear that they cannot indefinitely sustain in a longer time. In this study, membrane-less microbial fuel cell (ML-MFC) with mediators-less and air cathode had potential solution to generate electricity power and at the same time could reduce the abundant of food waste (1.64 kg/daily, around 8 tonnes/year) which dumped in the landfill and it’s cost effective device. The ML-MFC operated electrochemically incorporate electrogenic bacteria (EB) acted as a biocatalyst in order to produce electricity. The performance and optimization performance of food waste was evaluated using one-factor-at-a-time (OFAT) method and it was focused to pH for power generation. To determine the generated electricity the polarization curve was used to evaluate the performance of ML-MFC. The chemical oxygen demand (COD) of food waste was studied. The optimization of pH condition in ML-MFC was ranging from 7 to 9. Results showed that pH 8 was the optimum pH for EB strain, Bacillus Subtilis, with the high voltage (807 mV), EB biomass (15.46 mg/L), and power density (373.3 mW/m²) generated. Clearly the pH environment condition affected the efficiency of ML-MFC performance. The increase in EB biomass also increased the voltage in the ML-MFC, proving that EB biomass and voltage were associated with growth.

1. Introduction

Currently there are more than 1.4 billion people around the world which lack access to electricity and about 85 % from the total are comes from the rural area. The world now mainly uses energy for their basic needs, thus it shows the electricity is the basic energy in our daily life. It is alarming that still many rural areas that lack access to electricity. Therefore solution for a cost effective and environment option to overcome the problem is needed. Most countries depends on non-renewable sources that renewable sources to gain energy. There are two major problems from using non-renewable sources. Firstly, non-renewable energy source will be depleted and also when it is happens, the price would sky rocketing. Secondly, the emission of greenhouse gas from the combustion of non-renewable energy (natural gas, coal, fossil fuel, etc) lead to the air pollution and global warming [1].
One of the options for the solution is alternative sources. The major alternative sources are renewable energy (hydrogen from biomass, solar power, wind energy, hydropower energy, etc.). Since year 1980 our country, Malaysia, already started their renewable energy strategy with Four Fuel Diversification Strategy that aims to balance the utilization of oil, coal, gas and hydro in the energy mix. While in year 2011, Renewable Energy Act and Feed-in-Tarrifs (FiT) was implemented to accelerate growth in the renewable energy (RE) sector. Then in year of 2018, The Malaysia Government targeted 20% RE usage increase in the energy mix by 2025 [2].

Membrane-less microbial fuel cell (ML-MFC) has been one of the considerations from alternative renewable bioenergy technology that seems promising over the time. First demonstrated by M. C. Potter, a professor of botany at the University of Durham in 1911 discovered that organisms could generate a voltage and delivered current electrical [3]. This discovery demonstrated using cell cultures of *Escherichia coli* and *Saccharomyces* using platinum electrodes. The studies show that while microorganisms degraded the organic compounds, there was electrical energy generated at the same time [4]. Substrates that were commonly used for ML-MFC are acetate, glucose, wastewater and other many substrates that have organic compound inside. Problem regarding abundant of food waste is very alarming according to Solid Waste And Public Cleansing Management Corporation (SWCorp), Malaysia had an average of 1.64 kg/day or around 8 tonnes/year per person abundant food waste were generated (Abd Razak, 2017) [5]. Which later on will be dumped to the landfill. Bigger landfill would be needed, thus expense would be higher. This is the main reason to considered using food waste to generate electricity, as one of the solution to reduce waste and alternative energy. There is lack of information on effect of pH in membrane-less microbial fuel cell thus the project was carried out.

2. Methodology

2.1 Sample characterization

Sample of food waste obtained from E-Idaman Sdn Bhd and the collected sample was kept at 4°C and thawed to room temperature (27 °C) before being used in the study. The characterization of the food waste was carried out using an elemental analyzer (PerkinElmer 2400 Series II), atomic absorption spectroscopy (AAS) (Shidmadzu AA-6650), and a COD digester (Checkit Direct, Lovibond) to analyze the macro-nutrients, micro-nutrients and organic compounds.

2.2 Analytical methods

2.2.1 COD analysis

In the 30 mL falcon tube a minimum of 1 g of dewatered sludge containing food waste has been dissolved into 9 mL of deionized water. The sample was then filtered with a syringe filter (MF — Millipore Millex GS syringe filter with 0.22 mm pore size). The COD vials containing premixed chemicals from kit were then added to a minimum of 2 mL of filtrate. A blank sample was prepared with 2 mL of deionized water applied to the vials. Digested the COD vials for 2 hrs at 150 °C. The contents of the vials cooled down to room temperature after 2 h. The COD Lovibond kit had been used to measure the COD.

2.2.2 Biomass of Bacillus Subtilis species

Determination of the biomass in ML-ML-MFC was monitored using cell dry weight or/and absorbance measurement reading. The methods for measurement of cell dry weight using centrifugation are label, weigh and note the weight of each pre-dried Eppendorf tube. Then, Pipette accurately (in duplicate), 1 or 1.5 mL samples into the tubes. Centrifuge in the ultracentrifuge at 6000 to 10,000 rpm for 5 mins. Decant out the supernatant. Repeat to increase the volume of culture used, and the bacterial cells that will be weighed. Remember to note the total volume used. Wash the pellet by adding in saline equivalent to the original volume of the sample used. Mix by vortexing and
continue to centrifuge with the same configuration as before. Decant the supernatant and dry the tubes in the oven at 90 °C for 20 hours or at 110 °C for 8 - 10 hours or until constant weight. A lower temperature is preferable to avoid cell decomposition by heat. After drying, remove the tubes from the oven and transfer to the desiccators containing drying agents such as phosphorus pentoxide or silica gel. Let the tubes cool to room temperature in dry air or sample will absorb moisture from the atmosphere, thus affecting the measurement of cell dry weight. Reweight all tubes that have been dried and cooled to room temperature. For determination of cell dry weight, cell dry weight, $X$

$$X = \frac{\text{weight of dried filter membrane or tube} + \text{cell (g)} - \text{Wt of dried filter membrane or tube (g)}}{\text{Sample volume (ml)}}$$  

(1)

2.3 Construction of ML-ML-MFC

An ML-MFC was built using cylindrical PVC reactors (diameter: 10 cm; height: 10 cm). The anode electrode was placed at bottom of the reactor and food waste (acted as membrane; separate the anode and cathode) was placed on to a depth of 6 cm, and the cathode was placed on top of it, with its upper surface exposed to air. The graphite felt electrodes (anode and cathode) had radiiuses, thicknesses, and surface areas. The chamber was then closed with a lid and set at room temperature (27°C). Generation of electricity was measured using a digital multimeter (UT33D, UNI-T, Hong Kong) that connected the probe to the anode and cathode wires in the ML-MFC.

2.4 Determination of power using polarization curve technique

The polarization curve is a conventional method to evaluate the performance of ML-MFC. The ML-MFC was connected to a multimeter to record cell voltage at different external resistance (47, 100, 220, 470 and 1000 Ω) and its power was determined based on Ohm’s law ($R = \frac{V}{I}, P = IV$). The polarization curve was plotted throughout the voltage and current measurements. The peak of the power curve was the maximum power of the ML-MFC.

2.5 Experimental design

2.5.1 Optimization of electricity generation using one-factor-at-one-time (OFAT)

One-factor-at-one-time (OFAT) is a method where experimenting while involving the testing of factors, or parameter, one at a time instead of multiple factors simultaneously.

2.5.2 Effect of pH

To evaluate the effect of pH variation. The pH of food waste ranged between 7 and 9 by changing the sodium hydroxide (NaOH 1 M) and hydrochloric acid (HCL 1 M) concentrations.

3. Result and Discussion

3.1 Preliminary study

3.1.1 Characteristics of food waste

The characteristics of the food waste were determined in order to check the usefulness of food waste acted as source of substrate (Table 1). It is necessary to know its basic physical and chemical properties such as contents of organic, trace element and inorganic compounds characteristics. To analyze characteristic of food waste by using AAS method and elemental analyzer.
Table 1. Compounds analyze in food waste

| Contents        | Compound      | Value  |
|-----------------|---------------|--------|
| Macronutrient (%)| Carbon (%)    | 30.02  |
| Nitrogen (%)    | 6.7           |
| Hydrogen (%)    | 3.7           |
| Micronutrient (mg/L) | Phosphorus (mg/L) | 43.3   |
| Potassium (mg/L) | 2.5           |
| Iron (mg/L)     | 1.4           |
| Trace element (mg/L) | Zinc         | 4.3    |
| Cadmium         | 0.1           |
| Manganese       | 1.8           |
| Nickel          | 15.6          |

From Table 1 shows that carbon has the highest value that will help with degradation of the cells. While, high trace elements like iron (Fe), zinc (Zn), and manganese (Mn) concentrations of these metals and heavy metals can be harmful to certain microbial species in some metabolic reactions linked to bacterial physiology by means of redox reactions. But small quantities of this entire compound are still needed as it is for building compound and proton energy generation in the bacterial cells [6].

3.2 ML-MFC performance

3.2.1 Effect of pH in ML-ML-MFC
One of the optimization conditions in ML-MFC is pH condition, using OFAT method. The pH inside the ML-MFC was controlled to the respective values pH of 7, 8, and 9. ML-MFC other condition remain constant throughout the experiment with moisture content was at 20 % (vol/wt), electrode distance at 3 cm, and temperature at 35 °C.

3.2.2 Effect of pH on EB Voltage generation and substrate degradation efficiency (SDE) in the ML-MFC
The daily open circuit voltage (OCV) was read with a digital multi-meter. Voltage was achieved because of difference in the potential of anode and cathode. Theoretically, ML-MFC could achieve maximum voltage generation at 1.2 V because the reduced biomolecules were minimum of -0.4 V at anode and redox potential of oxygen was 0.8 V at cathode [6]. Voltage generation in ML-MFC result as shown in Figure 1, initial time there was fluctuation until \( t = 12 \) h as there were significant drop and increased as the EB enter its lag phase. This happened as lag phase EB of the microbes were adjusted to new conditions. In lag phase, degradation also happened because breakdown of the cells bond. Thus generated protons were passed to the cathode, and electrons (currents) moved from anode to cathode [7]. The data shows around \( t = 18 \) and \( t = 24 \) most of the ML-MFC drop their voltages, which pH 7 and 8 showed the most significant dropped which were 207 mV and 212 mV, respectively.

While during \( t = 24 \) to \( t = 48 \) the pH 8 enter its log phase where rises the voltage up to 641 mV whereas other pH stays stagnant. And at its peak of each pH based on Figure 1, pH 7, 8, and 9 generate the highest voltage at \( t_{144} = 762 \) mV, \( t_{120} = 807 \) mV, and \( t_{120} = 755 \) mV respectively. The highest voltage generation was from ML-MFC with pH 8. Result on Table 2, shows that pH 8 had the highest SDE (69.42 %) and COD removal (495 mg/L), while the lowest is pH 9 (SDE = 16.27 %, COD removal =
116 mg/L). The COD analysis was done within 24 h as to monitor how the process of hydrolysis took place and the result shown in figure 2. The EB in adaptation phase thus could see the EB managed to break down the complex matter in dewatered sludge thus the simpler compound dissolve in the electrolyte in ML-MFC thus captured by the increment of COD value. Clearly after 18 h in ML-MFCs the COD value of each ML-MFC recorded a declination of COD value and the data of COD removal illustrate in Table 2. Overall the voltage generation reflected the COD removal by the bacteria with the more bacteria oxidized (consumed) compounds at the anode, the higher the anode-cathode potential would be [7].

![Figure 1. Voltage generation of all varied pH.](image1)

![Figure 2. COD profile ML-MFCs (pH 7, 8 and 9).](image2)
Table 2. Result of voltage generation and COD removal using one-factor-at-a-time (OFAT).

| Parameters       | Varying Parameter |
|------------------|-------------------|
| Voltage generation (mV) | COD removal | Substrate degradation efficiency |
| mg/L | % |
|------------------|------------|
| Varying: pH      | 7          | 762          | 422          | 59.18 |
| Moisture content: 20 % (vol/wt) | 8          | 807          | 495          | 69.42 |
| Electrode distance: 3 cm | 9          | 755          | 116          | 16.27 |
| Temperature: 35 °C |            |              |              |      |

3.3 Effect of pH on EB growth in the ML-MFC.
Based on preliminary studies that were conduct, bacillus was the best EB to be used in the ML-MFC. EB biomass was measured by standard biomass value from equation \( y = 0.0451x - 0.025 \) which obtained from correlating OD and biomass graph. The biomass of EB was obtained by matching the absorbance with the linear graph of the curve, matching with the concentration of standard of food waste concentration.

Figure 3 display biomass values in working ML-MFC, which at time \( t = 0 \) to \( t = 12 \) h all ML-MFCs went through the lag phase where bacillus subtilis were trying to adapt the new conditions. The biomass in ML-MFCs seemed gradually stably after 24 h (entering log phase cycle of the microbe) and achieved the maximum biomass at \( t = 96 \) for MFC pH 9 (increased from 8.7 to 13.92 mg/L), \( t = 144 \) h for MFC pH 7 (increased from 9.72 to 14.53 mg/L) and MFC pH 8 also achieved highest biomass at \( t = 144 \) h (increased from 10.52 to 15.46 mg/L).

![Biomass profile of ML-MFC with varied pH.](image)

3.4 Effect of pH on Voltage generation and biomass growth in the ML-MFC.
Voltage generated and biomass correlation at optimum pH 8.0 could be viewed in Figure 4. As seen in the figure, as the inoculum inserted there was fluctuate voltage and biomass while in lag phase. Voltage plumbing down to 212 mV, and is the lowest voltage generated throughout the experiment.
and lowest biomass is at \( t_{d2} = 8.98 \text{ mg/L} \). After two days, voltage and biomass went through log phase, where increased rapidly to reach maximum growth and optimum voltage. Log phase time was about 4 days before reached peak which was at \( t_{PE} = 807 \text{ mV}, 15.46 \text{ mg/L} \), voltage and biomass value respectively. At day 7, both biomass and voltage decreased simultaneously due to the voltage generated and biomass correspond to each other. Increased biomass will result increased in voltage too. The voltage dropped phenomenon at \( t = 96 \text{ h} \) maybe happened due to the activation energy needed for an oxidation/reduction reaction, activation losses (or activation polarization) occur during the transfer of electrons from or to a compound reacting at the electrode surface [8].

3.5 Performance of ML-ML-MFC

Polarization curve is used to illustrate the current density as a function of voltage (the electric potential of the electrodes). In Figure 5 comparison of each pH was elaborated. From Table 3, pH 8 had the highest power density (373.3 mW/m²) followed by pH 9 (366.8 mW/m²) and pH 7 (321.6 mW/m²). In this study the EB growth shows that it leaned more toward base pH which mean pH 9 should give higher results than that pH 8. But this can happen because a phenomenon that happened in pH 9 as power density correlated with voltage generated, because of pH 8 had the higher voltage generated than pH 9. Mass transfer losses that happened in pH 9 also play a role, it was energy loss due the mass transfer (or flux of the substrate representing the reactants to the anode is most of the time insufficient [11]. This happened as pH biomass grew faster but producing lower voltage than pH 8. To overcome mass transfer losses during experiment, using an efficient proton exchange membranes that facilitate the migration of protons to the cathode while maintaining a relatively enough buffer capacity [12].

| Resistor (Ohm) | pH 7 | pH 8 | pH 9 |
|---------------|------|------|------|
| 0             | 0    | 0    | 0    |
| 47            | 48.8 | 40.9 | 41.4 |
| 100           | 89.7 | 94.3 | 99.5 |
| 220           | 192.6| 179.5| 224.8|
| 470           | 321.6| 373.3| 366.8|
| 1000          | 363.6| 336.6| 309.2|

**Table 3.** Power density at each pH.
ML-ML-MFC with pH of 8 was chosen to explain the phenomenon happens in the ML-MFC. Figure 6 there were three characteristic regions of voltage decline in ML-MFC; 1) a rapid voltage dropped as current flows through the circuit; 2) an almost linear voltage decline; 3) a second rapid voltage decline at high current density. This ML-MFC complies with all of the above mentioned characteristics. The activation potential for the ML-ML-MFC was happened when the current was from 1.6 to 3.2 mA and the voltage dropped from 765 mV to 722 mV. An activation loss was when energy loss due to the migration of electrons from the bacteria to the anode surface directly or indirectly [12]. To overcome this problem could be done by increasing the temperature in experiment [7]. Next, when current increased from 3.2 mA to 7.02 mA, there were a constant voltage drop was plotted (722 mV to 702 mV). Here this called Ohmic losses as transfer of electrons from the electrode through wires and the point of contact of the electrodes and the conducting wire causes energy loss due to the internal resistance of the electrode material and the wire or in short electrical resistance in the cell components[13].Therefore, increasing the solution conductivity we might as well reduce the Ohmic losses. In addition, the smaller the distance between the electrodes the lower Ohmic losses will be found. However, Ohmic losses were sometimes inevitable [10]. Then, when the current increased from 7.02 mA to 9.7 mA, the voltage went rapidly dropping from 702 mV to 457 mV due to large oxidative forces at the anode. This area was called mass transfer losses as it arise when a species mass transport rate to or from the electrode limits current output. It usually occurs at high current densities due to the minimal mass transfer by diffusion of chemical species to the electrode. So insufficient mass transport causes depletion of reactants or accumulation of products [14]. Optimization of ML-MFC operating conditions, electrode material, and cathode compartment design can minimize mass transfer limitations and other performance losses and it is to be tackled in future studies to produce better power generation of ML-MFC.

**Figure 5.** Graph of power density over varied resistance of varied pH.

![Graph of power density over varied resistance of varied pH.](image-url)
4. Conclusions
Microbial fuel cells represent a new promising technology that gives hope to the future generations and using food waste as substrate for ML-MFC was a great choice as it reduced abundant food waste produced by humans, and conserved the environment. ML-MFC was chosen for this experiment with pH varying from 7 to 9 and the results show that pH 8 was the most suitable pH for *Bacillus Subtilis* to grow in the system with the voltage generated was 807 mV, biomass 15.46 mg/L, and power density 373.3 mW/m². In conclusion, pH environment condition in ML-MFC will affect the efficiency of performance for energy production. The incremental increase in EB biomass also increased the voltage in the ML-ML-MFC, proving that EB biomass and voltage were associated with growth. ML-MFC using food waste as substrate would be brilliant alternatives to reduce food waste at the same time treated the pollutant.

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