Journal of Thermal Engineering
Yildiz Technical University Press, Istanbul, Turkey
Vol. 2, No. 6, Special Issue 5, pp. 1029-1033, December, 2016.

http://eds.yildiz.edu.tr/journal-of-thermal-engineering/Articles
Manuscript Received January 21, 2016; Accepted March 29, 2016

This paper was recommended for publication in revised form by Regional Editor Lian-Ping Wang

BIOENERGY PRODUCTION FROM FREEZE DRIED CHLORELLA VULGARIS BIOMASS VIA MICROBIAL FUEL CELL

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Keywords: microbial fuel cell, algae, freeze dried
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ABSTRACT

Algae biomass has strong and complex cell wall structure that is a hindrance for microbial digestion. In this work, two extracted algae biomass, which are freeze dried and spray dried Chlorella vulgaris biomass is applied to investigate the generation of bioelectricity by using single chamber air-cathode Microbial Fuel Cell (MFC). MFC was fed with freeze-dried algae powder to produce energy and determine its degradation efficiency. MFC with freeze-dried algae biomass was generating voltage around 739 mV from bacterial metabolism with algae substrate and phosphate buffered medium. Based on the power curve obtained, the maximum power density is 159 mW/m^2 with 2.5 g/L of substrate concentration. The Chemical Oxygen Demand (COD) removal efficiency is 54.2% and Coulombic efficiency (CE) obtained is 28.4%.

INTRODUCTION

Recently, most of world energy is mainly produced by the combustion of fossil fuels. However, its limited sources and the emission of greenhouse gases remains as a long term issue. Therefore, researchers need to find alternative energy which is renewable and environmental friendly [1–3]. One of the potential alternative energy is energy derived from the degradation of biomass by involving bacteria. Biomass is a product form from the combination of water, carbon dioxide, and solar energy. Photosynthetic microorganism that is known as microalgae uses the reaction. The cells are grown in aqueous condition, so they have more access to water and more predictable process variables (such as sunlight and temperature) compared to higher plant systems. This allows them to extrapolate easily from one site to others, even climatic condition. Microalgae also grow faster than higher plants and much less area requirement [4]. Microalgae become good candidates for biofuels production

because of their higher advantages of higher photosynthetic efficiency, higher biomass production and faster growth compared to other energy crops.

Microalgae are autotrophic singular cellular microorganisms that have chlorophyll, lipids, proteins and carbohydrates. They have a rapid growth rate and productivity [5]. For these reasons, algae is preferred to be used as energy sources, such as biodiesel, methane and hydrogen production via fermentation or microbial anaerobic digestion. Most preferred algae species is the one that has a high lipid content such as Chlorella species. Microalgae lipid is required for biofuel and bioelectricity. To obtain its lipids, a multi-steps process is required, such as photoautotrophic cultivation, harvesting, biomass dewatering, and lipid extraction. Light, carbon dioxide, inorganic nutrients, and water are necessary for microalgae growth. In commercializing the production of microalgae, harvesting and dewatering are important steps. Freeze drying is common used for dewatering microalgae biomass. Freeze drying preserves cell constituents without destroying its cell wall. Lipid is extracted by using physical or chemical methods or both methods. Physical methods are autoclave, bead-beating, sonication, microwave and osmotic shock. Solvent extraction is a chemical method. Furthermore, a combination of physical or mechanical methods with solvent extraction is commonly used for oil extraction [6–9].

Dry algae biomass is able to produce higher maximum power density compare to other substrates in generating bioelectricity via Microbial Fuel Cell (MFC) due to its high carbon sources for its lipid content [10]. However, the bacterial digestion of algae biomass is not easy due to algal strong and complex cell wall structure which is becoming difficult for microbial digestion. Therefore, an algae biomass extraction and dewatering is needed to break the cell wall structure to facilitate the digestion process. Freeze drying is preferable due to its method of conserving algae cell constituent while dewatering for microbial consumption to generate bioelectricity, compare to other methods which may degrade during pre-treatment process. In this work, freeze dry pre-treated algae biomass is applied to generate bioelectricity by using single chamber MFC with commercialized air-cathode. Air-cathode is much more practical and attractive other than cathodes due to no aeration required and generate higher power densities [11].

EXPERIMENTAL

MFC Construction and Operation

The MFC reactor was designed and fabricated from glass material (Fig. 1). It was a 1500 ml chamber with a net liquid volume of 1200 ml. For the start-up, a manganese based catalyzed carbon electrode (E-4, Electric Fuel Ltd.) used as an air cathode. Its thickness is 0.5 mm in diameter of 6 cm. The catalyzed side was placed and contacted with anodic solution with carbon side where it is directly exposed to air. Activated carbon fiber fabric (Carbon Technology Co., Ltd. Taiwan) with a projected surface area of 100cm^2 was used as for anode without any pre-treatment. It was placed in the chamber with a distance of 17 cm from the air cathode. The single chamber was inoculated with anaerobic sludge which is collected from wastewater treatment plant located at Universiti Teknologi MARA, Shah Alam, Malaysia. The reactor was fed with medium of phosphate buffer solution (PBS). 50 mM phosphate buffer medium consists of 4.576 g Na_2HPO_4, 2.452 g Na_2HPO_4, 0.31 g NH4Cl and 0.13 g KCl, 12.5 ml of minerals and 5 ml of vitamins solution. After inoculation, 2.5 g/L freeze-dried Chlorella Vulgaris biomass powder (Algaetech International Sdn. Bhd. Malaysia) was mixed with 50 mM PBS and fed into the MFC. Microalgae biomass were extracted by the bead-milling method and dewatering by using the freeze dry method. The same MFC operation was conducted for different algae biomass feedstock concentration of 1.0 g/L and 5.0 g/L.

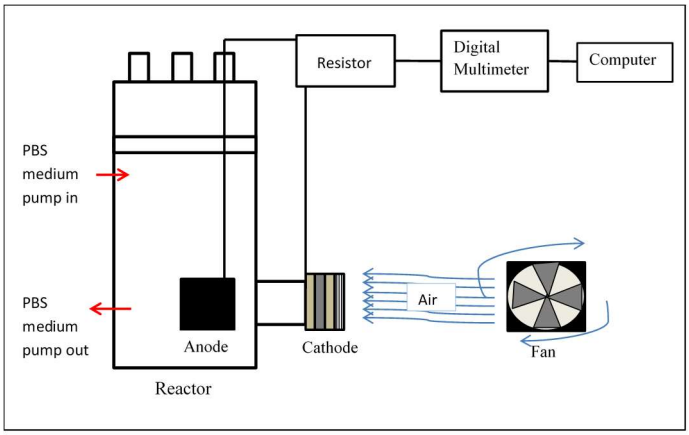

Figure 1. A schematic diagram of glass MFC device with fabricated anode and air-cathode

Data Collection and Analysis

The voltage across an external resistor of 1 kΩ was recorded every hour by connecting the electrodes to a digital multimeter (UT803, Uni-Trend Technology Ltd. China) and a computer with data logger software installed. A variable resistor was applied to the system (from 10 MΩ to 2 Ω) to determine its polarization curve during voltage stabilization. Each voltage were recorded (delayed about 10 seconds) for every resistance applied, starting from Open Circuit Voltage (OCV). Ohm's Law, $I = E_{cell} / R_{ext}$ was used to determine its current where E_{cell} is the cell voltage generated for each load, I is the current for each load, and R_{ext} is the external load resistor. Power curve was determined by using the formula $P = I / E_{cell}$, where P is power generated for each load, I is the current for each load and E_{cell} is the cell voltage for each load. Current and power is expressed as current density and power density where each value is divided by the total surface area of electrode used (100 cm^2). For every initial and final of MFC operation, some sample was taken to determine its chemical oxygen demand (COD), in mg.L^{-1}, by using a reactor digestion method (High Range, 20-1500 mg/L, HACH Co., USA). COD removal efficiency (ΔCOD) was calculated based on $\Delta COD = (COD_{int} - COD_{end})/COD_{int} \times 100\%$, where COD_{int} is the initial COD concentration of feedstock (mg. L^{-1}) and COD_{end} denotes the final COD concentration of the batch test.

Coulombic efficiency was analyzed, as fed batch system according to CE (%) = $C_P/C_T \times 100\%$, where C_P represents the total Coulombs as a result of integration of current over time, while C_T is the amount of Coulombs theoretically from the result of COD removal with assumption of four moles of electrons transferred over mole of COD.

RESULTS AND DISCUSSION

Bioelectricity Generation with Freeze-Dried Algae Biomass

The anode compartment of MFC was inoculated with wastewater and PBS nutrient buffer medium for 14 days. After that, the voltage generation was recorded in every hour. The recorded data are shown in Figure 2.

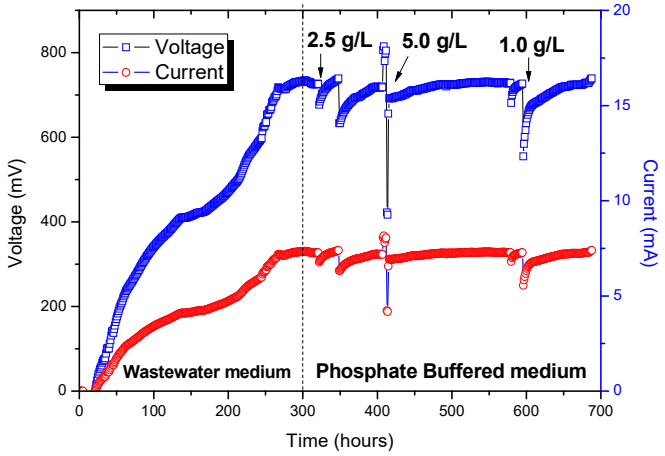

Figure 2. Voltage and current generation over time (hours). Pre-acclimation of wastewater and PBS medium for 14 days and followed by the addition of 2.5 g/L, 5.0 g/L and 1.0 g/L of freeze-dried algae biomass.

After 14 days of inoculation, voltage generation was stabilized around 731 mV. Then, wastewater was replaced with 2.5 g/L freeze-dried algae biomass and dissolved in PBS buffered medium. The voltage was unstable at first, and then increasing gradually, until its achieving a stabilization around 739 mV. Then, the concentration of algae biomass changed to 5.0 g/L and voltage was stabilized around 728 mV. The concentration of 1.0 g/L is then applied, which has voltage stabilized around 733 mV. Voltage generation is corresponding to the growth curve of microbial consortia in the anode chamber. At the beginning of the MFC operation, the voltage is increased due to exponential growth of microbes. The exponential growth represents a formation of biofilm occurs on the surface of the electrode. Sufficient organic matter (in this case, algae biomass) and nutrients in the sludge encourage a biofilm to form. The stabilized voltage generated means that the microbial growth is in stationary phase where biofilm formation is stabilized. Finally, the decrease of voltage is due to the competition between microorganisms in order to obtain their limited food from the organic matter and nutrients in the activated sludge. The decrease of voltage represents the death phase of microbes due to limited nutrients present in the chamber [12,13].

Polarization Curves between Different Freeze Dried Algae Biomass Concentrations

Three different substrate concentration is tested with variable resistor to examine the polarization power curve during the voltage stabilization. A difference of maximum power point is determined (Fig. 3). Based on polarization power curves (Fig. 3), the power curve shows the highest maximum power point is 159.9 mW/m^2 where 2.5 g/L of concentration of freeze dried algae biomass (substrate) was pumped into the MFC. 5.0 g/L of freeze dried algae biomass concentration shows power curve with maximum power point of 60.2 mW/m^2 while 1.0 g/L of freeze dried algae biomass concentration shows 98.5 mW/m^2. In this case, different substrate concentrations have an influence on the power generation. The 2.5 g/L substrate concentration generates more power than 1.0 g/L substrate concentration.

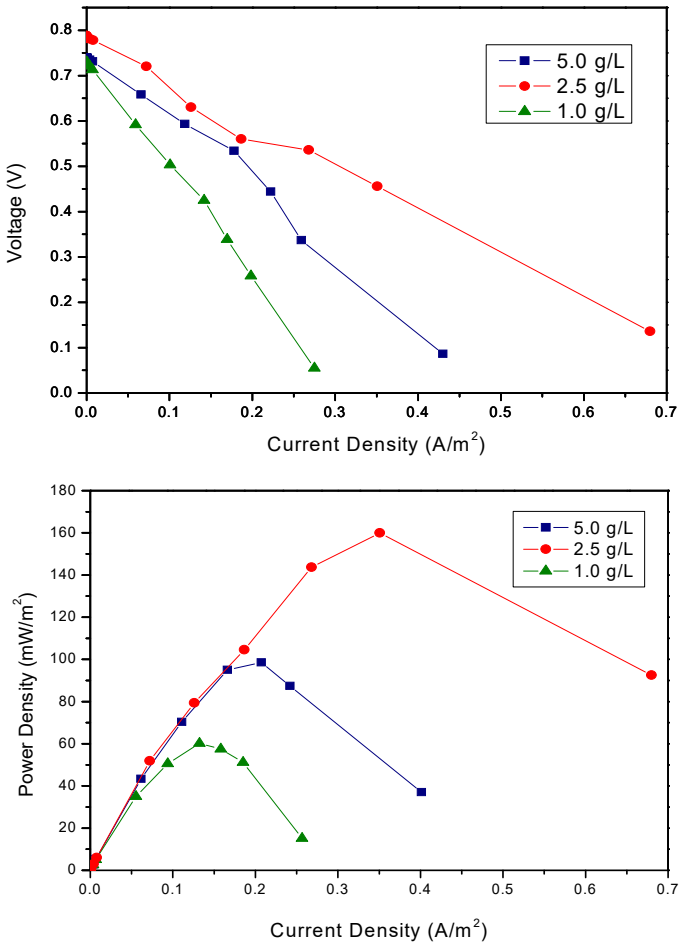

Figure 3. Three different polarization curves corresponding to different freeze algae biomass concentrations as feedstock for MFC. 1.0 g/L, 2.5g/L and 5.0 g/L of freeze dried algae biomass concentrations were used.

Consequently, the more concentration of substrate is added, the more power is generated by the MFC [14]. The concentration of freeze dried algae biomass of 5.0 g/L produces

a low power density compare to 2.5 g/L, perhaps due to many reasons such as the anode, cathode, chemical species in the electrolyte, proton exchange membrane (PEM), application of microbes species, the configurations of fuel cell and the condition of the operation [15]. Another reason is the algae suspected to produce concentrated toxicity along with concentrated algae biomass due to lipid extraction of algae body cells [10]. Chlorella species is identified, where it has a substance that resistant to degradation, namely as algaenan [16]. Furthermore, with probably several factors like the sizes of the anode electrode, types of algae species, substrate concentrations and internal resistances are likely to cause the large differences of maximum power density [17].

Chemical Oxygen Demand (COD) Removal and Coulombic Efficiency

The initial chemical oxygen demand (COD) and final COD of MFC operation is taken to determine its percentage removal and coulombic efficiency (CE) of the MFC. This evaluates performance of the MFC in generating bioelectricity and treat wastewater simultaneously.

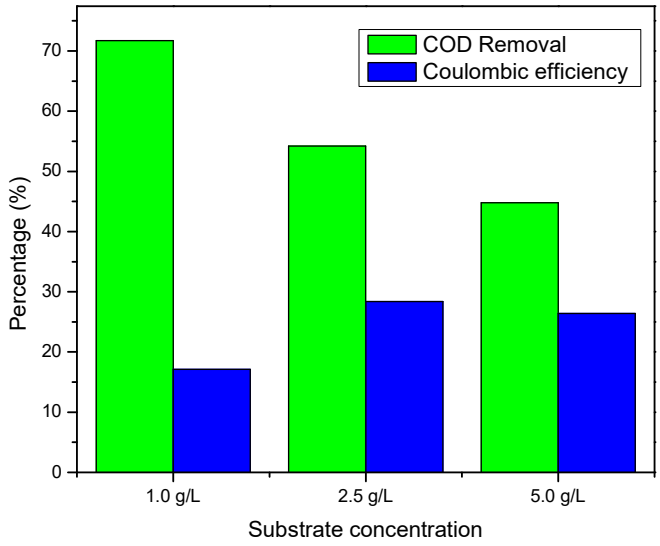

Figure 4. Chemical Oxygen Demand (COD) removal and Coulombic efficiency (CE) from three different substrate concentrations which are 1.0 g/L, 2.5g/L and 5.0 g/L of freeze dried algae biomass.

Three different substrate concentrations (freeze dried algae biomass) are applied to MFC (Fig. 4). The percentage of COD removal at 1.0 g/L of substrate concentration is 71.7%, 2.5 g/L shows 54.2% and 5.0 g/L shows 44.8%. The differences of COD between the initial and final of MFC operation determines the coulombic efficiency (CE). At 1.0 g/L of substrate concentration, CE is about 17.1%. At 2.5 g/L, the CE result is 28.4%, while 5.0 g/L only produce CE about 26.4%. This result proves that MFC power generation is able to treat wastewater and increase the quality of water. According to Fig. 4, 1.0 g/L shows highest COD removal, but lowest CE while 2.5 g/L shows highest CE compare to others. 5.0 g/L has a lowest COD removal, but higher CE than 1.0 g/L and a little bit lower than 2.5 g/L. These differences show that low COD removal has relatively high CE significantly, between 1.0 g/L and 2.0 g/L. The distinction between 2.5 g/L and 5.0 g/L is not so much (CE is differs about 2.0%). According to Velasquez-Orta et al. [14], the relationship between COD removal and CE shows that the CE value is high (28% for C. Vulgaris and 23% for U. Lactuca) at low COD removal (the range is 100 to 500 g/L). Beyond 600 mg/L of substrate concentration, CE reached 10 % plateau and declined. Therefore, the more substrate concentration is applied, the lesser COD removal efficiency. Meanwhile, CE is increased as substrate concentration increases. However, at certain concentration, CE reached plateau and decreases afterwards. On the other hand, a report by Kondaveeti et al. [17], their MFC has shown 7.8% CE in 66% TCOD removal and 13.4% CE in 59% COD removal (0.42 g/L substrate concentration). However, similarly in this study, their results are lower than CE and COD removal values than Velasquez-Orta et al. [14]. The decrease of COD removal at low power generation is probably due to the large size of organic matter for fermentation, aerobic respiration and bacterial growth [17]. The decrease of 2.0% CE value between 2.5 g/L and 5.0 g/L substrate concentration, perhaps due to electron transfer are used for microbial growth, instead of being used for bioelectricity generation. However, a further investigation is needed to understand the behavior of bacteria in degrading the composition of microalgae biomass, in order to achieve the optimization of bioenergy produced.

CONCLUSION

Freeze dry pre-treated microalgae, Chlorella vulgaris was demonstrated in a single chamber Microbial Fuel Cell (MFC) with air cathode to generate bioelectricity. Freeze dry is a common pre-treatment method due to its high lipid recovery, by preserving the algal cell constituents. Therefore, the maximum power density is 159.9 mW/ m^2 and COD removal efficiency of 54.2% with 2.5 g/L of substrate concentration. MFC with freeze dried algae substrate concentration of 1.0 g/L, 2.5 g/L and 5.0 g/L has a coulombic efficiency of 17.1%, 28.4% and 26.4%, respectively. Therefore, the bacterial substrate consumption of freeze dry pre-treated Chlorella vulgaris algae biomass is able to generate bioelectricity and also very efficient in wastewater treatment.

ACKNOWLEDGEMENT

The authors are grateful thanks to Ministry of Education (MOE) for supporting this research under the funding of NRGS, RAGS and Universiti Teknologi MARA (UiTM) for the facilities provided in succeeding this research.

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