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Comparison of Energy and Performance from Biodegradation of Freeze Dried and Spray Dried Algae Biomass

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ABSTRACT

Many kinds of substrates have been used to investigate bioelectricity production with Microbial Fuel Cell (MFC). Dry algae biomass has the highest maximum power density compared to other substrates due to high carbon sources from its lipid. However, the bacterial digestion of algae biomass is not simple because of the complexity and strength of the algal cell wall structure. An algae biomass extraction is needed to break the cell wall structure and facilitate digestion. Spray drying method is commonly used in high-value products but may degrade some algal components which are crucial for microbial degradation in MFC, while the freeze-drying method is able to preserve algal cell constituents. The MFC was fed with freeze dried and spray dried algae biomass to produce energy and determine the degradation efficiency. Results showed the average voltage generated was 739 mV and 740 mV from freeze dried and spray dried algae biomass, respectively. The maximum power density of freeze dried algae biomass is 159.9 mW/m^2 and spray dried algae biomass is 152.3 mW/m^2. Freeze dried algae biomass has 54.2% of COD removal and 28.4% of Coulombic Efficiency while spray dried algae biomass has 50.1% of COD removal and 24.9% of Coulombic Efficiency.

Keywords: Algae biomass, energy storage and conversion, freeze dry, Microbial Fuel Cell, spray dry

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INTRODUCTION

A review by Zhao et al. (2009) states that generally Microbial Fuel Cell (MFC) produces low power (less than 6 W m^{-2} or same and less than 500 Wm^{-3}) because of some factors such as anode, cathode, chemical species in electrolyte, proton exchange membrane (PEM), application of microbe species, the configurations of fuel cell and the condition of the operation. These 'acceptable loss' in lab scale, are still far from reaching the level of commercial scale. In this study (Zainal et al., 2016), the maximum power density is found to be lower than that recorded by previous studies on algae biomass (Kondaveeti et al., 2013; Rashid et al., 2013; Velasquez-Orta et al., 2009). The large differences of maximum power density is because of the same reason given by Kondaveeti et al. (2013), which is probably due to several factors such as size of the anode electrode, type of algae species, substrate concentration and internal resistances. Although MFC has the potential to generate electricity, the materials and substances used and applied for its configuration have limited MFC from reaching their real potential to generate power.

Dry algae biomass as a substrate can produce high maximum power density compared to other substrates in generating bioelectricity via MFC. It has high carbon sources from its lipid. Rashid et al. (2013) did apply sonication, thermal and unpre-treated to break down cell wall and facilitate algae degradation by microbes, and found unpre-treated algae biomass has the highest cell voltage profile. A premature conclusion is made that lipid extracted algae cannot be used for substrate degradation to generate electricity. Also, un-pre-treated algae biomass mixture has produced a maximum voltage of 0.604 V and pre-treated mixture has produced a maximum voltage of 0.290 V. The reason of the negative effect of sonication is still unknown (Rashid et al., 2013). More investigations are needed to be carried out pertaining to pre-treatment method algae species biomass.

Microalgae lipids are required for biofuel and bioelectricity. To obtain 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 also needed for the purpose of microalgae growth. In commercializing the production of microalgae, harvesting and dewatering are important steps. Harvesting methods involves flocculation, filtration, floatation, centrifugation and any combination of these methods. Upon harvesting, the wet biomass need to be freeze dried, drum dried, oven-dried, spray-dried and fluidized bed-dried in order to increase the viability of biomass for lipid extraction. Spray drying method causes deterioration of some algal components such as pigments. Furthermore, high temperature pre-treatment can cause further degradation and denaturation of desired products (Hammed et al., 2013; Sander & Murthy, 2009). Freeze drying is commonly used for dewatering microalgal biomass while preserving cell constituents and cell wall (Brennan & Owende, 2010; Chen et al., 2009; Guldhe et al., 2014; Halim et al., 2012), allowing for better power generation by MFC. In this paper, freeze dried and spray dried pre-treated algae biomass are compared to ascertain their energy production and performance.

METHOD

MFC Construction and Operation. A 1500 ml glass chamber with a net liquid volume of 1200 ml was used as an MFC reactor (Figure 1). A manganese based catalysed carbon electrode (E-4, Electric Fuel Ltd.) was applied as an air cathode (thickness is 0.5 mm in diameter of 6 cm). The catalysed part was positioned towards the anodic solution and carbon side in the direction of air. For the anode, a projected surface area of 100 cm^2 of activated carbon fibre fabric (Carbon Technology Co., Ltd. Taiwan) was used, without any pre-treatment. The distance between anode and air cathode is about 17 cm. The single chamber was filled and inoculated with anaerobic sludge (collected from wastewater treatment plant Universiti Teknologi MARA (UiTM), Shah Alam, Malaysia). A medium of 50 mM phosphate buffer medium (PBS) consists of 4.576 g Na_2HPO_4, 2.452 g Na_2HPO_4, 0.31 g NH_4Cl and 0.13 g KCl, 12.5 ml of minerals and 5 ml of vitamins solution was made to feed the MFC. After 14 days of 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. Microalgal biomass was extracted using the bead-milling method and dewatering by the freeze dry method. The same MFC operation was conducted for 2.5 g/L spray dried *Chlorella vulgaris* biomass. Spray dried *Chlorella vulgaris* biomass were purchased (Jarrow Formulas).

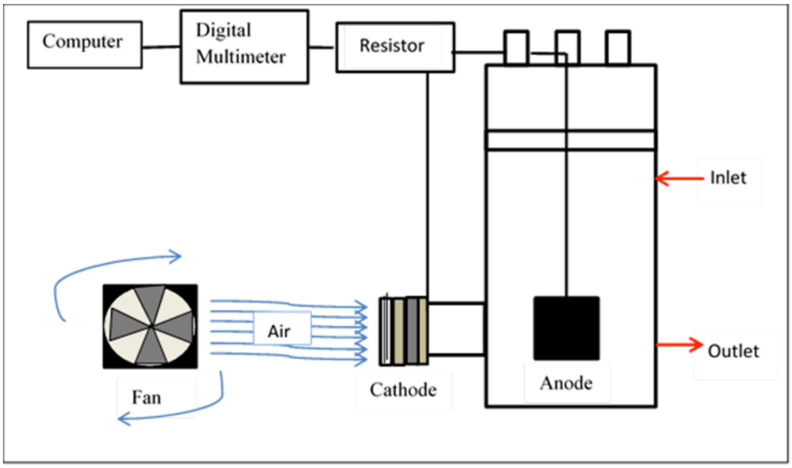


Figure 1. A schematic diagram of glass MFC device with fabricated anode and air-cathode

Data Collection and Analysis

A digital multimeter (UT803, Uni-Trend Technology Ltd. China) and a computer with data logger software was installed to measure voltage for 21 days, simultaneously which a variable resistor was connected to the system (from 10 MΩ to 2 Ω) to determine power density and current density during voltage stabilization. Starting from Open Circuit Voltage (OCV), each voltage was recorded (delayed about 10 seconds). The current was calculated using Ohm's Law,

$I = E_{cell} / R_{ext}$ where E_{cell} is cell voltage generated for each resistance, I is the current for each resistance, and R_{ext} is the external load resistor. A formula, $P = I \times E_{cell}$ was used to calculate power, where P is power generated for each resistance, I is the current for each resistance and Ecell is the cell voltage for each resistance. The total surface area of electrode (100 cm^2) was used to determine the current and power, as current density and power density. 2 ml sample was taken to determine its chemical oxygen demand (COD) during the initial and final of MFC operation, in mg/L, by using the reactor digestion method (High Range, 20-1500 mg/L, HACH Co., USA). COD removal efficiency (ΔCOD) was calculated according to where COD_{int} is the initial COD concentration of substrate (mg/L) and COD_{end} is the final COD concentration of the batch test.

$$\Delta COD = \frac{(COD_{int} - COD_{end})}{COD_{int}} \times 100\% \qquad [1]$$

As fed batch system, a formula [2] was used to analyse Coulombic efficiency where ΔCOD is change of COD concentration (mg/L), I is current (A), t is change in time (s), V_{An} is working volume (volume liquid in anode compartment, L), F is Faraday's constant (96,500 C mol^{-1} e-), and 8 is a constant, according to $M_{O2} = 32$ for the molecular weight of oxygen and b = 4 for the number of electrons transferred per mole of oxygen.

$$CE\ (\%) = \frac{8\int_0^t I\,dt}{FV_{An}\,\Delta COD} \qquad [2]$$

Environmental Scanning Electron Microscope (ESEM) Image

Environmental Scanning Electron Microscopy (Quanta 450 FEG ESEM, USA) was performed at Imaging Centre, Faculty of Pharmacy, Universiti Teknologi MARA (UiTM) Puncak Alam campus. A 2 mm x 2 mm section of carbon cloth was cut (taken out of the fuel cell) using a sterile scalpel. The carbon cloth was placed in a sterile falcon tube filled with 4% phosphate buffered glutaraldehyde in distilled water. The sample was immersed for 4 hours after which it was rinsed gently with 50 ml distil water for 1-2 minutes. The rinsed sample was placed in the Peltier cooling chamber device inside the ESEM chamber. The temperature inside the ESEM chamber was maintained at about 4°C, and water vapour pressure was between 4.5 and 5.5 Torr, to ensure the sample was maintained in a moist condition.

RESULTS AND DISCUSSION

Voltage Generation from Freeze Dried and Spray Dried Pre-Treated Algae Biomass

The anode compartment of MFC was inoculated with wastewater for 14 days. Then, the wastewater was replaced with PBS medium and 2.5 g/L of substrate (freeze dried and spray dried algae biomass). The voltage generation from both substrates is shown in Figure 2.

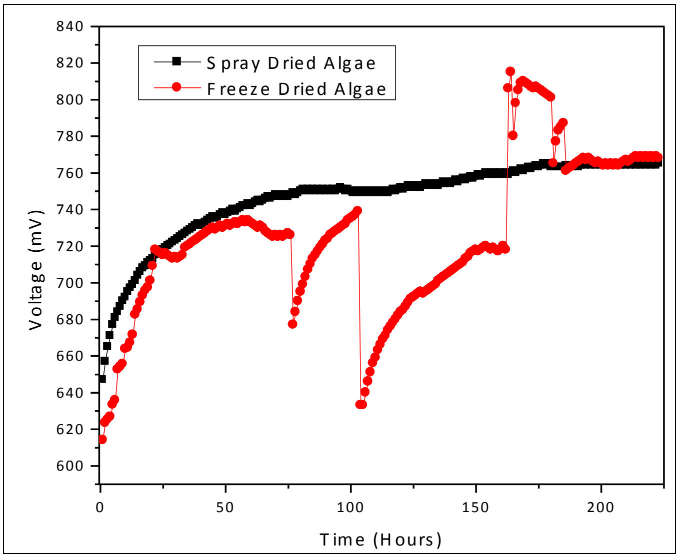


Figure 2. Voltage generation over time (hours) as result of degradation of both 2.5 g/L of freeze dried and spray dried algae biomass

From Figure 2, spray dried algae biomass was generated a stable voltage averagely about 740 mV while that of freeze dried algae biomass was unstable, averagely about 739 mV for 200 hours. The highest voltage recorded was 820 mV by freeze dried algae biomass, until its voltage was stable as the voltage generated from spray dried algae biomass, from 175 hours onwards. The voltage generation by MFC is related to the growth curve of microbial consortia in its anode compartment. Firstly, voltage increase is the product of exponential growth of microbes to form biofilm on top of the surface of the electrode (carbon cloth) in the anode compartment. Secondly, maintained biofilm formation causes voltage stabilisation. Lastly, the voltage decreases when microbes are in the death phase (Nair et al., 2013; Venkata Mohan et al., 2008). The unstable voltage generated by freeze dried algae biomass is probably due to the large size of the organic matter which makes the process of degradation more difficult (Kondaveeti et al., 2013).

Maximum Power Density from Freeze Dried and Spray Dried *Chlorella Vulgaris* Biomass

Two different pre-treatment algae biomass (freeze dried and spray dried) was used to compare power density generation (Figure 3). Both have similar concentrations of 2.5 g/L of algae biomass, and the MFC was connected to a variable external load resistor (range of 0.5 Ω to 10 MΩ), to determine power density by starting at Open Circuit Voltage (OCV). The OCV of freeze dried algae biomass is about 795 mV while the OCV of spray dried algae biomass is 765 mV. During an open circuit condition, no current is generated, therefore no power is produced. When the current is increased, power is also increases until reached the maximum power point. Beyond the point, the MFC is in a state of short circuit condition where ohmic loss and the electrode overpotential is increased, until no power is produced. In Figure 3, the maximum power density of freeze dried algae biomass is 159.9 mW/m^2 and spray dried algae biomass is 152.3 mW/m^2. Therefore, freeze dried algae biomass produces higher power than spray dried algae biomass. However, there was no significant difference in power generation between freeze dried and spray dried algae biomass in this study probably due to the capability of exoelectrogens growing inside of MFC. Therefore, the application of different pre-treated algae biomass in the MFC is not very effective in increasing power generation (Lee et al., 2015).

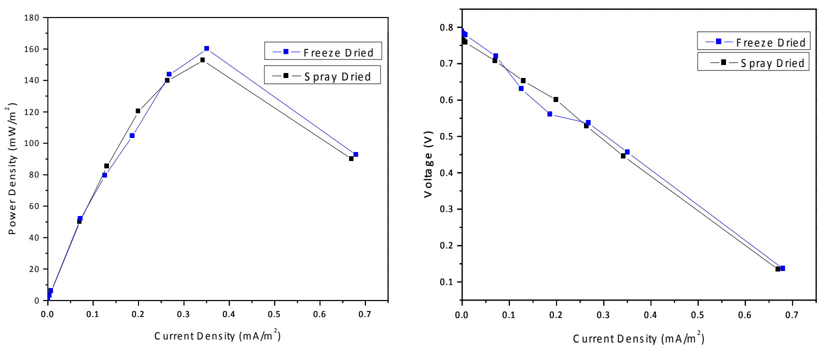


Figure 3. Power density and voltage generation against current density as a result of external load resistance control to determine maximum power density from freeze dried and spray dried algae biomass

Chemical Oxygen Demand (COD) removal percentage and Coulombic efficiency

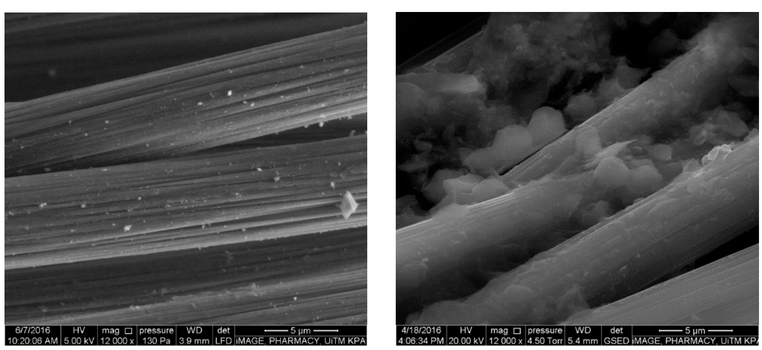
To determine the degradation of algae biomass the anodic solution of MFC was tested for wastewater treatment efficiency, which is known as Chemical Oxygen Demand (COD) removal percentage. COD removal is a measurement of organic matter degradation efficiency. COD removal was recorded is 79.8% in MFC compared to 59% in the control experiment, proving that COD removal from MFC is better than COD removal without power generation (Kondaveeti et al., 2013). COD removal is also required to calculate Coulombic efficiency. Coulombic efficiency is a measure of maximum total coulombs transferred from substrate towards the anode to generate power (Logan et al., 2006). Table 1 shows that freeze-dried algae biomass has 54.2% of COD removal and 28.4% of Coulombic Efficiency while spray dried algae biomass has 50.1% of COD removal and 24.9% of Coulombic Efficiency. Therefore, freeze dried has higher COD removal percentage and total coulombs transferred to the anode compared to spray dried algae biomass. However, the differences of pre-treated algae biomass were not significant. The coulombs may be limited by a requirement growth of exoelectrogens and only some coulombs were transferred to the anode surface for power generation, although substrate used are not the same (Lee et al., 2015). In the anode biofilm community, fermenting microbes have sufficient retention time to dominate the anode-respiring bacteria, and consuming electrons for reduced products. Thus, the electron cost reduced coulombic efficiency (Logan et al., 2006).

Table 1
Chemical Oxygen Demand (COD) removal percentage and Coulombic Efficiency determination from both freeze dried and spray dried algae biomass degradation in the MFC

Substrate concentration	2.5 g/L Freeze Dried Algae Biomass	2.5g/L Spray Dried Algae Biomass
Chemical Oxygen Demand (COD) removal	54.2%	50.1%
Coulombic Efficiency	28.4%	24.9%

Environmental Scanning Electron Microscope (ESEM) image on the surface of the anode

Figure 4(a) shows Environmental Scanning Electron Microscope (ESEM) image of the surface of carbon cloth fibre (as the anode) before MFC operation. Figure 4(b) shows a formation of biofilm on top of the surface of the anode. The biofilm covers the anode with a kind of monolayer to multilayer structure with variable thickness on the surface of carbon fibre. Sufficient organic matter (algae biomass) and nutrients from PBS medium favours growth of biofilm. Biofilm formation consists of three basic components: (1) surface for biofilm growth attachment; (2) microbes acting as the unit for biofilm; and (3) glycocalyx, which is a secreted protecting polymer matrix by microbes to form biofilm (Dunne, 2002). The biofilms play an important role in transferring electrons directly to the anode surface, as a result of biochemical reaction between biofilm and the substrate.



(a) (b)

Figure 4. Environmental Scanning Electron Microscope (ESEM) image of the anode surface. The anode surface of carbon fibre (a) before; and (b) after MFC operation

CONCLUSION

The energy and performance of freeze dried and spray dried *Chlorella vulgaris* biomass was compared using single camber air-cathode Microbial Fuel Cell (MFC). Freeze dry pre-treatment was able to conserve algae biomass constituents and help in increasing power generation compared to spray dried algae biomass. As a result, maximum power density of freeze dried algae biomass is 159.9 mW/m^2 and spray dried algae biomass is 152.3 mW/m^2. The average voltage generated is 739 mV and 740 mV from freeze dried and spray dried algae biomass, respectively. The COD removal percentage of freeze dried algae biomass is 54.2% and spray dried algae biomass is 50.1%. The Coulombic Efficiency for freeze dried algae biomass is 28.4% and spray dried algae biomass is 24.9%. Therefore, freeze dried algae biomass has potential as pre-treated substrate to improve energy production in MFC.

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REFERENCES

Brennan, L., & Owende, P. (2010). Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews, 14*(2), 557–577. http://doi.org/10.1016/j.rser.2009.10.009

Chen, P., Min, M., Chen, Y., Wang, L., Li, Y., Chen, Q., … Ruan, R. (2009). Review of the biological and engineering aspects of algae to fuels approach. *International Journal of Agricultural and Biological Engineering, 2*(4), 1–30. http://doi.org/10.3965/j.issn.1934-6344.2009.04.001-030

Dunne, W. M. (2002). Bacterial adhesion: seen any good biofilms lately? *Clinical Microbiology Reviews, 15*(2), 155–66. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/11932228

Guldhe, A., Singh, B., Rawat, I., Ramluckan, K., & Bux, F. (2014). Efficacy of drying and cell disruption techniques on lipid recovery from microalgae for biodiesel production. *Fuel, 128*, 46–52. http://doi.org/10.1016/j.fuel.2014.02.059

Halim, R., Danquah, M. K., & Webley, P. A. (2012). Extraction of oil from microalgae for biodiesel production: A review. *Biotechnology Advances, 30*(3), 709–732. http://doi.org/10.1016/j.biotechadv.2012.01.001

Hammed, A. M., Jaswir, I., Amid, A., Alam, Z., Asiyanbi-H, T. T., & Ramli, N. (2013). Enzymatic Hydrolysis of Plants and Algae for Extraction of Bioactive Compounds. *Food Reviews International, 29*(4), 352–370. http://doi.org/10.1080/87559129.2013.818012

Kondaveeti, S., Choi, K. S., Kakarla, R., & Min, B. (2013). Microalgae Scenedesmus obliquus as renewable biomass feedstock for electricity generation in microbial fuel cells (MFCs). *Frontiers of Environmental Science and Engineering*. http://doi.org/10.1007/s11783-013-0590-4

Lee, D. J., Chang, J. S., & Lai, J. Y. (2015). Microalgae-microbial fuel cell: A mini review. *Bioresource Technology, 198*, 891–895. http://doi.org/10.1016/j.biortech.2015.09.061

Logan, B. E., Regan, J. M., Potter, M. C., Kim, B. H., al., et, Kim, B. H., … Lovley, D. R. (2006). Electricity-producing bacterial communities in microbial fuel cells. *Trends in Microbiology, 14*(12), 512–8. http://doi.org/10.1016/j.tim.2006.10.003.

Logan, B. E., Verstraete, W., & Rabaey, K. (2006). Critical Review Microbial Fuel Cells: Methodology and Technology †, *40*(17), 5181–5192.

Nair, R., Renganathan, K., Barathi, S., & Venkatraman, K. (2013). Performance of salt-bridge microbial fuel cell at various agarose concentrations using hostel sewage waste as substrate, *2*(5), 326–330.

Rashid, N., Cui, Y.-F., Saif Ur Rehman, M., & Han, J.-I. (2013). Enhanced electricity generation by using algae biomass and activated sludge in microbial fuel cell. *The Science of the Total Environment, 456-457*, 91–4. http://doi.org/10.1016/j.scitotenv.2013.03.067

Sander, K., & Murthy, G. (2009). Enzymatic degradation of microalgal cell walls. *ASABE Annual International Meeting, Reno*, 0300(09). Retrieved from http://www.researchgate.net/publication/228865662_Enzymatic_degradation_of_microalgal_cell_walls/file/d912f508732a29f4a6.pdf

Velasquez-Orta, S. B., Curtis, T. P., & Logan, B. E. (2009). Energy from algae using microbial fuel cells. *Biotechnology and Bioengineering, 103*(6), 1068–76. http://doi.org/10.1002/bit.22346

Venkata Mohan, S., Mohanakrishna, G., Srikanth, S., & Sarma, P. N. (2008). Harnessing of bioelectricity in microbial fuel cell (MFC) employing aerated cathode through anaerobic treatment of chemical wastewater using selectively enriched hydrogen producing mixed consortia. *Fuel, 87*, 2667–2676. http://doi.org/10.1016/j.fuel.2008.03.002

Zainal, M. H., Hassan, O. H., Ab Samad, L. S., Ali, A. M. M., & Yahya, M. Z. A. (2016). Energy conversion from biodegradation of non-thermal pre-treated algae biomass for microbial fuel cell. *Journal of Mechanical Engineering, 13*(1), 26-31.

Zhao, F., Slade, R. C., & Varcoe, J. R. (2009). Techniques for the Study and Development of Microbial Fuel Cells: An Electrochemical Perspective, (0), 1–54. Retrieved from http://epubs.surrey.ac.uk/chemistry/61