International Journal of Innovative Research in Engineering & Management (IJIREM)
ISSN: 2350-0557, Volume-2, Issue-5, September- 2015

Sequester of CO_2 and Power Generation in Photosynthetic Fuel Cells of *Chlorella vulgaris*

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ABSTRACT
The Photosynthetic Fuel Cell (PFC) is considered a promising new technology. This kind of Microbial Fuel Cell (MFC) uses microalgae as electron acceptors attached to the cathode compartment to decrease the operational costs with conventional MFC generating energy. Besides generate energy the microalgae have the ability to sequester atmospheric carbon dioxide by photosynthesis, and turn it into value-added biomass where the most valuable by-products are currently starch and lipids, which are the basis of the manufacture of biofuels such as bioethanol and biodiesel. In the present study the microalgae *Chlorella vulgaris* was used as an electron acceptor in a cathode compartment, where during ten days of experiments showed the amount of CO_2 captured by the algae cells (7mg L of CO_2). At the same time, the composition of the biomass was produced starch (3%) and lipids (70%), and electrochemical parameters such as coulombic efficiency (C_E = 33.1%) and the maximum current density (Id max = 147 mA cm²). The results confirmed the high potential of *C. vulgaris* in power generation PFC, and in the generation of products of industrial interest.

Keywords
Photosynthetic cathode, Biofuel cell, Microalgae.

1. INTRODUCTION
The modern world is totally dependent on fossil fuels; around 80% of all energy consumed in the world comes from this non-renewable energy source. Their use through the combustion process releases million tons of carbon dioxide into the atmosphere each day, aggravating the global warming process (Medeiros et al 2015).

Aiming to reduce the consumption of these fuels, several alternative technologies have been developed, among which we highlight the microbial fuel cell (MFC), which utilize the oxidation process of organic matter by micro-organisms to generate electricity (Rahimnejad et al., 2011).

However, in recent years, a range of MFCs has been drawing considerable attention from researchers, calls the Photosynthetic Fuel Cells (PFC), which are photo bioreactors that utilize photosynthetic microorganisms as microalgae for the production of electricity. In this type of MFC, microalgae are used as electron acceptors in the cathode compartment where simultaneously atmospheric CO_2 is converted into biomass and O_2, helping to reduce the excessive amount of this gas into the atmosphere (Zhou et al, 2012).

The aim of the present study with microalgae *Chlorella vulgaris* was utilized in the cathode compartment of a photosynthetic fuel cell using atmospheric CO_2, as a single source of carbon for energy production and analysis of the biomass by-products such as polysaccharide starch and total lipids.

2. MATERIALS AND METHODS
2.1 Configuration of the PFC
A bi-compartmentalized fuel cell was used as: a cathode compartment of 1L, an exploded carbon plate electrode with an area of 660 cm² immersed in the mineral culture medium, and the initial cell density of $3x10^3$ cell/mL^{-1} and exploded carbon electrode. Anode of1L, with a exploded carbon electrode immersed in a potassium ferricyanide solution 20 mmol/L^{-1} and as a cation exchange system was used a salt bridge of 5 cm on agar with KCl 3 M connecting the two compartments.

2.2 Photosynthetic Culture
The microalgae *C. vulgaris* was grown according to the modified method of Hernández 2014 in mineral medium with a relation C:N = 0,104 : 4,12 g/L^{-1} (Table 1), in 500 ml Erlenmeyer flasks with constant aeration, which were grown at room temperature (25° C) and illumination with photoperiod of 12 h – 12h (light / dark).

Cells were counted in a Neubauer chamber until they reached a density of 3 x 10^{-3} Cell/ml^{-1}. The suspension was centrifuged, resuspended in distilled water, centrifuged again, and resuspended in mineral medium used in the cathode compartment of the PFC. The cathode was maintained at room temperature, continuous illumination and constant aeration.

Table 1. Composition of mineral medium used in the experiments with *C. vulgaris*

Components	g/L
K_2HPO_4	75.00 x 10^{-3}
KH_2PO_4	1.75 x 10^{-3}
$MgSO_4$	75.00 x 10^{-3}
Urea	1.16 x 10^{-3}
$CaCl_2$	25.00 x 10^{-3}
NaCl	25.00 x 10^{-3}
EDTA	0.50 x 10^{-3}
KOH	3.10 x 10^{-3}
$FeSO_4$	498.00 x 10^{-3}
$H2SO_4$	1x 10^{-3} (mL)
Boric Acid	0.70 x 10^{-3}
$ZnSO_4$	706.00 x 10^{-3}
$MnCl_2$	116.00 x 10^{-3}
$CuSO_4$	126.00 x 10^{-3}
$Co(NO_3)_2$	0.40 x 10^{-3}
$(NH_4)_2MoO_4$	0.96 x 10^{-3}

2.3 Chronoamperometric Analysis

The potential (E) vs. time (hours) It was recorded using a Fluke 8080 multimeter with data acquisition software FlukeView® (Fluke Corporation, USA). The data of the chronovoltammetry as potential were converted to current density (Id) using Ohm's Law equation (Equation 1), since an external load resistor of 1 kΩ was used.

$$Id = E \times R \quad (1)$$

2.4 Coulombic Efficiency Calculation (C_E)

The coulombic efficiency (%) was calculated according to Equation 2. where CT is the theoretical amount that is obtained from each substrate and CR correspond to the actual amount obtained from each substrate and can be calculated by equation 3.

$$C_E = CR/CT \quad (2)$$

$$C_T = NZF \quad (3)$$

Where N is the number of moles of substrate, Z is the number of moles of electrons from the substrate and F is the Faraday constant (96.485.4 C mol^{-1}).

For a microbial fuel cell, it uses an integrated model Id vs. Time, generating Equation 4. Where M is the molar mass of the substrate, A = electrode area, V = total volume of the cathode compartment and ΔS the final concentration of the substrate (Morant et al 2014).

$$C_{E=} (M\int_0^{tf} Id\ dt\ A)/(FzV_{AC/CC}\Delta S) \quad (4)$$

2.5 Measurement of CO_2 Dissolved

Carbon dioxide was quantified with Compact Kit® for CO_2 quantification of Alfakit, using 10 mL of the cultured medium every day for 10 days, obtaining the results in mg L^{-1} CO_2.

2.6 Starch Content

The measurement of the amount of starch was carried out according to the proposed method in the article Appenroth 2010 which is based on a colorimetric method, where 200 mg of fresh biomass is homogenized in 4 mL of HCl at 18%. The suspension was stirred for 1 hour at 5 ° C and centrifuged for 20 min at 5000 g. Withdraw an aliquot which is mixed with the same volume of Lugol's solution (0,5% w / v of KI and 0,25% w / v of I2 in water) and measure the absorbance at 605 and 530 nm. The amount of starch was calculated according to Equation 5.

$$S = ([Cs \times Vol\ (Ext)] \times 100)/Fw \quad (5)$$

Where = A605/(0.07757 x P+4.463) , P=(7.295 x A605/A530-4.463)/(7.757-0.729 x A605/A530) x 100, the V(ext) = Seaweed extract volume after homogenization (mL), FW = fresh weight (mg).

2.7 Extraction of Total Lipids

To determine the percentage of lipids contained in microalgae cells, we used the method of Deven and Manocha (1980). Lyophilized biomass (100mg) was used for extraction total lipids using as solvents chloroform and methanol respectively in the following proportions, 2:1; 1:1 and 1:2 v/v. The extracts were evaporated using liquid nitrogen until total evaporation. The total lipids were calculated using the Equation 6, where T1 is the weight of the flask, and T2 is the weight of the flask after evaporation of the solvents, and B is the deep freeze lyophilize biomass until constant weight expressed in g/L.

$$\text{Total Lipids (\%)} = (T2\text{-}T1)/B \times 100\% \quad (6)$$

3. RESULTS AND DISCUSSION

3.1 CO_2 Consumption

The consumption of CO_2 by the microalga C. vulgaris t was accompanied by the end of the experiment showing an average daily consumption of 0.7 mg/L, consuming in the end of ten days of the experiment a total of 7 mg / L of CO_2 (Figure 1) which can be considered a good result taking into account of the volume and time of the experiment. Because is already a scientific knowledge that microalgae are responsible for the attachment of more than 50% of these gas in nature, as it have a photosynthetic efficiency 100 times higher than terrestrial plants (Pienkos and Darzins, 2009; Mendes et al., 2012).

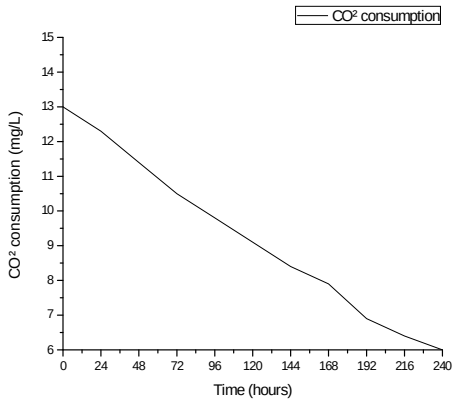

Figure 1. CO_2 consumption by *C. vulgaris* during ten days of experiments in PFC.

3.2 Biomass Analysis

Cell growth was quite high throughout the experiment, growing exponentially until it reaches a maximum cell density of 156 x 106 Cell/mL^{-1} (Figure 2), which shows a good adaptation to culture conditions and therefore a good accumulation of reserve material.

By analyzing, the composition of the biomass there was a small amount of starch, only 3%. However, the total lipid analysis revealed that the accumulation of this kind of storage material reached 70% of the total cellular. It is estimated that to produce 1kg of microalgae biomass, the fixing of about 1.83 kg of carbon dioxide is required (Jiang et al, 2013, Cheah et al 2015).

The accumulation of lipids may be influenced by various factors such as the initial amount of inoculum, lighting, pH, temperature and especially the C: N: P relations. For this ability to produce and accumulate lipids, C. vulgaris has been the target of several studies, as its fatty acids are good for the production of biodiesel as well as its biomass is rich in other components such as proteins which leads to a food highly nutritious (Schenk, 2008).

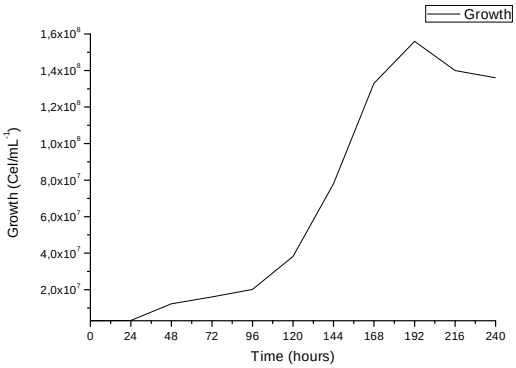

Figure 2. *C. vulgaris* growth profile in PFC bioanode.

3.3 Electrochemical Analysis

The results of chronoamperometry (Figure 3) show an increasing power generation during the 10-day experiment, with two peaks (86 hours with 120 mA/cm² and 144 hours with 130 mA/cm²) followed by a small loss and resumption of growth reaching a maximum current density production, Id max, of 147 mA/cm² and a CE = 33.1%, suggesting that the microalgae got a good efficiency in the use of CO2 as a substrate for power generation. As a superior performance to the results reported by other authors, such as Caprariis in 2014, who obtained values of 0.20 mA/m², equivalent to 0.00002 mA/cm² using the same organism and similar experimental conditions and lower than the results obtained in conventional microbial fuel cells. Even with a yield slightly lower, the PFC have some advantages, such as not requiring an organic substrate, they are powered exclusively by light, not emitting gases and consuming atmospheric carbon dioxide.

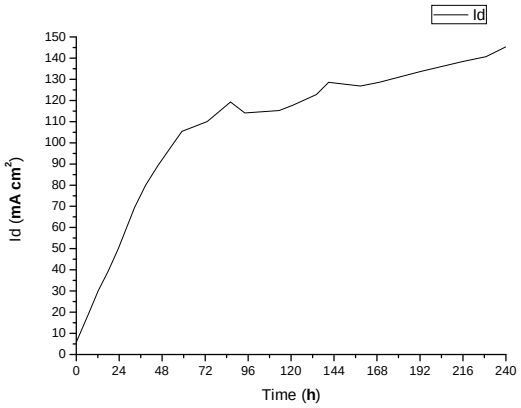

Figure 3. Chronoamperometric profile obtained from at PFC experiment with photosynthetic cathode of *C. vulgaris*.

4. CONCLUSION

The date obtained in this experiment further reinforce the great potential of the Photosynthetic fuel cells as an alternative to generate clean, renewable energy. Confirming that the use of a microalgae cathode as electron acceptor is feasible. The analysis of biomass also demonstrated that the microalgae has a great potential to sequester CO_2, which is a major cause of global warming, transforming it into commercially valuable products such as lipids which may be used in multiple areas and particularly in the generation of biofuels such as biodiesel.

5. ACKNOWLEDGMENTS

Our This work was financially supported by Higher Education Personnel Improvement Coordination (CAPES), National Counsel of Technological and Scientific Development (CNPq), Support Foundation Science and Technology Pernambuco (FACEPE) and We are also grateful to the Nucleus of Research in Environmental Sciences and Biotechnology (NPCIAMB), Catholic University of Pernambuco (Recife-PE, Brazil) for the use of its laboratories.

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