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Anodic pH Evaluation on Performance of Power Generation from Palm Oil Empty Fruit Bunch (EFB) in Dual Chambered Microbial Fuel Cell (MFC)

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The performance of dual chambered microbial fuel cell (MFC, Nafion 117, non-catalysed graphite electrodes) in concurrence with anodic pH microenvironment was evaluated based on bioelectricity generation from palm oil empty fruit bunch (EFB). Experiments were carried out at different anodic pH microenvironments (acidic (5), neutral (7) and alkaline (9)) using potassium permanganate catholytes with mixed consortia as anodic biocatalyst. In addition, power and microbial growth were also evaluated in order to connect the link between pH changes and MFC performance.

1. Introduction

Microbial fuel cell (MFC) is an alternative technology being developed in the laboratory that is capable of producing power or electricity from many kinds of organic substrates and treat wastewater at the same time. Di Palma et al. (2015) reported that by using both small laboratory based and scale-up based H-type MFC, the treatment of digested agricultural waste lead to approximately 60 % of volatile solid removal, with significant large amount of power generated in the small-scale based MFC. The MFC system includes the organic matters, electrolytes, both anode and cathode electrode, and ion-exchange membrane if applicable (Wang et al., 2015). The anodic environment is very important for the overall performance of MFC. It can influence the bacterial activity such as the degradation capacity and production of electron and protons and the overall electron transfers to the anodic electrodes (Cheng et al., 2008).

Previously, studies have been conducted using a modified single chamber MFC to utilise EFB as fuel for power generation. Results indicated that the utilisation of EFB as fuel in the MFC can generate a maximum power of approximately 0.7 W/m^2 (Nik Mahmood et al., 2015), which was 5-fold higher compared to a simple substrate such as glucose (Rossi et al., 2015). Others biomass which were subjected to pre-treatment prior to the use in MFC produces almost similar power density (i.e. steam exploded corn stover produces 0.4 W/m^2 (Wang et al., 2009). In a similar designed MFC, cassava peels were subjected to power generation with a value of 0.029 W/m^2 of power density (Adekunle et al., 2016).

In real situation, bacteria respond differently when there are changes in their internal and external environment, especially the pH changes. It was reported that neutral sternly remains the best pH condition which most microbial activity can adapt and progress to produce electricity in MFC. There are reports on the potential acidic or alkaline tolerant microorganism(s) that produced reasonable amount of power (Prasetsung et al., 2012). Some microbes will have to adjust due to the alteration of their normal environment, primarily in growth and degradation process (Batlle-Vilanovaa et al., 2014). The power output was reported to be elevated

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with the presence of catholyte such as ferricyanide (Raghavulu et al., 2009) or potassium permanganate (Eliato et al., 2016) in the cathode side of the MFC.
In the present study, the ability of two microbes mixed in a MFC to withstand the changes in the pH environment to produce electricity was investigated. The ability of these mixed microbes to extract electricity from complex substrates such as empty fruit bunch (EFB) was reconfirmed and compared with the pH changes.

2. Materials and Methods

2.1 Cell culture preparation and EFB pre-treatment

The microorganisms used were cultured and maintained in Luria-betani broth which was stored as aliquots in -80 °C. Prior to use, stock bacilli E1 and Clostridium cellulolyticum (CC) were thawed and each of the cell suspensions in total of 12.5 mL each were mixed thoroughly before it was transferred in the anodic side of a dual chamber MFC. For the preparation of EFB, dried EFB was obtained at local palm oil mill and was subjected to size reduction using a mill grinder and subsequently sieved to obtain particle size of between 250 mm to 400 mm sizes. Next, the EFB was subjected to alkaline pre-treatment as conducted previously (Nik Mahmood et al., 2015) to reduce most lignin content in the EFB. The physically treated EFB was soaked in excess of distilled water in a hot bath at 80 °C in order to soften it. Next the water was filtered and softened EFB was mixed with 2.5 M NaOH and autoclaved for 15 min at 121 °C. After filtration to separate the alkaline solution, addition of sodium hypochlorite (6 – 14 % active chlorite) was carried out for bleaching or delignification process. Finally, the EFB fibres were washed with access of tap water until the pH was neutralised.

2.2 MFC preparation

The two chambers MFC contained carbon electrodes with a Nafion 117 membrane (DuPont) in between to provide division of the chambers. The set-up was illustrated in Figure 1. The carbon electrodes were made of reticulated carbon cloth with a surface area of 20 cm^2 and connected with a copper wire to the auto-logged multimeter. Total amount of electrolyte which in this case, 0.1 M potassium phosphate (Kpi, pH 7.0) or otherwise stated was 250 mL for each compartment. In the anode compartment, the mixture of microbes was also mixed with 5.0 g EFB in 0.1 M Kpi. For the cathodic compartment, 0.005 M Potassium permanganate (KMn_4O_7) was added.

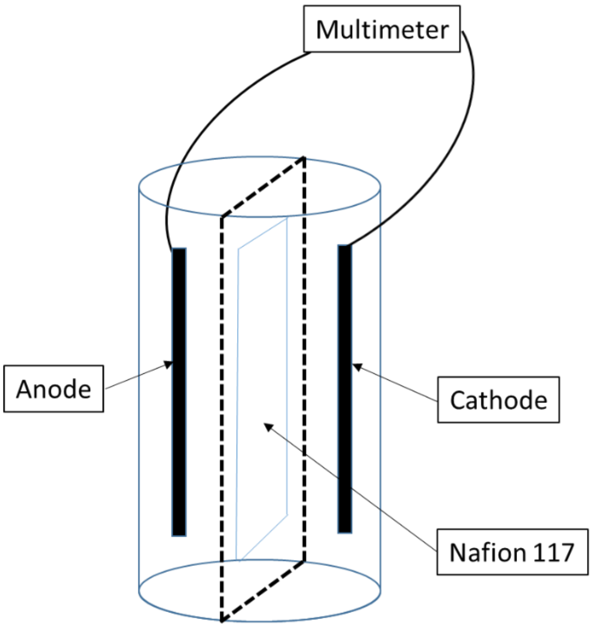

Figure 1: Schematic diagram of the dual chambered MFC.

2.3 MFC operation

Firstly, the MFC was operated in open circuit condition where no load was applied to the system in a batch mode. It was observed that after three cycles of operating in this condition, the OCV was stabilised. Subsequently, the circuit was connected to 1,000 Ω after a stable maximum OCV was achieved and voltage was measured as CCV data using auto-logged multimeter. Power and current were calculated based on the Ohm's Law, P = V × I and I = V/R. Power was normalised by the surface area of the anode electrode to obtain power density.

2.4 Microbial growth analysis

Growth of microbes was done by culturing both microbes in a MFC reactor with the same conditions as above without any multimeter connected. Samples were discarded from MFC every 2 h and immediately measured for its turbidity using UV/Vis spectrophotometer at wavelength of 600 nm.

3. Results and discussion

3.1 OCV profiles

Maximum OCV is considered as the true maximum achievable voltage for fuel cell system such as MFC (Logan et al., 2006). In thermodynamics term, electron motive force or E_{mf} can be evaluated via the OCV obtained and it was observed that more or less uniform voltage was produced in pH 7 cell compared to pH 5 and 9 as shown in Figure 2. This is due to the microbes' ability to adapt to different pH environment. The same observation applies with the CCV profile. However, in terms of power evaluation, OCV cannot be used as an indicator for the efficiency of a MFC system.

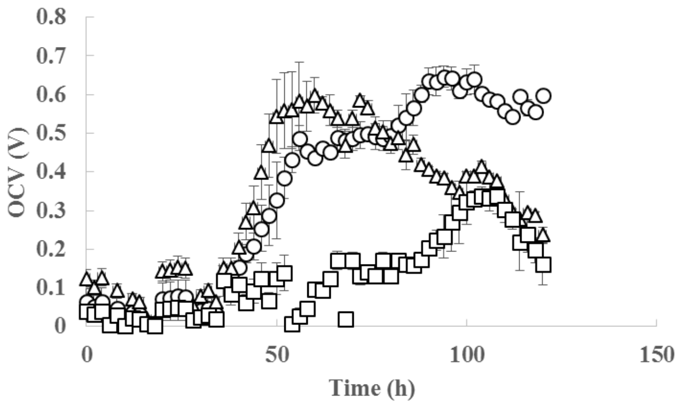

Figure 2: OCV profiles for different pH operated. The dual chamber MFC was operated twice for each pH values. Both first and second trial of each pH tested was plotted accordingly. '○', '□' and 'Δ' show the system were operated in pH 7, 5 and 9.

3.2 CCV profiles

In response to the load applied to the MFC system, a steady-state voltage was observed after 3 h of operation as shown in Figure 3.

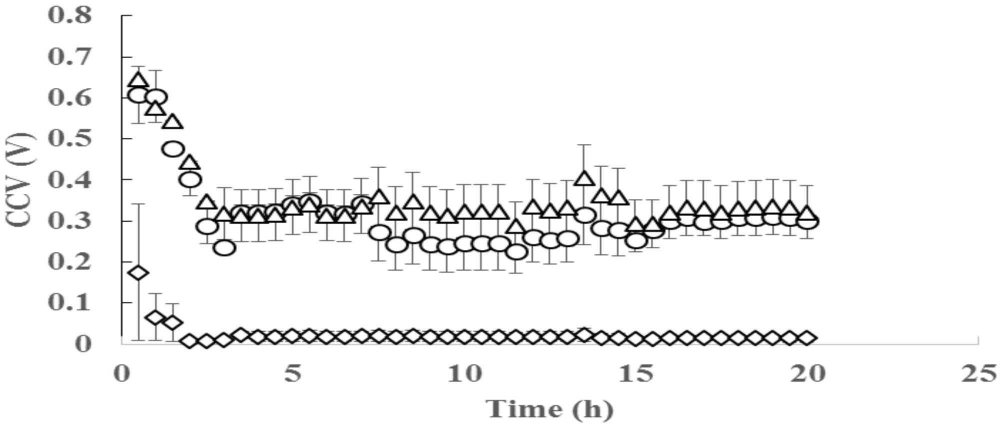

Figure 3: CCV profile for different pH. '○', 'Δ' and '◊' were pH 7, 9 and 5 respectively and each trial was done twice.

The system with pH 5 achieved the lowest voltage value compared to pH 7 and 9. The voltage produced was significantly low as what was observed in OCV results. If it is based on microorganisms' adaptability, the similarities for both OCV and CCV imply that both E1 and CC probably did not function efficiently in pH 5. CC was known to be able to adapt to acidic environment and sporulate efficiently in a low pH environment (Devausx and Petitdemange, 2002). However, E1 was not able to grow at low pH condition (data not shown) and OCV profiles as shown in Figure 2 did not show significant increment in the voltage either. This implies even if CC can actually degrades the pre-treated EFB and modulates further degradation of producing electrons, electrons cannot be transferred to electrode due to the minimum growth of E1. In contrast, at pH 7 and pH 9, the OCV and CCV were stable with a value two times higher compared with at pH 5 and considered to be suitable for the MFC to be operated using the culture mixture.
The calculated power density for all pH was summarised in Table 1 and compared with some of the reported power densities to date. The power densities at pH 7 and 9 shows comparable power density with other dual chambered MFC and are much higher than a fed batch mode of a complex substrate, CMC using two different microbes for electricity generation (Ren et al., 2007) was also the case in the present study. Some microorganisms did tolerate an initial pH as high as 10 to produce more than 0.4 V of voltage value (He et al., 2008) and pH 9 in the present day.

Table 1: Comparison of power densities of different substrates based MFC.

Type of MFC	Substrate or fuel	Condition of pH	Power densities (W/m^2)	References
Single chamber	EFB	7	0.7	(Nik Mahmood et al., 2015)
Dual chamber	Date syrup	7	0.06	(Ghoyeshi et al., 2011)
Dual chamber	Carboxymethyl cellulose (CMC)	7	0.143	(Ren et al., 2007)
Dual chamber	EFB	7 and 9	Average (0.32 – 0.33)	Present data

Several factors could have contributed to the effect of low voltage production. It was reported that acidification and alkalinisation occurred over time due to the proton diffusion phenomenon through the membrane (Olievera et al., 2013). Both acidification at the anode and alkalinisation will cause changes in the microbial metabolism activity and growth that effects the electron transfer efficiency (Zhang et al., 2011) and in (Yuan et al., 2011). Recent development in MFC reveals that pH gradient between anode and cathode could be solved by adding microbes in the cathodic side which can overcome the challenges of pH changes and poor oxygen reduction. However, further investigation in these two ways of microbial involvements in producing power should be conducted to investigate the overall differences.

3.3 Growth analysis

The microenvironment of anodic MFC was one of the determinant for efficient microbial growth and metabolism. pH changes may have altered one or both microbes present in the anode. Periodically samples were taken to access the microbial growth and is shown in Figure 4. It was clear that overtime no growth was observed in pH 5 but microbes seem to grow very well in pH 7 and 9. CC was not known to be able to grow in alkaline environment and growth trials showed less growth compared to pH 7 (not shown). In contrast, E1 has no effect in growth in alkaline condition but do not grow in more than pH 10 (data not shown). It was difficult to explain the similarities in voltage production for pH 7 and pH 9 as observed in Figure 2 as CC did not grow well in alkaline pH environment.
In a different study, specific growth coefficient has been proven to coincide with the growth of microorganisms in a fuel cell (Ledezma et al., 2012). Though the MFC system reported was operated in a fed-batch manner (which was different from the present MFC operation) with carbon source, the study proves that the maximum power output was produced at which microorganism grew at the maximum cell biomass production.

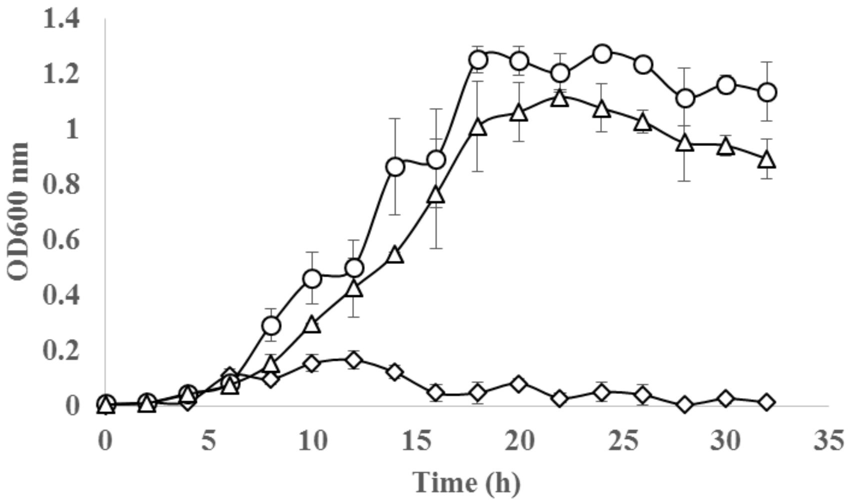

Figure 4: Microbial growth curve for mixture of E1 and CC. The evaluation was based on optical density values and measurement was done for growth in pH 5, 7 and 9 as indicated with symbols '◊', '○' and '∆'.

4. Conclusions

In the nutshell, the adaptability of microorganisms with the microenvironment pH is an important factor for power production. In response to pH changes, the MFC produced high voltage at pH 7 and 9 compared to pH 5 which gave low voltage in both open circuit and closed circuit orientation. These results were supported with the microbial growth analysis which indicates that at no significant growth was observed at pH 5 as compared to pH 7 and 9.

Acknowledgments

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