Treatment of Palm Oil Mill Effluent in Microbial Fuel Cell Using Polyacrylonitrile Carbon Felt as Electrode

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Abstract—**Palm oil mill effluent (POME) is an organic waste material produced at the oil palm mills. It is highly polluting due to its high content of biological and chemical oxygen demand. In the present paper, POME was treated using double chamber microbial fuel cell with simultaneous generation of electricity. Polyacrylonitrile carbon felt (PACF) was used as electrode and anaerobic sludge was used as inoculum throughout the MFC experiments. Various dilutions of raw POME were used to analyze the MFC power generation, COD removal efficiency and coulombic efficiency. Among the raw POME and different concentrations of POME used, the PACF with raw POME showed the maximum power density and volumetric power density of about 45mW/m^2 and 304mW/m^3 respectively but it showed low coulombic efficiency and low COD removal efficiency of about 0.8% and 45% respectively while PACF with 1:50 dilution showed higher COD removal efficiency and coulombic efficiency of about 70% and 24% but showed low power density and low volumetric power density of about 22mW/m^2 and 149mW/m^3 respectively. The results show that MFC possesses great potential for the simultaneous treatment of POME and power generation using PACF as electrode.**

Index Terms—**microbial fuel cell, Polyacrylonitrile carbon felt, palm oil effluent, wastewater treatment**

I. Introduction

Palm oil mill effluent (POME) is an organic waste material produced at the palm oil mills. During the production of 1 ton crude palm oil, more than 2.5 tonnes of POME is produced [1]. Typically, the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the POME are in the range of 15000 - 100000 mg/l and 10250 - 43750 mg/l respectively [2]. Over the past decades, several economically viable technological solutions have been proposed for the treatment of POME, including simple skimming devices [3], land disposal [4], chemical coagulation and flotation [5] aerobic [1] and anaerobic biological processes and other specialized treatments. Of these technologies, anaerobic treatment followed by aerobic biological processes are most widely used because of their particular advantages, such as low biomass yield, low nutrient requirement, and high volumetric organic loading. Recently, MFC emerged as one of the promising sustainable technologies; MFC is a bioreactor which converts chemical energy into electrical energy through catalytic reactions of microorganisms under anaerobic conditions [6]. As a result of the improvements in the last ten years, the power density of MFCs increased by 10000 fold [7]. Electrode is the key component in affecting the performance and cost of MFC. For all the types of electrodes, their base materials must generally be of good conduction, good chemical stability, high mechanical strength and low cost [8]. Microorganisms and substrates also the key factors which influences in the performance of MFC. Mixed cultures or microbial consortia have been shown to be robust and more productive than single strains and their extraction can be easily achieved from natural sources [9]. Complex substrates are hard for the microbes to digest so when complex materials used as substrates power generation will be generally lower than acquired from simple substrates. POME is one of the complex substrates comprising amino acids, inorganic nutrients such as sodium, potassium, calcium, magnesium, short fibers; organelles, nitrogenous constituents, free organic acids and a mixture of carbohydrates ranging from hemicelluloses to simple sugars etc [10]. In this study, performance of MFC with POME as substrate was investigated and also its power generation, COD removal efficiency and the effect of initial chemical oxygen demand on coulombic efficiency were analyzed. Anaerobic sludge was used as inoculum throughout the experiment and it showed potential in treating POME as well as generated bioelectricity. Polyacrylonitrile carbon felt (PACF) was used as electrode material in all the MFC experiments which is not reported elsewhere.

II. Materials and Methods

A. MFC Construction

The MFC was made of glass material (borosilicate) and was fabricated in china (Shangai sunny scientific, China). It consisted of two compartments; anode and cathode, with working volume of 450mL. PACF (Shangai sunny scientific, China) was purchased and used as electrode material for all the experiments. Equal size of

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PACF (4.9 x 0.9 x 5) was used as electrode in each compartment of dual chamber MFC. The anode and cathode compartments were separated by a Nafion 117 membrane (Dupont Co., USA). POME was charged in anode chamber and was inoculated with anaerobic sludge under N_2 atmosphere. The anode and cathode electrodes were connected by using copper wires with a resistor to form a circuit. Cathode was operated with $KmNO_4$ solution and its concentration was kept constant throughout the experiment. The fuel cells were operated at ambient temperature from 25 to 28 ℃. The schematic diagram of microbial fuel cell is shown in Fig. 1.

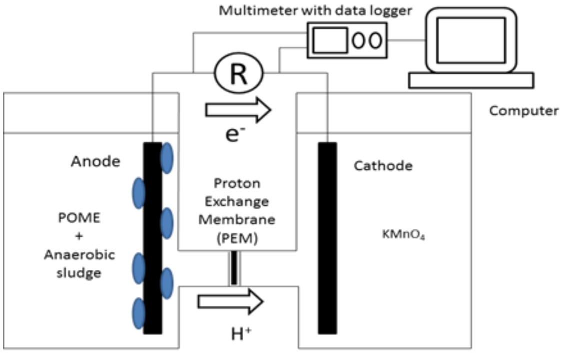

Figure1. Schematic diagram of double chamber Microbial fuel cell

B. Measurement and Analyses

The voltage and current across external 1kΩ resistor was measured every 15 min by using digital multimeter with data logger (Fluke 289). The polarization curves and power density curves were plotted using the voltage and current data. Power density (Pv, W/m^3) normalized by volume and power density normalized by surface area (P_A, W/m^2) were measured and calculated using the following The voltage and current is across an external 1kΩ resistor equations:

$$P = VI$$

$$P_{An} = \frac{V^2}{A_{An}R}$$

$$P_v = \frac{V^2}{vR}$$

where A = area of anode electrode (m^2), P = power (W), V = the potential (V), v = Working volume of anode (m^3), R = external resistance (Ω) and I = current (A). Polarization curves of the MFC were obtained by varying the external resistance (50 - 200000 Ω) and recording the steady-state potential after a period of 15 minutes.

C. COD Removal Efficiency and Coulombic Efficiency

COD was periodically analyzed by taking small amount of sample from the anode effluent for every 24hrs. The COD removal efficiency (η) was calculated using the following equation:

$$\eta = \frac{COD_0 - COD_t}{COD_0}$$

where COD_0=initial COD of the effluent in anode chamber, mgL^{-1} and COD_t = COD of the effluent in anode chamber at any time. The COD of the anode effluent was determined using COD cell test kit (0 -1500- mg/l range; Hach, USA) and measured using a COD reader (Hach DRB 200, USA).The CE for complex substrates can be calculated for a fed batch system [11] as :

$$CE = \frac{8\int_0^t Idt}{FV_{An}\Delta COD}$$

where ΔCOD = Change in COD concentration (mg/L), I= current (A), t = change in time (s), V_{An}= volume of liquid in anode compartment (l), F= Faraday's constant (96485 C/mol e$^-$). In Eq. 5, 8 is a constant, based on M_{O2} = 32 for the molecular weight of oxygen and b = 4 for the number of electrons exchanged per mole of oxygen.

D. Sampling and Wastewater Characterization

Raw POME and anaerobic sludge were collected from Felda palm oil industries located in Kuantan, Malaysia. The samples were transported to the laboratory in sterile 1000 mL Schott bottles placed in ice and stored at 4 ℃ until use. The wastewater characteristics such as chemical oxygen demand (COD), biological oxygen demand (BOD), total solids, total suspended solids, ammoniacal nitrogen, nitrate nitrogen and total dissolved solids were analyzed by standard methods [12].

E. Scanning Electron Microscope

Parts of the polyacrylonitrile carbon felt were cut and removed from the anode chamber then rinsed with a sterile medium, and followed the method described by Chae et al (2008) [13]. Desiccated samples were sputtered with platinum and observed using a JEOL JSM7800F field emission SEM at 3 kV.

III. Results and Discussion

A. Performance of MFC with POME

TABLE I. Efficiency of MFC Treatment with PACF

Parameters	Before MFC treatment with PACF (mg/L)	After MFC treatment with PACF (mg/L)	Removal % (MFC with PACF)
COD	60600	33200	45.21
BOD	24000	13200	45
Total solids	24050	9986	58.47
Total suspended solids	10040	2920	70.91
Ammoniacal nitrogen	23	10	56.52
Nitrate nitrogen	160	78	51.25
Total dissolved solids	12900	5320	58.75

POME was collected and characterized as shown in Table I. Wastewater treatment efficiency of the MFC with POME were evaluated by comparing before and after treatment values of wastewater parameters as shown in Table I. It can be seen that after 15 days of operation about 45.21 % of COD were removed from raw POME. The results are in accordance with the report in literature [14].

B. Current and Power Generation

MFC was operated with raw POME for simultaneous wastewater treatment and power generation. Current and power density vs. time from raw POME is presented in Fig. 2. The initial current generation, as well as the power generation with raw POME showed significantly higher which confirms the initial biological activity of the microorganisms. Thereafter, the power generation increased because of increased biological activity, and showed a plateau after 8 days of operation. Fig. 2 reveals that the current and power generation in the batch mode included the ascending phase followed by the stationary phase which is in accordance with the report in literature [15]. As the initial COD of the raw POME was very high, more substrates were available for the microorganisms to utilize it. However, most of the substrates were converted into fermentation products subsequently most of the electrons were not available for the power generation. Substrates in POME that are difficult to metabolize could be the reason for lower current in the MFC.

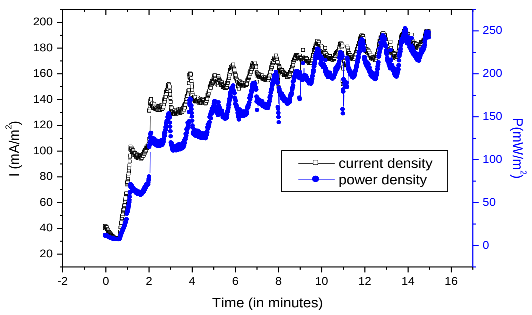

Figure 2. Profile of current densities and power densities of Raw POME in PACF MFC (1kΩ) with time

There are other several factors which affects the power generation of MFC. MFC with POME forms a thick biofilm on the electrode surface which interrupts the electron transfer from microbes to the electrode surface and it could be a reason for low power density produced by MFC with complex POME compare to MFC with simple substrates. Members of Proteobacteria have often been reported to predominate mesophilic MFCs [16] and the diverse bacterial populations in MFC anode electrode was obviously affected by the highly complex nature of POME substrate. It is generally known that fermentative bacteria are required to metabolize the complex organic materials of POME into fermentation products [17] of which EAB (electrochemically active bacteria) can oxidize and generate bioelectricity. The lack of electrochemically active bacteria could also be the reason for incomplete utilization of POME.

C. Effect of Initial COD on CE

Fig. 3 depicts the coulombic efficiency and power density of MFC with PACF varies with different dilutions of initial COD. As can be seen that coulombic efficiency increases with the decrease of initial COD and power density decreases with the decrease of initial COD, among the samples, PACF with 1:50 dilution showed higher coulombic efficiency than PACF with 1:1, 1:25 and without dilution. Low CE has been reported as a common issue in the MFC systems fed with real or complex wastewater.

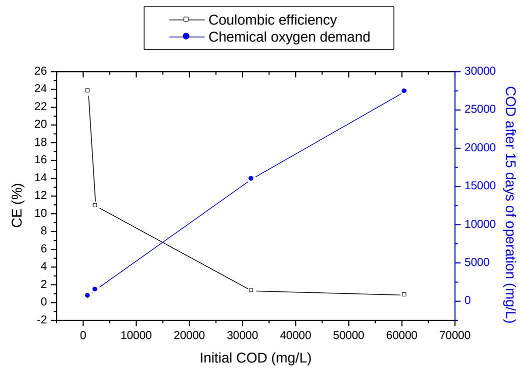

Figure 3. Effect of initial COD of POME on coulombic efficiency

The main reason for this has been proposed to be other available electron acceptors in POME consuming electrons, thus lowering coulombic efficiency [18]. While among the samples PACF with undiluted sample showed higher power density than PACF with 1:1, 1:25 and 1:50. Higher power density obtained due to more availability of electrons from complex POME with higher COD content but still large number of electrons were not available since which were locked inside the fermentation products produced by fermentative bacteria [17]. We have successfully shown that using the MFC, power density of about 95.39mW/m^2 acquired from the 1:50 diluted POME and also 24% of the available electrons were recovered as current whereas power density of about 241.53mW/m^2 were obtained from the undiluted POME and only 0.8 % of the electrons recovered as current after 15days of operation.

D. Effect of Initial COD on Wastewater Treatment

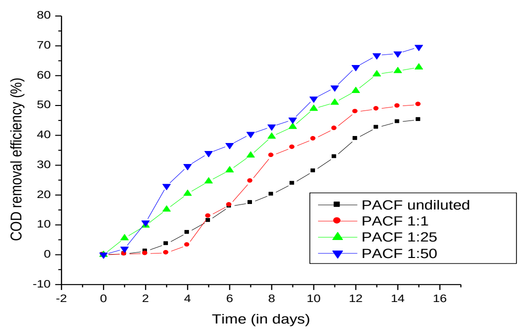

Figure 4. COD removal efficiency of PACF MFC at different dilutions of raw POME with time

The COD removals of the palm oil mill wastewater in the MFC system over time are shown in Fig. 4. The figure shows that COD removal efficiency increases with increased dilution of initial COD. As time increased, the efficiency increased and reached a maximum of approximately 70%, 63%, 50% and 45% for PACF MFC with 1:50, 1:25, 1:1 and without dilution of initial COD respectively after 15days. Besides that PACF with 1:50 dilution of initial COD has acquired higher COD removal efficiency than PACF with 1:25, 1:1 and without dilution of initial COD.

E. Polarization and Power Density Curves

Polarization and power density curves were obtained for MFC with polyacrylonitrile carbon felt as anode and cathode at different dilutions. The open circuit potential (OCV) was higher in the case of PACF with undiluted initial COD than PACF with different dilutions of initial COD as shown in Fig. 5. MFC with PACF at 1:1 dilution, 1:25 dilution, 1:50 dilution and without dilution produced maximum power densities of about 27 mW/m^2, 25mW/m^2 , 22 mW/m^2 and 45mW/m^2 respectively whereas, maximum volumetric densities produced about 183 mW/m^3, 169 mW/m^3, 149 mW/m^3 and 304 mW/m^3 respectively. MFC with undiluted POME showed maximum power density than other diluted POME samples. Increased dilution results in decreased power production and increased coulombic efficiency. When comparing the energy obtained from the current system to literature, it seems that palm oil mill wastewater has a great potential to benefit from the use of MFCs to simultaneously treat and generate electricity.

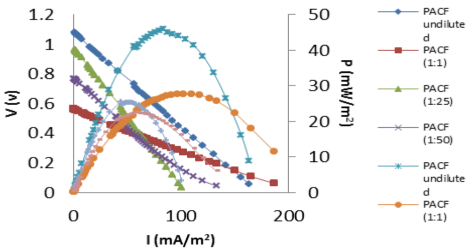

Figure 5. Polarization and power density curves of PACF MFC at different dilutions of raw POME

F. Biofilms on the Anode

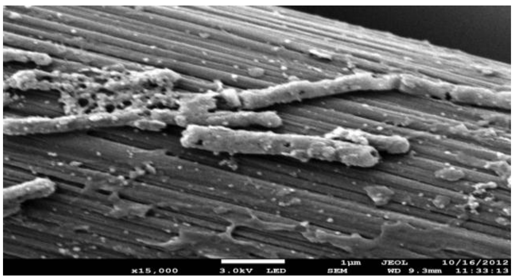

Figure 6. SEM images of bacteria growing on anode PACF in the MFC fed with POME as electron source for 15 days

In order to confirm the presence of biofilm on the electrode surface, SEM of the anode after 15 days of operation in MFC is conducted and the results are presented in Fig. 6. As shown in Fig. 6, different types of bacteria were attached to the electrode surface, which acted as biocatalyst to transfer electrons to the electrode. Bacteria growing on the anode appeared to be heterogenous (Fig. 6). Biofilms were sparsely distributed on the PACF along with highly complicated structures comprised of morphologically different cells. Rod shaped cells seemed to be abundant than other types of cells.

IV. Conclusion

In this study, polyacrylonitrile carbon felt, a new type of electrode material in MFC was used to treat palm oil mill wastewater whilst generating electricity. COD removal efficiency of approximately 45% was achieved in the MFC system with undiluted POME (raw POME). Maximum power density achieved about 45 mW/m^2 in MFC with raw POME but CE of the MFC operated with raw POME was found very low (~1%) and the CE was increased with the decrease in initial COD of the POME. For 1:50 dilution the CE was found as 24% after 15 days of operation. Further works including the development of MFC systems that are able to utilize both fermentative and nonfermentative substrates in POME are crucial to better utilize this type of highly complex and abundant organic feedstock for electricity generation.

Acknowledgements

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