Evaluation of electricity generation and wastewater treatment from Palm oil mill Effluent using single and dual chamber microbial fuel cell

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Abstract— Microbial Fuel Cells (MFCs) can be simultaneously used for the treatment of wastewater and generation of electricity. In this study, single chamber air-cathode MFC (sMFC) and double chambered MFC (dMFC) were compared for the palm oil mill effluent (POME) treatment and generation of electricity while *Pseudomonas aeruginosa* (ATCC – 27,853) was used as inoculum and POME used as substrate. The dMFC was efficient and found to be producing maximum power density of 4.2 W/m^3 whereas sMFC produced a maximum power density 1.7 W/m^3. Moreover, the dMFC showed higher COD (54%) removal when compared with sMFC (41%). The significant power generation and COD removal efficiency observed in dMFC might be attributed to the microbial catalyzed and reversible electrochemical reactions occurring in the anodic chamber and cathode chamber of dMFC. These results suggest that dMFC is efficient than sMFC in producing electricity as well as in treating wastewater.

Keywords— Microbial fuel cell; Palm oil mill effluent; Energy recovery; Dual chamber MFC; Single chamber air-cathode MFC.

1. INTRODUCTION

Microbial fuel cells are gaining more and more interest as an alternative eco-friendly energy source that generates electricity, simultaneously cleaning up environmental pollutants [1]. The depletion of fossil fuel, global warming and various dimensions of environmental pollution are the major ecological challenges in recent days. In this context, an MFC becomes a fascinating green technology because of its ability to recycle environmental wastes by utilizing organic substances contained in them using microorganisms as biocatalysts [2].

Palm oil mill effluent (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.[3]. It is an organic waste material produced at the palm oil mills. During the production of 1 ton crude palm oil, more than 2.5 tons of POME is produced[4]. Typically, the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the POME are in the range of 15,000–100,000 mg/L and 10,250– 43,750 mg/L, respectively. Due to its acidic nature (pH 3.4–5.2), high values of chemical oxygen demand and BOD, POME can cause considerable environmental problems if discharged without effective treatment [5, 6].

Generally, MFCs often consist of two compartments, the anode and cathode, which are often separated by a proton-exchange membrane (PEM). The anode chamber contains microorganisms that oxidize the available substrate (i.e., the electron donor). However, incomplete reduction of oxygen leads to low energy conversion efficiency and produces reactive intermediates and free radical species which can be destructive. While the electrons travel through the circuit, the corresponding protons migrate to the cathodic compartment through a proton exchange membrane to maintain charge neutrality. At the cathode an electron acceptor (e.g., oxygen) is reduced by the electrons via the circuit and the protons via the membrane [7].

Several types of MFCs have been developed, including two-chamber, single-chamber, up flow membrane-less and tubular designs. Among the different types of MFCs that have been developed, the sMFC is the most likely configuration to be scaled up for wastewater treatment due to its high power output, simple structure, and relatively low cost[8]. Moreover, the mass transport loss is minimized due to direct oxygen supply from ambient air to the electrode. Although several conveniences have been reported for sMFC but some severe cruxes such as sluggish reaction rate in cathode, cathode flooding via anodic solution and aerobic microbial growth has not been resolved thus leading to mass transfer losses resulting low power output of air-cathode MFCs. In addition, oxygen depletion and substrate loss are occurred in the cathode due to the growth of heterotrophic aerobic bacteria[9].

In this study, the treatment efficiency of POME (real complex wastewater) has been accomplished using sMFC and dMFC. The electricity generation and wastewater treatment efficiency with time evaluated and compared between sMFC and dMFC.

2. MATERIALS AND METHODS

2.1 Inoculum preparation

The pure culture *P. aeruginosa* (ATCC - 27853) was used as an inoculum. Enrichment of the cultures was carried out by preparing an overnight culture in LB broth (10% v/v) incubated at 37^o C with shaking at 150 rpm. The overnight culture (10% v/v) was used as inoculum in the anode compartment. Additional nutrients were not given for microorganisms except the nutrients present in the POME.

2.2 MFC fabrication operation

Single chamber and double chamber MFC were constructed as shown in Fig.1. The reactors were constructed using non-reactive plexi glass with dimensions of 5 X 5 X 5 cm. Carbon brush was used in both anode and cathode as electrode material. The electrodes were connected by using titanium wire. The anode and cathode compartments were separated by a Nafion 117 membrane (Dupont Co., USA). Prior to use, nafion membrane was soaked overnight in dilute HCL and then heated at 100^{o}C for an hour to remove organic impurities. The solution was allowed to cool at room temperature. Thereafter, the Nafion membrane was drenched in deionized water for 24 hours followed by washing with DI water several times. The POME was fed to the anode chamber and Potassium permanganate (catholyte) was fed to the cathode chamber in dMFC. In sMFC and dMFC, similar anode conditions were maintained. In sMFC, the electrocatalyst, MnO_2 and the electrode were prepared using the method as described by Woon et al. 2015 [10]. In brief, the catalyst ink was prepared by mixing as-prepared MnO_2 with 0.15 mL of 5 wt% Nafion solution and 0.15 mL of isopropanol. The catalyst ink was ultrasonicated for 20 min. The prepared MnO_2 ink was evenly dispersed onto a 2 mm thick Polyacrylonitrile carbon felt (PACF) surface with the dispersion area of 7 cm^2.The Nafion 117 membrane (Dupont Co., USA) with a dimension of 5 cm × 5cm was boiled in 0.1 M H_2SO_4 solution for 30 min, followed by boiling in deionized water for 1 h. Pre-treated membranes were kept in deionized water overnight at room temperature before use. The membrane-electrode-assembly (MEA) was prepared by hot pressing catalyst/PACF with the pre-treated Nafion 117 membrane for 2 min at both sides. The press temperature and pressure were set at 100 °C and 1 bar, respectively. The electrodes were placed in the chambers, then were sealed and made air tight. Both the reactors were checked for water leakage.

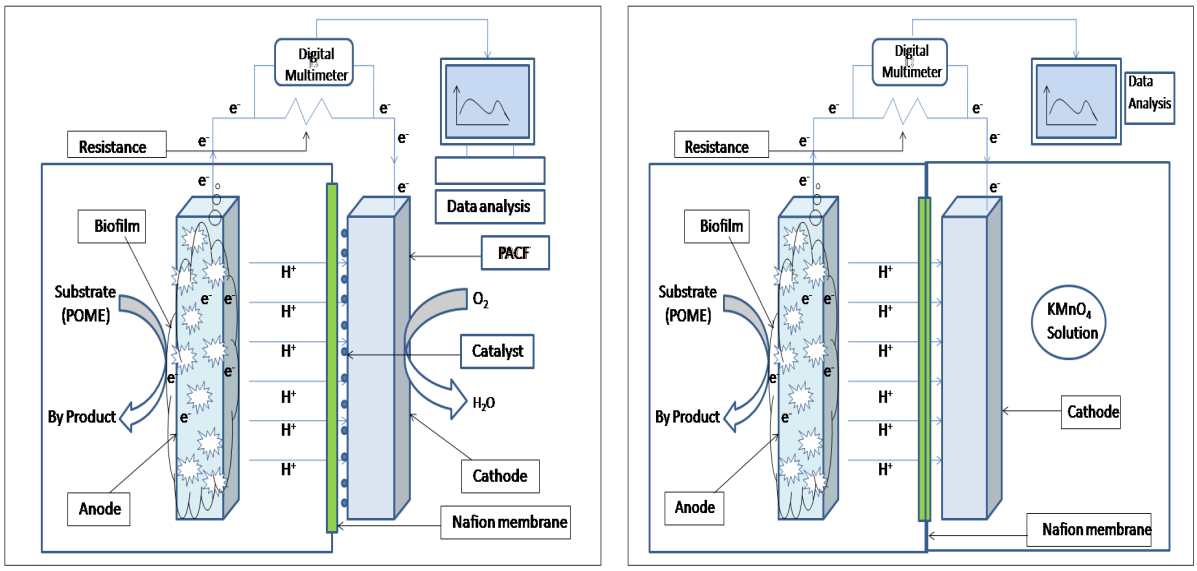

Figure 1: Schematic diagram of sMFC and dMFC

2.3 Measurement and analyses

The voltage (V) and current (I) across an external resistor (1 kΩ) in the MFC circuit was monitored (15 mins intervals) using a digital multimeter with data logger (Fluke 289 True RMS Multimeter, USA) connected to computer through USB cable adapter. External resistance was varied from 50 to 20,000Ω to obtain polarization curve. Power density normalized by surface volume (P_V, W/m^3) were mentioned and calculated using the following equations

$$P = VI \quad (1)$$

$$P_V = V^2/vR \quad (2)$$

The COD removal efficiency (mg/L) and CE of the complex substrates were calculated as described by Baranitharan et al. [11]

2.4 POME Characterization

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].

3. RESULTS AND DISCUSSIONS

3.1 Performance of MFCs

The electrochemical performance of sMFC and dMFC were investigated using MFC fed with 50% POME (COD=26,260 mg/L) and inoculated with 1 mL of *P. aeruginosa* (ATCC – 27853) broth culture. The power density curve of sMFC and dMFC are shown in Fig 2. On day 1, maximum power density was obtained from sMFC 482 mW/m^3 whereas dMFC obtained 948 mW/m^3 which is about 2 fold higher than sMFC. Power generation gradually increased with time in both sMFC and dMFC until 7 days of operation could be due to increased execretion of phenazine-based compounds such as pyocyanin produced by *P. aeruginosa*. These naturally-produced redox mediator (electron shuttle) may be involved in facilitating the extracellular electron transfer, thus resulting in the increase in electricity generation [13]. On day 7, sMFC reached maximum 1677 mW/m^3 alternatively dMFC reached 2130 mW/m^3. After 7 days of operation, sMFC power generaion started decreasing might be due to increase in the microbial growth in air face cathode surface as well as in cathode catalyst that possibly hindered proton accumulation from anode as well as increased internal resistance [2]. A thick biofilm on catalyst layer may adversely influence the cathode performance through several mechanisms: (1) it may function as a diffusion barrier to the transfer of H^+ and charged ionic species to the catalyst sites (3) the aerobic bacteria may consume a portion of the available oxygen at the catalytic sites and thus reduce the oxygen reduction reaction (ORR) kinetics (4) the extra-cellular secretions (e.g. proteins, polysaccharides) of the attached microorganisms may change the physicochemical properties of catalysts (e.g. surface functional groups, pore size distributions and hydrophilicity), thus reduced their ORR catalytic activity[14]. As a result, the suppressed cathode performance, an increased internal resistance coupled with a decreased electricity (power) generation of MFCs after long term operation was observed in many studies[15, 16]. Moreover, The electrochemical reaction irreversibility happened that affect MFC performance and enhenced activation losses, ohmic losses, and mass transport losses. [7]. However, in dMFC, power generation still increasing until 11 days of operation due to lack of cathode limitations. After 10 days of operation, dMFC achieved maximum power generation of 4140 mW/m^3. Thereafter, power generation started decreasing for dMFC might be due to resulting of multilayered biofilm which interrupted electron shuttle mechanism of *P. aeruginosa.* Although, biofilm is a crucial component of MFC that allows considerable conversion capacity and opportunities for extracellular electron transfer[17] but an increase in the thickness of the inactive biofilm layer over time could reduce the electricity generation might be due to less electrical conductivity of the dead biofilm compared to the viable biofilm, as well as greater diffusion path needed for electron transport from live cells to the surface and depletion of the substrates at the electrode surface[18, 19]. Polarization and power density curve for sMFC and dMFC as shown in Fig. 3. It can be observed that sMFC obtained maximum power density 1677 mW/m^3 whereas dMFC obtained 4140 mW/m^3 which is about 2.5 times higher than sMFC.

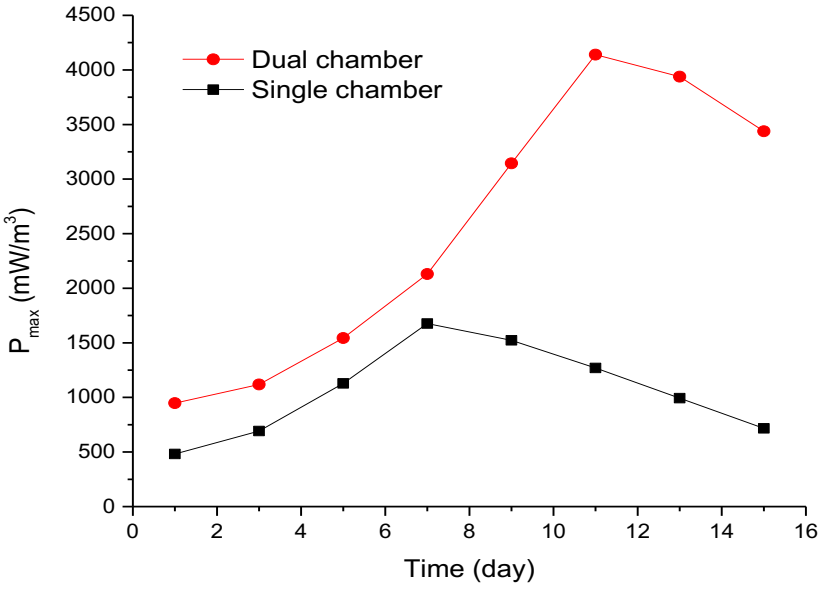

Figure 2: Maximum power densities of sMFC and dMFC vs. time

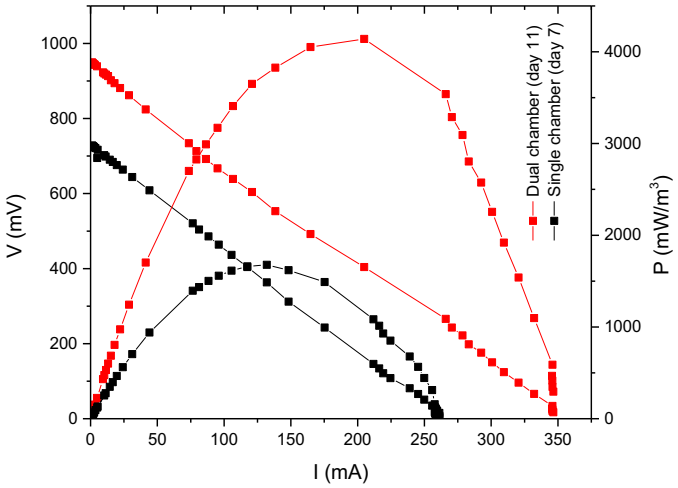

Figure 3: Polarization curves of sMFC on 7th day and dMFC on 11th day

3.2 POME treatment efficiency

Table 1: Efficiency of POME treatment using sMFC and dMFC

Parameters	**Before treatment (mg/L)**	**Treatment using dual chamber (mg/L)**	**Treatment using single chamber (mg/L)**	**Removal efficiency using dual chamber (%)**	**Removal efficiency using single chamber (%)**
COD	26,260	12,150	15,280	54	41
BOD	11,238	4,622	5,352	59	52
NH_3 - N	18	9	11	50	38
TS	12,224	5,118	6,225	58	50
TSS	4,267	1,356	1,829	68	57
NO_2-N	72	37	48	48	33
TDS	6,321	3,161	4,123	50	35

*COD - Chemical oxygen demand, BOD - Biological oxygen demand, NH_3-N – Ammonical nitrogen, TS – Total solid, TSS – Total suspended solid, NO_2-N – Nitrite nitrogen, TDS – Total dissolve solid.

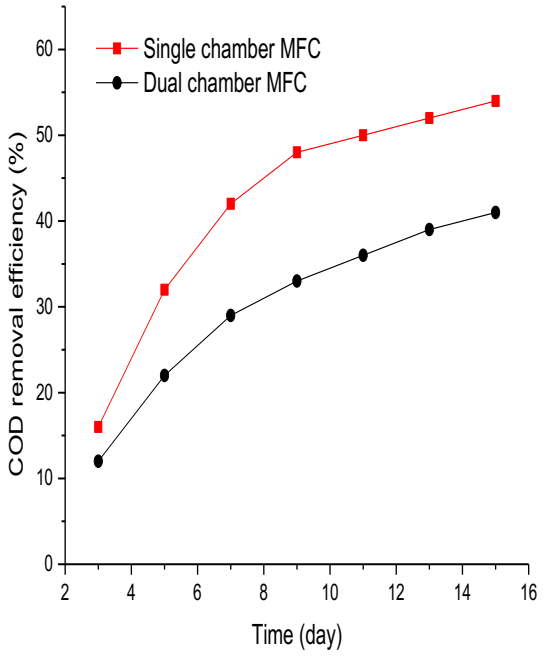

Figure 4: The COD removal efficiency after different days of operations using sMFC and dMFC

Analysis of the POME treatment using sMFC and dMFC were evaluated by comparing wastewater parameters before and after treatment as shown in Table.1. The dMFC was found to be effective for wastewater treatment compare to sMFC. The COD removal efficiency in both MFC is shown in Fig 4. The maximum COD removal was achieved 41% and 54% using sMFC and dMFC respectively. The COD removal using dMFC was higher than that of sMFC. Similar results were achieved by Hampannavar et al., 2011 [20] using distillery wastewater as a substrate. The sMFC achieved lower COD removal efficiency perhaps incomplete reduction of oxygen due to microbial growth in cathode which leads to low energy conversion efficiency. Ammonia reduction has previously been observed in fed-batch mode single and two-chamber MFCs by Kim et al. 2008 [21]. In the present study, the dMFC was found to be effective at removing ammonia (NH3–N). Generally, the biological nitrification would occur in the cathode compartment of the MFC, which was probably the primary route of ammonia removal. Moreover, The cathode plays an important role in the consumption of electrons by reducing electron acceptors such as nitrate [22]. The dMFC promotes nitrogen removal by both biological nitrification and denitrification might be due to the good reversibility of anode and cathode in dMFC [23].

4. CONCLUSIONS

The outcome of the work indicates that effective treatment of POME using dMFC and sMFC. The dMFC proves to be more effective to produce significant electricity generation as well wastewater treatment when compared with sMFC owing to complete reversible electrochemical reaction. Further beneath study is needed to elucidate the complete cathode mechanism and contribution in electrochemical performance of sMFC and dMFC .

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