Application of OPEFB Fibre Based Electrode in Microbial Fuel Cell System for Electricity Generation and Chlorophenol Degradation

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Abstract. Microbial fuel cell (MFC) has emerged as one of the potential technologies for sustainable bioelectrical energy recovery and reduction of recalcitrant wastes. The MFC performance is greatly influenced by the anode materials which serve as the support for exoelectrogenic bacteria attachment. In this study, oil palm empty fruit bunch (OPEFB) is proposed as an alternative anode material prepared via a direct carbonization process using tube furnace owing to its good conductivity property. The carbonization process was conducted under nitrogen gas flow at 900°C with a constant heating rate of 5°C/min. The anode was prepared by mixing the carbonized OPEFB with polytetrafluoroethylene (PTFE) binder. When used in MFC, the OPEFB-anode generated a maximum current density of 97.30 mA/m², which is comparatively higher than that of the conventional carbon cloth anode (76.24 mA/m²). Our MFC system had also resulted considerable chemical oxygen demand (COD) and 2-chlorophenol reductions of 77% and 75%, respectively. This study could support future research on freely-available OPEFB materials for high performance MFC anode.

1. Introduction
A microbial fuel cell (MFC) is a bioelectrochemical device that harnesses the microbial metabolic energy to convert organic waste into electricity [1]. Nowadays, there is an increased interest in MFC technology due to the exceptional benefits in energy conversion efficiency and mild reaction conditions to be applied in wastewater treatment and electricity generation [2]. The typical MFC reactor consists of an anode and cathode chambers, which hold the electrodes, and a bridge containing a proton exchange membrane (PEM) through which the protons (H⁺) pass from anode to cathode for circuit stabilization [3].

Electrode plays an important role in MFC. The electrode especially anode in MFC is not only used as conductor but also acts as a support for the formation of bacterial biofilms and therefore needs to be biocompatible with the bacterial cells in the MFC [4]. The power generation efficiency, cost, and performance of MFC are greatly influenced by the electrodes materials in the MFC [5].

Carbon materials such as carbon cloth, carbon rod, carbon mesh are frequently used as anodes for their stability in microbial cultures, wide surface area, and high electrical conductivity [6]. Besides, carbon materials also have good biocompatibility, high efficiency in heterogeneous electron transfer kinetics, and excellent chemical stability [7]. However, the price of the refine-carbon based electrode

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materials has been estimated for over half of the overall cost of MFC reactors [8]. Therefore, it is important to find a low-cost electrode material with high efficiency for sustainable MFC usage.

Malaysia is known as one of the countries in South East Asia with the largest production of palm oil in the world. Large production of palm oil resulted abundance of oil palm empty fruit bunch (OPEFB) as by-products. The annual production of OPEFB in Malaysia is 8.5 million tons [9]. However, only small amounts of OPEFB is used as fuel in boilers and fertilizers in palm oil plantations, while most of them were disposed of in landfills [10]. A previous study conducted by Farma [9], shows that carbon materials can be obtained from EFB fibre and has been used as an electrode in supercapacitors.

A biomass-derived electrode is advantageous because it has a porous structure, low-cost, high conductivity, and eco-friendly properties [8]. The carbon materials from OPEFB can be obtained through the carbonization method. The carbonized OPEFB fibres are then bonded with a conductive binder and pressed to form an electrode. The strong, stable and highly porous electrode for bacterial attachment is a key element in MFC operation for optimum electricity generation and contaminant removal.

Phenols are harmful organic contaminants that contain a hydroxyl (-OH) group attached to the benzene ring. Phenols and phenolic compounds are mostly present in the wastewater effluent of numerous industrial activities such as resin and plastic manufacturing, oil refineries, cooking plants, pharmaceuticals, and petroleum industries [11]. Phenol and phenolic compounds are listed as priority pollutants by the US Environmental Protection Agency (EPA) and Malaysian Environmental Quality Regulations, due to their acute toxicity, carcinogenicity, and resistance to decomposition in the environment [12]. Besides, after being released into the environment, the phenol will react with water and transformed into phenolic compound such as chlorophenols, alkylphenol, and methyl phenol that are more recalcitrant, toxic, and persistent than phenol [13].

Therefore, it is vital to treat phenolic contaminated wastewater before it could pose more harmful effect to the environment. This study investigated the ability of the OPEFB electrode in generating electricity and reducing COD and phenolic compounds simultaneously. The OPEFB electrode was electrochemically tested by polarization curve and coulombic efficiency analyses to determine its potential as an ideal MFC electrode with good bacterial attachment property.

2. Materials and methods

2.1 Electrode fabrication

Palm oil empty fruit bunches (EFB) and palm oil mill effluent (POME) were obtained from Malpom Industries Sdn. Bhd.,Nibong Tebal, Penang, Malaysia. EFB fibres were treated using 0.4 M sulfuric acid (H₂SO₄) at 80°C for 2 h to remove any impurities from the fibre surfaces and to generate a porous structure in the carbonaceous material for high carbon yield [14]. Then, the fibres were washed with distilled water to obtain neutral pH and dried overnight in an oven at 80°C. After drying, the EFB fibres were carbonized in a tube furnace at 900°C under nitrogen gas (N₂) at a flow rate of about 300 mL/min for 2 h. Then, the EFB fibres were grinded manually in a mortar to obtain carbonized EFB powder.

EFB electrode was prepared by mixing 70 wt% of carbonized EFB powder with 30 wt% polytetrafluoroethylene (PTFE) to form a slurry and compressed by using a metal compressor. The materials obtained were dried in an oven at 100 °C for 1 hour. Then, a piece of titanium wire was bonded to the EFB electrode with a conductive epoxy fixative to form electrical connections and to be used as anode electrode in the MFC [8].

2.2 MFC setup and operation

A double chamber MFC was constructed by two 500 mL Schott bottles, joined by glass tubes that consist of a cation exchange membrane (CEM) (2.5 cm in diameter) between the chambers. The anode chamber consisted of 30% v/v of POME inoculum and 70% v/v of growth media. The growth media was composed of chemicals: 0.3 g CaCl₂, 0.53 g K₂HPO₄, 1.07 g K₃HPO₄, 1 g NaCl, and 0.2 g MgSO₄.
mixed with glucose and 2-chlorophenol (50 mg/L) in 1000 mL distilled water. Nitrogen gas was sparged into the anode chamber and the chamber was tightly closed to ensure strict anaerobic conditions.

The cathode chamber was filled with 100 mM phosphate buffer solution and was fully opened for aeration. The carbonized EFB electrode was used as anode and cathode electrodes with a dimension of 5 cm × 5 cm. A titanium wire was connected to both anode and cathode with external resistance (1 kΩ) and the voltage output was monitored by using a computer. The MFC system was operated on a magnetic plate to ensure well mixing and to maintain the temperature at 30-35°C. A control MFC was similarly set up with a commercial carbon cloth (5cm × 5 cm) as the electrode.

2.3 Electrochemical analysis
The current generated by the MFC was measured and recorded across the external resistance (1 kΩ) by using a multimeter (ASAKI) for over five days. The polarization curve was developed by applying different external resistance within a range from 10 Ω to 100 kΩ when the voltage was at steady-state conditions [15]. The recorded current was divided by the external resistance value to obtain the voltage value based on Ohm’s law where V=IR. The voltage and current value was used to derive the power output. The power density (mW/m²) and current density (mA/m²) were determined by dividing power and current by anode surface area in m².

2.3.1 Coulombic efficiency. The coulombic efficiency (CE) for both of the MFC systems was calculated by using the following formula:

\[
\text{CE} = \frac{\text{MI}}{\text{Fbq} \times \Delta \text{COD}}
\]

where M is 32 g/mol which is the molecular weight of oxygen, I is the highest current density, F is Faraday’s constant, q is the volumetric influent flow rate and \( \Delta \text{COD} \) is the difference between the initial and final COD readings taken on the first day and at the end of MFC operation, respectively.

2.4 Phenolic degradation
2-Chlorophenol (50 mg/L) was used as the main carbon substrate with intermittent glucose addition for steady growth, hence electrical generation. 5 mL of samples were collected every 24 h and were centrifuged at 4000 rpm and 4 °C for 10 min. The supernatant was used to analyze the degradation of 2-chlorophenol (2-CP) by the MFC. The degradation of 2-chlorophenol was analyzed by using Folin-Ciocalteau method.

2.5 Folin-Ciocalteau method
To examine the 2-chlorophenol degradation using Folin-Ciocalteau’s method, 1 mL of the supernatant was mixed with 5 mL of Folin Ciocalteau’s reagent (diluted tenfold) and 4.0 mL of sodium carbonate solution (75 g/l). After 30 minutes, the absorbance was determined at 765 nm by using a spectrophotometer and were compared with the 2-chlorophenol standard calibration curve [16]. The phenolic degradation (%) was determined as the difference between the initial \((C_0)\) and final concentration \((C_f)\) of 2-CP, based on the samples taken at the first and the last day of MFC operation, respectively.

2.6 COD removal
COD removal is an important parameter to evaluate the MFC treatment efficiency. The COD removal was determined by using the colorimetric method. The COD reading was measured daily by using a COD kit. 2.5-mL samples from the AC and MFC anode chamber were added into COD reagent vials and heated at 150 °C using block digester for two hours. After two hours, the COD value was measured with a COD spectrophotometer (HACH Company, Colorado, USA).
3. Results and discussion

3.1 Electricity generation

The MFC was operated by using OPEFB electrode as the anode and cathode in the double chamber MFC. The control MFC was operated using commercial carbon cloth electrode. The performance of the OPEFB electrode used as the anode in double chamber MFC was investigated for over five days. The current density generated by both MFCs with respect to time was illustrated in Figure 1. 2% of glucose solution is added into the MFC every 24 hours. The result showed that the current density gradually increases as the glucose is added to it. The maximum current density is generated on the third day of operation where MFC equipped with OPEFB electrodes produced 97.3 mA/m² higher than the carbon cloth electrode which generated 76.24 mA/m².

Based on Figure 1, the current density value increased once glucose is added until the third day of operations. However, after the fourth day, the current density kept decreasing until the last day of operations. The decreased current produced might be due to recalcitrance and toxicity of the 2-chlorophenol that hindered the bacterial growth in the MFC [17]. The biofilm formed on the surface of the OPEFB electrode and the current density produced by the MFC indicates that the OPEFB electrode has the potential to be used in MFC and is able to replace the commercial carbon electrode. The OPEFB electrode MFC was tested for the subsequent electrochemical analyses.

![Figure 1. Current density generated by MFC with OPEFB electrode (A) and control MFC (B). The arrows indicate glucose feedings.](image)

3.2 Polarization curve

The trend of MFC potentials can be demonstrated by a polarization curve that consists of the voltage as a function of the current density. Figure 2 illustrates the polarization curve with varying external resistances ranging from 10 Ω to 100 kΩ. The polarization curve also presents the MFC performance in maintaining its voltage as a function of the current production. The maximum power density occurred at a point where internal resistance equal to external resistance. From the power density curve in Figure 2, 1496 mW/m² power density was obtained at external resistance of 10,000 Ω in MFC with the OPEFB electrode and the corresponding current density is 13.68 mA/m². The power density curve describes the power as a function of current density. The power density started to drop beyond the maximum point due to the increasing ohmic losses. The power also drops because of the electrode over-potentials where no more power is produced [18].

In comparison with the previous researches that used biomass-derived electrode, our OPEFB electrode produced comparatively higher power density than loofah sponge [19] and chestnut shell [8] electrodes which produced 701 mW/m² and 850 mW/m², respectively. However, research conducted by Zhang et al. [20] used bamboo as an electrode in MFC and generated 1652 mW/m² power density.
The higher power density generated might be contributed by the higher surface area and porous structure of the electrode [8].

![Polarization curve](image_url)

**Figure 2.** Polarization curve.

### 3.3 Coulombic efficiency

Coulombic efficiency (CE) is a principle that demonstrates how well the recovery of electrons resulted from the oxidation of the substrate in the form of an electric current. It defines the quantity of actual amount of electrons that received from the bacterial utilization of substrate in the form of electricity against the theoretical amount of electrons that are donated by the bacteria based on the COD removal [21]. The CE hence describes the MFC performance in terms of power generation. In this study, the CE value for MFC with the OPEFB electrode is 17% while the CE in MFC with carbon cloth electrode is 15%. The CE values obtained in this study were relatively higher than that of those reported by Luo et al. [17] where their MFC only achieved less than 10% of CE. The previous study by Song et al. [22] also used phenol as the carbon source also generated a lower value of CE which is only 3.68%. These results occurred because of the different conditions, source of inoculum, and electrode used in the MFC. The relatively higher value of CE achieved by our MFC might be attributed by the lower oxygen diffusion of the membrane [23] and the capability of the biofilms formed on the anode causing high stability in electricity generation.

### 3.4 Phenolic degradation

The 2-chlorophenol concentration in MFC was observed for five days. The 2-chlorophenols were used as the carbon source for the bacteria in the MFC. It can be depicted from Figure 3 that both MFCs could degrade the 2-chlorophenol compound. However, OPEFB-electrode MFC performed better with 75% removal while MFC with commercial electrode removed only 44% of 2-chlorophenol in five days of operations. The MFC with the OPEFB electrode proved that the higher 2-chlorophenol degradation correspond to the higher electricity generations where the phenolic compound was used as the bacteria carbon energy. The results however showed a lower removal rate compared to the study conducted by Luo et al. [17] and Hedbavna et al. [24] which removed more than 90% of phenol from the MFC. The difference removal rate capability might be due to the different bacterial inoculum source which has adapted differently towards the toxic phenolic compound.
3.5 COD removal
In this study, the maximum COD removal was 77% and 66% achieved by MFC with OPEFB electrode and the control MFC, respectively. From Figure 4, it can be observed that MFC with the OPEFB electrode removed higher COD value compared to that of control MFC. This result proved that MFC with the OPEFB electrode is relatively more efficient in wastewater treatment. Besides, this study demonstrates a high COD removal with a high current generation compared to the previous study by Hanif et al. [18] which used the same source of POME inoculum but removed low COD despite the high current generation.
4. Conclusion

Electricity was successfully generated by the double chamber MFC with the OPEFB as the electrode. The highest current density produced by the MFC with the OPEFB electrode is 97.3 mA/m², higher than that of the control MFC with commercial carbon cloth at 76.24 mA/m². The MFC with OPEFB electrode could also remove 75% of recalcitrant 2-chlorophenol and 77% of COD suggesting that the electrode is relatively efficient for wastewater treatment. These results proved that the OPEFB electrode could be highly favourable as the alternative low-cost electrode for MFC application.

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