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Short Communication

Potential of Biochar-Anode in a Ceramic-Separator Microbial Fuel Cell (CMFC) with a Laccase-Based Air Cathode

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Abstract

A cost-effective biochar derived from rubber tree sawdust was prepared by low-temperature pyrolysis at 500ºC for 2 h. The biochar was placed as an anode electrode in the anode chamber of the novel model ceramic-separator microbial fuel cell (CMFC) with a laccase-based air cathode. The rubber wastewater (with 500 mg/L sulfate and 1000 mg/L COD) was used as an anolyte. Maximal volumetric power density (PD) of 3.26±0.08 μW/m^3, maximal volumetric current density of 3.20±0.07 mA/m^3, and system internal resistance of 1002 Ω were obtained. The post-treatment results showed sulfate removal and COD removal efficiencies of 88.26±1.29% and 89.77±0.45%, respectively. Our work provided a novel model of a low-cost and economically friendly MFC system. Moreover, this work demonstrated a potential route based on sustainable and economical biochar as a bio-anode for wastewater treatment in an MFC.

Keywords: csawdust, yeast, rubber wastewater, sulfate, electricity generation

Introduction

A Microbial fuel cell (MFC) can directly convert the chemical energy in a substrate to electricity by anode reaction. This technology can be used as a wastewater treatment system and can simultaneously removal xenobiotics [1]. In the MFC, the proton exchange membrane (PEM) such as Nafion, is a significant factor that affects the cost of the development (reaching 3000 USD per m^2) and the performance both in xenobiotic removal and electricity production. Therefore, a low-cost and environmentally friendly cation separator is essential [2]. Previous studies have established that ceramics can offer stability, improve power and treatment potential, create a better condition for the exo-electrogenic bacteria

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to reach resource recovery and even remove pathogens from the wastewater [3-4].

Biochar is a carbon-rich material produced from a biomass pyrolysis process in a low-oxygen condition [5]. It is a cost-effective material for several areas such as management and rehabilitation of infertile soil [6-8]. Moreover, a previous study has indicated that the biochar provides a high surface area for exo-electrogenic biofilm to generate electricity with low-cost operation [9].

Natural rubber is the raw material for the broad range of products such as tires, adhesives, and gloves [10]. In the rubber industry, a massive volume of rubber wastewater is discharged. It is usually treated by stabilization pond methods. In this system, the sulfuric acid is added for rubber particles recovery, and it can convert to sulfate under an anaerobic condition that is harmful for human health [11-12]. Moreover, the stabilization pond system requires a vast installation area and emits a green gas [13].

This study aimed at developing the novel model of a low-cost MFC system with laccase-based cathode by using ceramics as a cation separator. The saw dust-biochar was used as an anode in a bio-electricity generation and simultaneous removal of sulfate from rubber wastewater.

Experimental

To prepare the ceramic chamber, the ceramic clay was used to create a chamber. The external diameter was 12.0 cm, inner diameter was 11.6 cm, thickness was 0.2 cm and height was 10.0 cm. It was prepared according to Gajda et al. [14]) at 800ºC for 3 h in an electrically heated furnace. The ceramic chamber was soaked in deionized water (DI water) overnight before it was used.

To prepare the laccase-based air cathode, the 5.0 g of sterile weight constant coconut coir was inoculated by 3.5 mL 7-day-old yeast *G. reessii* in potato dextrose broth (initial moisture of 70%). Then it was incubated at 30ºC for 7 days to produce an extracellular laccase [15]. To prepare the rubber tree sawdust biochar, it was prepared according to a modified method of previous studies [16-17] at 500ºC for 2 h in an electrically heated furnace. The sawdust biochar was sterilized to remove a contaminated bacteria before it was used.

The 10 cm^2 of stainless steel mesh was used as an air-cathode, and 10 cm^2 of sawdust biochar was used as an anode. The electrodes were linked by 1.0 mm diameter stainless steel wire. The anode chamber was made by 1.5 L of the glass cylinder. The ceramic chamber was inserted at the top of the anode chamber, and the diagram of the CMFC is shown in Fig. 1. The rubber wastewater (500 mg/L sulfate and 1000 mg/L chemical oxygen demand (COD)) was prepared according to Chaijak et al. [15].

To operate a CMFC, the 0.9 mL of rubber wastewater was filled into the anode chamber. The

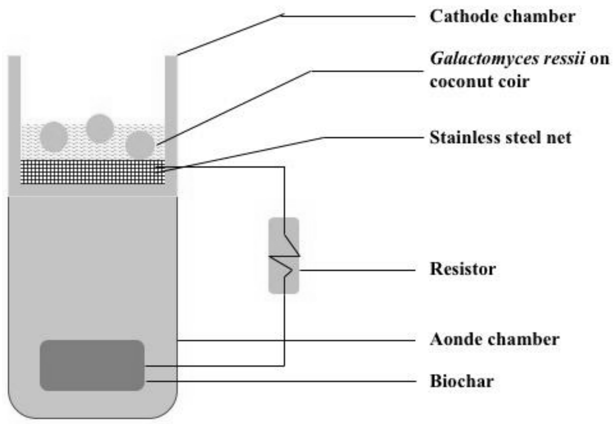

Fig. 1. Diagram of the novel model CMFC with a sawdust biochar anode.

rubber wastewater sludge was collected from the local rubber industry in Southern Thailand. The microbial community was described in Chaijak et al. [15]. The fermented coconut coir with laccase-producing yeast *G. reessii* was planted on the top of a stainless steel mesh electrode to catalyze the reduction reaction on a cathode surface. The open circuit voltage (OCV) was monitored by LabView software (National Instruments, United States) and the data was collected every 10 mins for 24 hrs. The closed circuit voltage (CCV) was studied by connecting with seven different resistors (33, 150, 270, 330, 390, 1002, 2150 Ω). The power density (PD), current density (CD) and the power curve were calculated by the previous study [2, 15].

The COD was determined by a Hach 21259-25 COD test kit (Hach, United States). COD removal (%) was calculated following Eq.1:

$$\text{COD removal (\%)} = [(COD_A - COD_B)/COD_A] \times 100 \tag{1}$$

…where COD_A and COD_B are the initial COD and final COD. The sulfate concentration was monitored by the turbidimetric method [18]. Sulfate removal (%) was calculated following Eq. 2, where A and B are the initial and final sulfate concentrations.

$$\text{Sulfate removal (\%)} = [(A-B)/A] \times 100 \tag{2}$$

Results and Discussion

Developing cost-effective and highly applicable material for electron acceptance is essential to increasing the electrical production of a bio-electrochemical system [19]. In our study, the sawdust biochar was prepared at 500ºC for 2 h and was used as a bio-anode of the novel model CMFC with the low-cost laccase-based air cathode. This study provided the two novel points: 1) it was the first work to apply the CMFC with a biochar-anode to treat a rubber wastewater (sulfate and COD removal) and simultaneously generate a bio-electrical

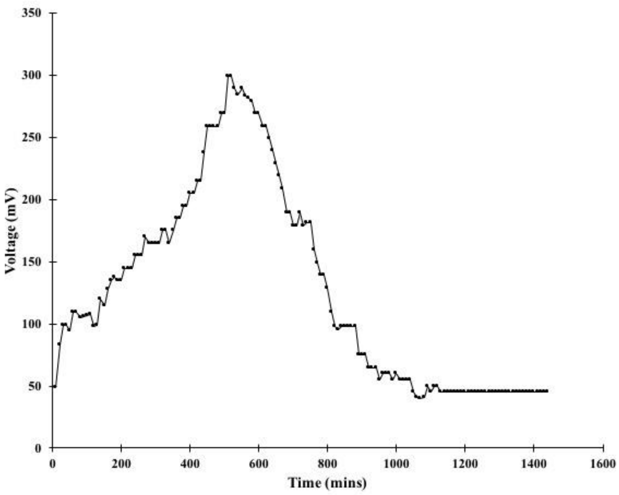

Fig. 2. OCV of the novel model CMFC with a sawdust biochar anode.

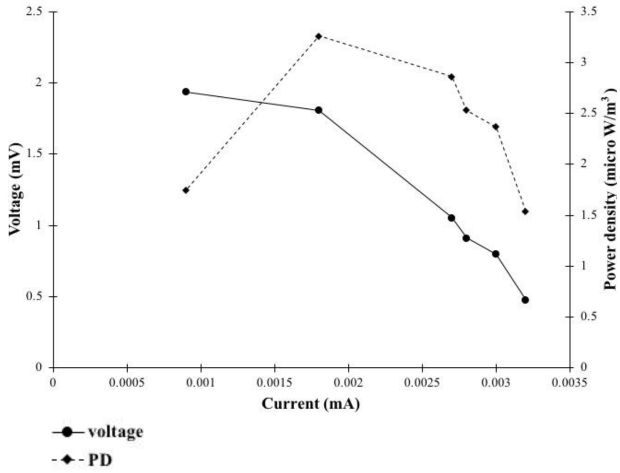

Fig. 3. Polarization and power density curves of the novel model CMFC with a sawdust biochar anode.

energy and 2) it used the whole-cell laccase-producing yeast *G. reessii* planted on cathode electrode of the CMFC to enhance electricity generation instead of high-cost platinum. Fig. 2 shows the novel model CMFC with a sawdust biochar-anode producing the maximal OCV at 278.83±17.32 mV (N = 3) at 500 mins. The maximal CD of 3.20±0.07 mA/m^3 (0.32±0.01 µA/cm^2) (N = 3) and maximal PD of 3.26±0.08 µW/m^3 (N = 3) were obtained (Table 1). Fig. 3 shows the polarization curve and power density curve of the CMFC with the biochar anode electrode, and this result indicated that the internal resistance of this system is 1002 Ω.

The rubber wastewater with the 500 mg/L sulfate removal and the 1000 mg/L COD was used as anolyte in an anode chamber to prove the wastewater treatment efficiencies of this CMFC system under 24 h of operation. The post-treatment data showed the sulfate removal of 88.26±1.29% (N = 3) and the COD of 89.77±0.45% (N = 3). To treat the rubber wastewater, several methods, including MFCs, had previously been used. Jiang et al. used the multi-membrane technology to treat the rubber wastewater. In this system, the rubber wastewater is pretreated by sand filtration and cartridge filtration. Then the filtrated wastewater is forced to pass through the ultrafiltration, nanofiltration and reverse osmosis membrane. The result showed this complex process achieved 99% of COD removal without generating energy production and sulfate removal. So, this system is limited by its cost of operation, complex process, and outcome [20]. The use of an ozone reactor in rubber wastewater treatment has been reported. In this system, the 22.7 mg/L of ozone was added into wastewater. The 71.80% of COD removal efficiency that was obtained [21] was lower than our study by 20.02% with the addition of an exogenous chemical.

To achieve both wastewater treatment and energy production, MFC technology has been interested. Our previous work used the conventional dual chamber MFC to generate electrical energy. The results indicated that this MFC system can produce the maximal OCV of 250 mV, which was lower than this study by 10.34%, while the sulfate removal and COD removal were not determined [15]. Sukkasem and Laehlah used the upflow bio-filter circuit MFC to treat rubber wastewater, but this system still used a commercial anode electrode. Their results showed that 70.00% of sulfate removal and 80.00% of COD removal were lower than our study by 20.69% and 10.88% [12]. Comparison of the sulfate and COD removal efficiencies of the CMFC system and other microbial fuel cells is shown in Table 2. However, CMFC performances were lower than some other works, reaching 7.09% to 10.30% [22-23], that use the commercial electrode as an anode.

To prepare the biochar, many biomass materials have been used. In other hands, the biochar was made from algae prepared at 750ºC for 2 h. It was used as a bio-anode to produce electrical energy. Their study used the well-known exoelectrogen Shewanella oneidensis. The mineral medium was used as chemical energy for a bacterium to convert to an electric. The result showed the maximal current density of 9.1 µA/cm^2,

Table 1. Electrochemical properties (N = 3) of the novel model CMFC with a sawdust biochar-anode.

Resistance	Voltage (mV)	Current density (mA/m^3)	Power density (µW/m^3)
33	--	--	--
150	0.48±0.01	3.20±0.07	1.54±0.06
270	0.8±0.01	2.96±0.04	2.37±0.06
330	0.91±0.00	2.77±0.01	2.53±0.02
390	1.06±0.01	2.71±0.02	2.86±0.04
1002	1.81±0.02	1.80±0.02	3.26±0.08
2150	1.94±0.05	0.90±0.02	1.75±0.08

Table 2. Comparison of sulfate and COD removal efficiencies and electrochemical properties of the CMFC system and other microbial fuel cells.

MFC type	Microbe	Anolyte	Membrane	Anode	OCV (mV)	Sulfate removal (%)	COD removal (%)	Reference
CMFC	Sludge	Rubber wastewater	Ceramic	Sawdust biochar	278.83±17.32	88.26±1.29	89.77±0.45	This study
Upflow Bio-filter circuit	Sludge	Rubber wastewater	None	Iron core carbon fiber brush	NA	70.00	80.00	[12]
Dual chamber MFC	Sludge	Rubber wastewater	Nafion 117	Carbon cloth	250.00	NA	NA	[15]
Dual chamber MFC	Sludge	Textile wastewater	Nafion 117	Carbon felt	580.00	95.00	NA	[22]
Multi-chamber MFC	Sludge	Sulfate-contaminated wastewater	Nafion 117	Iron core carbon fiber brush	NA	98.40	NA	[23]

but wastewater treatment efficiency was not provided [19]. Moreover, the previous study was presented using corncob biochar as a bio-cathode electrode in a single-chamber MFC. In their work, the biochar was prepared at 650ºC for 2 h. The maximal volumetric PD of 458.85 mW/m^3 was achieved while an anode was made from the commercial carbon felt [24]. Thus, our study indicated that the low-temperature prepared sawdust biochar can be used as a low-cost and environmentally friendly anode in the MFC.

Conclusions

The cost-effective CMFC model is an example of clean technology that uses low-cost biomaterials and biocatalyst (laccase). It enabled the treatment of sulfate and COD in wastewater like other MFC designs without energy consumption. The CMFC with a sawdust biochar anode can generate a volumetric maximal power density with 3.26±0.08 μW/m^3. However, the CMFC with a sawdust biochar-anode has to be developed in order to achieve more electrical power outcome in future work.

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Conflict of Interest

The authors declare no conflict of interest.

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