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RESEARCH PAPER

Power Recovery and Sulfate Removal from Rubber Wastewater with the Novel Model Multi-Electrode Microbial Fuel Cell

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ABSTRACT
Microbial fuel cell (MFC) is a well-known technology that can convert contaminated substrate in the wastewater to electrical power. To gain more power output, the multi-electrode MFC was developed owing to it has a high surface area for anaerobic microbe adhesion. Here we show the multi-anode was made from the bamboo charcoal was combined with laccase-based cathode in the ceramic separator MFC for the rubber wastewater treatment and enhancing the power generation. The untreated rubber wastewater with initial COD and contaminated sulfate concentration of 3,500 mg/L and 1,100 mg/L was used as a anolyte. The 843.33±5.77 mA/m^3 of CD, the 711.23±9.76 mW/m^3 of PD were generated. Moreover, this system reached 83.07±3.01% of sulfate removal when it was operated at 30 °C for 12 hr. This study recommended that multi-anode with laccase based MFC can more successfully produce energy from untreated rubber wastewater. it will be greater in terms of electricity generation and sulfate removal.

KEYWORDS: Laccase, Bamboo charcoal, Biocathode, Aerate-MFC, Electricity Generation.

INTRODUCTION

Natural rubber is one of the most important economic agricultural products in Southeast Asia including Thailand. Natural rubber processing factories discharge huge amounts of wastewater from several processes (Watari et al., 2015). The rubber wastewater contains chemical oxygen demand (COD), volatile fatty acid (VFA) and sulfate with 3,900 – 8,200 mg/L (Chaiprapat et al., 2011). Sulfate is a hazardous pollutant, the discharge of an excessive load of sulfate can affect public water supplies and human health. The upper concentration limit of sulfate in groundwater intended for human intake is suggested by approximately 250 mg/L. Hence, sulfate contaminated wastewater requires treatment before it is discharged to the environment (Blazquez et al., 2016). The natural rubber processing factories normally use the anaerobic-aerobic lagoon system for rubber wastewater treatment. Existing treatment processes have a high chemical oxygen demand (COD) removal of 90% . Though, this process requires a large operating area, expensive operating costs and long hydraulic retention time (Mohammadi et al., 2010; Nguyen & Luong, 2012).

Microbial fuel cell (MFC) relies on electroactive bacteria to utilize organic or inorganic material for a bio-electricity generation. It is a potentially useful method for wastewater

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treatment with simultaneous energy production. The main advantage of MFC for wastewater treatment include energy-saving, sludge volume reduction and bio-electric production (Zhang et al., 2019). The MFC with a stainless steel electrode has been reported in the rubber wastewater treatment. The results at days-18 of operation indicated that 40% of nitrogen removal and the net power output of 64 mW/m^2 were gained (Das et al, 2017). In the study of Selvaraj et al. (2020), the dual-chamber MFC has been used to treat an electro-Fenton pretreat rubber wastewater with 2,660 mg/L initial COD. The COD removal of 96.0% and high power output were gained. However, these processes still need the electro-Fenton reaction to drive the system. In Thailand, the upflow bio-filter circuit (UBFC) MFC has been applied to remove sulfate in the rubber wastewater. 70.0% of sulfate has removed by these systems, but only a small amount of electricity was generated (Sukkasem & Laehlah, 2015). In our previous study, the laccase-based cathode MFC has developed to generate electrical energy from the rubber wastewater. The data indicated that only a small amount of power density has been produced (Chaijak et al., 2018).

Normally, the MFC contains only a single set of electrodes. To investigate the scalability of MFC for enhancing electricity generation, the multi-electrode MFC is developed. The 8 separate anode electrodes are made from the graphite fiber brush. The results displayed the multi-electrode MFC can be scaled up based on the electrode area (Rader & Logan, 2010). The study of Ahn & Logan (2012) suggested the scaling up of MFC requires a compact reactor with multiple electrodes. It has interested to use for the distillery wastewater treatment. The maximum power output of 597 mW/m^2 is observed (Sonawane et al., 2013). Moreover, the multi-electrode is combined with a ceramic separator to design the low-cost reactor. It rewards low internal resistance and high power output when sucrose is used as a substrate (Ghadge et al., 2016).

Our previous study uses the laccase-based single-electrode ceramic separator MFC (CMFC) to recover an electron and remove contaminated sulfate molecule from the rubber wastewater. The maximal power output of less than a microwatt is produced (Chaijak et al., 2020). Thus, this study aims to combine the CMFC with multi-electrode for enhancing electricity generation through microbial metabolism. The electrochemical properties, COD removal and sulfate removal were determined and compared with the single-electrode CMFC.

MATERIAL & METHODS

The rubber wastewater was collected from the Platinum Rubber Company in Trang province, Southern Thailand by aseptic technique. It was preserved in the icebox, then transferred to the laboratory in the Department of Biology, Faculty of Science, Thaksin University, Phatthalung Campus. The wastewater was kept at – 4 °C until used. The characteristics of rubber wastewater used in this experiment were shown in Table 1.

Table 1. The characteristics of rubber wastewater used in this experiment.

Characteristic	Rubber wastewater	Unit
Sulfate	1,100 ± 59	mg/L
Nitrate	150 ± 32	mg/L
COD	3,500 ± 100	mg/L
Volatile fatty acid (VFA)	520 ± 12	mg/L
Alkalinity	1,200 ± 30	mg/L
pH	5.5	

Anaerobic seed enriched from the rubber industry sludge (Chaijak et al., 2018), was obtained from the Department of Biology, Faculty of Science, Thaksin University. For preparation, the 10 mL of anaerobic seed was inoculated into 90 mL of sterile nutrient broth (NB) containing 10 g/L peptone, 10 g/L beef extract and 5 g/L NaCl. It was incubated under the anaerobic condition at 30 °C for 2 days.

The colony of laccase producing yeast *Galactomyces reessii* (Chaijak et al., 2018) was inoculated onto a 2.0 mm-thick layer of potato dextrose agar (PDA) containing 4 g/L potato extract, 20 g/L dextrose and 15 g/L agar. It was incubated at 30 °C for 5 days to cover fully the surface of the medium. A 1.0 cm^2 of the colony-covered medium was cut to be placed on the cathode.

Fig. 1 schematically depicts the novel model CMFC with a multi-anode electrode. The anode chamber working volume of 100 mL was used. The eight anode electrodes (1.0 x 2.0 cm) were made by bamboo charcoal (100 – 250 µm of pore size) with 5 Ω of resistance. The 1.0 x 2.0 cm of carbon cloth (Fuel Cell Store, United States) was used as a cathode electrode. The 5.0 g of sterile dried coconut coir (1.0 cm length) was placed into cathode as yeast medium. The 2.0 cm^2 of a 1.0 mm-thick ceramic separator was inserted between the cathode and anode chamber for exchanging a proton. The stainless steel wire with 1.5 mm diameter was used to connect the electrode.

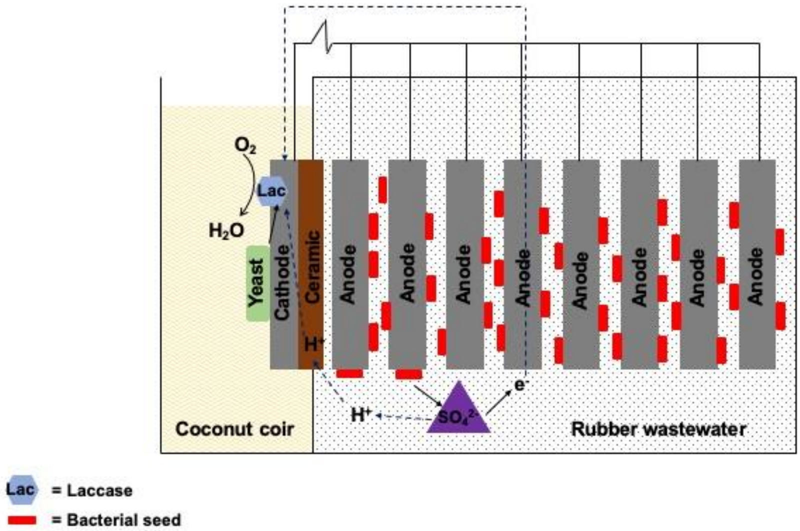

Figure 1. The novel model CMFC with multi-anode electrode

To operate an MFC, the 1.0 cm^2 of 5-days old *G. reessii* was inoculated into the cathode chamber. The 0.5 mL of PDB was added for adjusting the moisture content in the cathode chamber. The laccase producing yeast was grown for 5 days before operated an MFC. The 10 mL of 2-days old anaerobic seed (1.0 x 10^7 cell/mL) was added into the anode chamber. Then 90 mL of rubber wastewater was filled and incubated at 30 °C for 2 days for growing the biofilm on an anode surface. The incubated solution was fed out and the 100 mL of rubber wastewater was replaced. The hydraulic retention time (HRT) of MFC is 2 days. The open-circuit voltage (OCV) was collected every 10 min by Hantek 365F PC USB Digital Data logger (Hantek, China) for 12 hr. The closed-circuit voltage (CCV) at 1,000 Ω was determined for calculation of current density (CD), power density (PD) and internal resistance (R_{int}) followed Eq. (2), (4) and (5) respectively.

$$I = V/R \quad (1)$$

$$CD = I/V_w \quad (2)$$

$$P = IV \quad (3)$$

$$PD = P/V_w \quad (4)$$

$$R_{int} = (V_S \cdot R_L / V_O) - R_L \quad (5)$$

where I is the current (A), V is the CCV (V), R is the resistance (Ω), CD is the current density (A/m^3), the V_w is the working volume (m^3), the P is the power (W), PD is the power density (W/m^3), R_{int} is the internal resistance (Ω), V_S and V_O are the OCV and output voltage. At the load resistance (R_L) of 1,000 Ω.

The anode potential between the multi-electrode and single electrode was measured using a universal Ag/AgCl reference electrode (201 mV vs. SHE) at 30 °C.

The anolyte at 0 mins and 1,440 min were collected for used as a sample for COD and sulfate removal study. The COD removal was determined by High range plus COD digestion kit (Hach, United States). The sulfate removal was studied according to Chaijak et al., 2019.

RESULTS AND DISCUSSION

The materials used in the scaling up of MFC for wastewater treatment and electricity generation need to be low-cost. Carbon cloth or flat carbon can allow a small distance between electrodes and high power output with artificial wastewater (Liu et al., 2005). Though, it found unstable power output when it was used to treat the domestic wastewater (Hays et al., 2011). The study of Ahn & Logan (2013) used the graphite fiber brush anode in MFC to achieved a good rate of COD removal and stable power output owing to it has high surface area and porosity for growth of an anaerobic seed. The graphite fiber brush anode MFC has developed to gain more power output than a single-anode MFC (Ahn et al., 2014). However, the graphite fiber brush affected the high structural cost of the wastewater treatment system. Bamboo charcoal has been employed in the filtration and purification of a toxic gas for a long period due to its high area surface and high adsorption capacity. In the previous study of Moqsud et al. (2013) the bamboo charcoal anode is studied in bioelectricity generation in MFC compared with carbon fiber. Nevertheless, the potential advantage of the bamboo charcoal anode has not been established.

The dual-chamber laccase-based MFC with multi-bamboo charcoal anode was stared with the inoculated the laccase producing yeast *G. reessii* onto cathode surface with coconut coir supporter. The yeast was grown for 5 days to ensure it can cover the cathode area. Then, the anaerobic bacterial seed was inoculated into an anode chamber to accumulate an anaerobic bacterial biofilm into the anode chamber. For bioelectricity analysis, the 100 mL rubber wastewater with 1,100 mg/L of contaminated sulfate concentration and 3,500 mg/L of COD. One cycle of MFC is defined when the OCV is decreased under 50 mV (Wang et al., 2019). At the stationary phase of multi-anode MFC, the 960 – 985 mV of OCV was achieved at 200 – 530 min (Fig. 2). It gained 46.19% higher than the single-anode control (500 – 530 mV at 310 – 400 min). The 1,000 Ω of external resistance was used to determine the CCV and calculate the CD, PD and R_{int}. The 843.33±5.77 mA/m^3 of CD, the 711.23±9.76 mW/m^3 of PD were generated from multi-electrode, which higher than control of 60.08% and 84.05% respectively. The internal resistance of MFC is a key factor of MFC model designing owing to the high internal resistance that can limit the power output of MFC. The multi-anode MFC provided the 102.80±7.52 Ω of internal resistance that 82.14% lower than control. The single-anode MFC showed the 575.47±52.99 Ω of internal resistance.

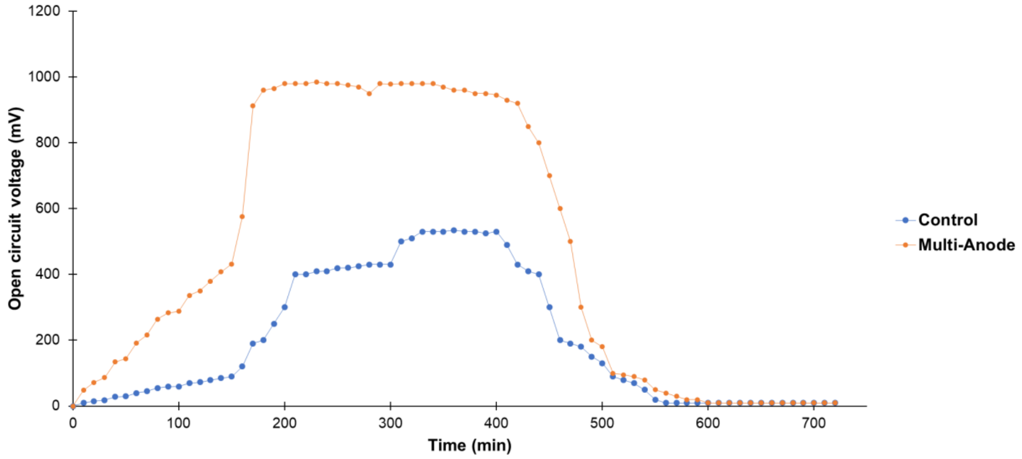

Figure 2. The open-circuit voltage (OCV) generated by the laccase-based CMFC with single anode (Control) and multi-anode

In the study of Kim et al. (2015), the three graphite fiber brushes have been constructed in the single-chamber MFC when the domestic wastewater has been used as an anolyte. Approximately 700 mW/m^3 of power output was achieved during operation. The six-carbon rods were used as anode electrode in single-chamber MFC. It generated a maximum power density of 56.25 mW/m^3 (Aparna & Meignanalakshmi, 2016). Furthermore, the multi-electrode MFC has combined with an anaerobic digester for swine wastewater treatment. The carbon cloth has been used as an anode electrode, the platinum-coated carbon cloth has been used as a cathode electrode. The maximum power density of 25 mW/m^3 was gained (Kim et al., 2020).

Half-cell potential measurements are an efficient method of characterizing electrode potential (Pant et al., 2011). The bamboo charcoal anode was connected with the universal reference electrode (Ag/AgCl) to determine anode potential. The half-cell potential of MFC was observed at the stationary phase. The results indicated that the multi-electrode MFC has 73.04% higher half-cell potential than single-electrode MFC.

The latex producing processes form the natural rubber is as energy-intensive processes and contributes to some environmental problems including toxicity from the additive chemicals (sulfuric acid and ammonia). Although, the anaerobic treatment system has been recommended in Thailand for the reasons of low operation cost and biogas production (Jawjit et al., 2015). Conversely, the anaerobic treatment system has been concerned by the emission of toxic gas hydrogen sulfide (H_2S). The UBFC has reported improving this problem (Sukkasem & Laehlah, 2015).

In this study, the 3,500 mg/L of initial COD and 1,100 mg/L sulfate concentration were removed through an anaerobic seed metabolism. The 90.05±12.30% of COD removal and 83.07±3.01% of sulfate removal were achieved when the multi-electrode MFC was operated at 30 °C for 12 hr. Where the control (single-anode MFC) was gained only 50.36±9.85% of COD removal and 23.73±0.52% of sulfate removal. The multi-anode MFC got 44.07% of COD removal and 71.43% of sulfate removal higher than control. Hien et al (2017) reported an anaerobic treatment process can degrade 61% of COD content from the rubber wastewater during 90 days of operating time. When the sulfate removal was not proved. Moreover, rubber wastewater has been treated by the coagulation-flocculation process combined with Fenton oxidation. The maximum COD removal of 78.26% was obtained under the treatment condition of 1,257 mg/L H_2O_2 and H_2O_2/Fe^{2+} ratio of 2.31 (Pendashteh et al., 2017). To remove contaminated sulfate from rubber wastewater, the micro-oxygen hybrid reactor has been used. 90.3% of sulfate removal and 93.0% of COD was gained at 10 days of operating time (Su-ungkavatin et al., 2019).

CONCLUSION

In conclusion, the multi-anode MFC provided a higher power output. The CD and PD of multi-anode MFC were higher than single-anode MFC (control) of 60.08% and 84.05% respectively. In terms of wastewater treatment, 90.05±12.30% of COD removal and 83.07±3.01% of sulfate removal were achieved. These results suggested that multi-anode MFC can more effectively generate energy from untreated rubber wastewater. it will be superior in terms of power generation and wastewater treatment.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

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LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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