

*Short Communication*

# Modified Water Hyacinth Biochar as a Low-Cost Supercapacitor Electrode for Electricity Generation From Pharmaceutical Wastewater

Pimprapa Chaijak<sup>1,2\*</sup>, Panisa Michu<sup>2,3</sup>

<sup>1</sup>Microbial Fuel Cell and Bioremediation Laboratory, Faculty of Science, Thaksin University, Thailand

<sup>2</sup>Microbial Technology for Agriculture, Food and Environment Research Center, Thaksin University, Thailand

<sup>3</sup>Department of Biotechnology, Faculty of Science, Thaksin University, Thailand

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## Abstract

The biochar electrode is an alternative low-cost electrode for electricity generation and wastewater treatment by the microbial fuel cell (MFC). In this study, the water hyacinth biochar (WHB) was prepared by pyrolysis at 350°C and activated by chemical immersion. The activated WHB was integrated with ceramic-separator MFC (CMFC) and used for the pharmaceutical wastewater (containing 100 µg/mL penicillin) treatment and electricity generation. The maximal power output and penicillin removal of 0.032±0.001 W/m<sup>2</sup> and 65.12±0.02% were achieved. This study gained new knowledge of using the WHB electrode coupled with the CMFC for pharmaceutical wastewater treatment and electricity generation.

**Keywords:** biochar, Penicillin, mioremediation, microbial fuel cell, Beta-lactam

## Introduction

Biochar is the solid product of biomass pyrolysis that can be used in a huge number of applications such as heating, soil improvement, metal removal, flue gas cleaning, and power generation [1]. During pyrolysis, the cellulosic matter in the agricultural waste can be converted to stable carbon in biochar [2]. Wood-based biochar has been reported in used as a sustainable material for microbial fuel cell (MFC) electrodes that provide a higher potential than graphite granules [3].

Jiang et al. showed that macroporous wood biochar has a high potential for ion movement than microporous wood biochar that can enhance electricity generation [4]. Various biomass substrates have been used for biochar production such as peanut shell [5], tea saponin [6], eucalyptus scraps [7], cotton rose [8], sugarcane bagasse [9], and others.

Water hyacinth (*Eichhornia crassipes*) is interesting as the worldwide harmful and aquatic invasive plant produced approximately 140 million daughter plants annually that causes a huge problem in water flooding led to the decline of aquatic animals [10]. The water hyacinth has been used for biochar production. The water hyacinth biochar (WHB) has been applied in different benefits like heavy metal adsorption [11],

\*e-mail: chaijak.pimprapa@gmail.com

soil improvement [12], and dye adsorption [13]. None of the previous studies has reported using WHB as an MFC electrode.

The pharmaceutical wastewater is the most emergency wastewater for treatment owing it contains several contaminants, anti-inflammatory drugs and antibacterial drugs [14]. Various methods have been developed for pharmaceutical wastewater treatment such as adsorption, membrane filtration, oxidation process and biological degradation [15]. Furthermore, the previous report of Vinayak et al. displayed the MFC process has a high potential for pharmaceutical wastewater treatment and generation of electrical power [16]. The  $\beta$ -lactam like cephalosporins and penicillin is the common type of antibiotics that are normally used in both humans and animals to avoid bacterial infection [17]. In this study, the modified WHB was prepared and used to produce electrical power from synthetic pharmaceutical wastewater using a dual-chamber ceramic separator MFC (CMFC).

## Experimental

### WHB Preparation

The water hyacinth stem (*E. crassipes*) was collected from the freshwater resource in Thaksin University, Phatthalung province, Thailand. The stem was separated and cleaned with tap water to remove the sediment. The sample was dried at 80°C until for 7 days and cut into 0.5 cm size pieces. The dried sample was pyrolyzed at 350°C for 30 mins (modified from Narayanan et al. [18]).

### Activation of WHB

The WHB was activated according to Jiang et al. [4], the WHB was immersed into the 0.5 M of  $\text{HNO}_3$  solution at room temperature for 12 hr. Then it was rinsed with deionized water to remove the covered particles before use (Fig. 1a).

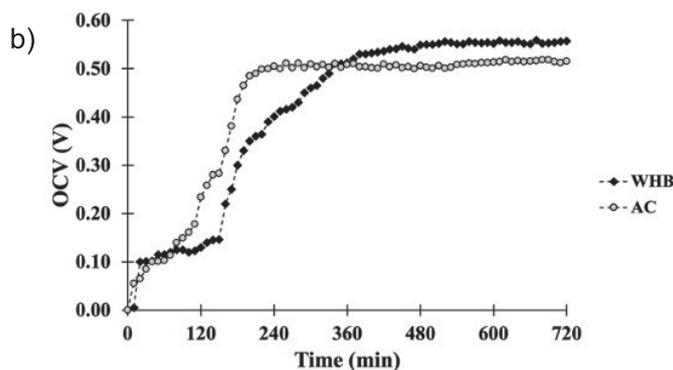
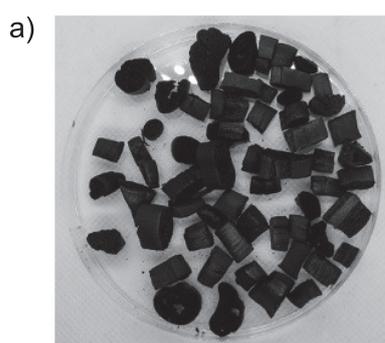


Fig. 1. The activated WHB was used in this experiment a), and the opened-circuit voltage (OCV) was gained from the CMFC with the WHB and AC electrode b).

## Pharmaceutical Wastewater

The synthetic pharmaceutical wastewater was prepared according to Khoshvaght et al. [19] and Yang et al. [20], contains 21.00 mg/L  $\text{MgSO}_4$ , 8.00 mg/L  $\text{KH}_2\text{PO}_4$ , 3.8 mg/L  $\text{CaCl}_2$ , 3.43 mg/L  $(\text{NH}_4)_2\text{SO}_4$ , 1.28 mg/L  $\text{K}_2\text{HPO}_4$ , and 100  $\mu\text{g/mL}$  penicillin.

### CMFC Construction and Operation

The CMFC was constructed according to the modified model of Chaijak et al. [21], the 50  $\text{m}^2$  of WHB (320  $\text{m}^2/\text{g}$  of specific surface area) was used as an anodic electrode. while the 50  $\text{m}^2$  activated carbon granule (1,000  $\text{m}^2/\text{g}$  of specific surface area) was used as a positive control. The 30% silica modified ceramic plate with 2 mm of thickness was used as a proton separator.

For operation, the 4 mL of penicillin degrading consortium was inoculated into the anode chamber, then the 36 mL of synthetic wastewater for CMFC was filled and incubated for 48 hr to immobilized the bacterial on the electrode surface. The anolyte was fed out and replaced with fresh synthetic pharmaceutical wastewater. The 1 M  $\text{KMnO}_4$  was used as a catholyte. The opened-circuit voltage (OCV) was collected every 10 mins for 12 hr. The closed-circuit voltage was monitored at 1-5,000  $\Omega$  for plotting the polarization curve. The current density and power density were calculated according to Ohm's law.

### Penicillin Removal

The effluent was fed out every 3 hr, and centrifuged at 5,000 rpm for 10 mins at 4°C. The supernatant was collected and used for penicillin residue determination. The quantitative evaluation of penicillin was monitored according to Yang et al. [20], the absorbance was measured at 325 nm using UV-Vis spectrophotometry (Shimadzu, Japan) with the limit of operation of 0-200  $\mu\text{g/mL}$  penicillin and the detective limit of 0.01  $\mu\text{g/mL}$  penicillin.

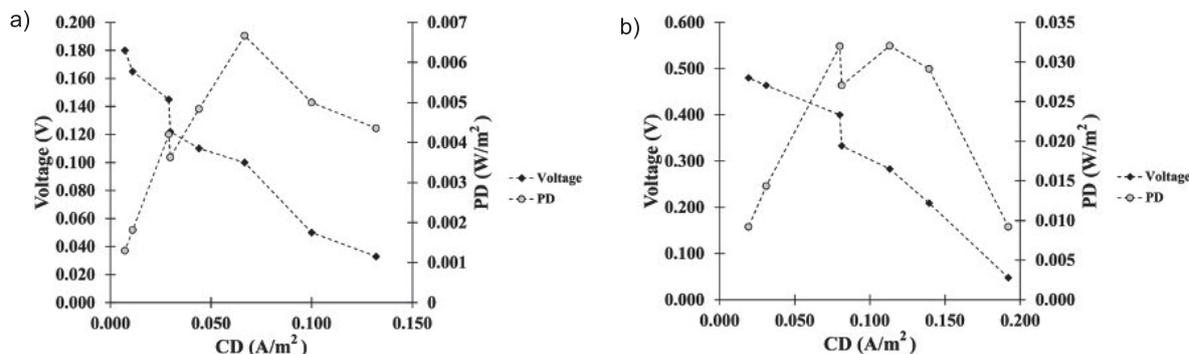


Fig. 2. The polarization curve of the CMFC with the WHB a) and AC b).

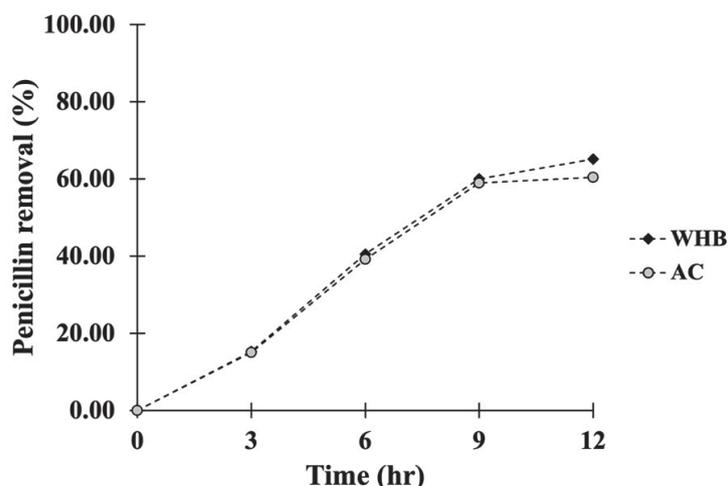


Fig. 3. The penicillin removal of the CMFC with the WHB electrode and the AC electrode.

### Results and Discussion

For this experiment, the WHB biochar supercapacitor was prepared by pyrolysis at 350°C for 30 mins for use as an alternative low-cost MFC electrode. The penicillin degrading consortium was grown in the anode chamber for 48 hr before the system was operated. The active consortium was coated on the surface of the anode electrode and releasing of oxidoreductase enzyme for penicillin degradation. The OCV of CMFC with the WHB and activated carbon granule (AC) was displayed in Fig. 1b). The maximal OCV of 0.554±0.003 V was

gained from the CMFC with the WHB electrode. While the maximal OCV of 0.515±0.002 V was produced from the CMFC with AC (control).

According to the polarization, the maximal CD and PD of the CMFC with the WHB electrode based on the electrode area were 0.192±0.001 A/m<sup>2</sup> and 0.032±0.001 W/m<sup>2</sup>. while the maximal CD and PD based on the working volume were 33.250±0.001 A/m<sup>3</sup> and 4.422±0.002 W/m<sup>3</sup> respectively. Although the maximal CD and PD of the CMFC with the AC electrode (control treatment) were 0.132±0.000 A/m<sup>2</sup> (16.500±0.001 A/m<sup>3</sup>) and 0.007±0.000 W/m<sup>2</sup> (0.833±0.001 W/m<sup>3</sup>) respectively.

Table 1. Comparison of biochar-based electrodes used in MFC.

MFC Types	Biochar substrate	Pyrolysis temperature (°C)	PD (W/m <sup>2</sup> )	Reference
CMFC	Water hyacinth	350	0.032±0.001	This study
Single chamber MFC	Water hyacinth	900	0.027	[25]
Single chamber MFC	Egg plant	800	0.667	[26]
Stack MFC	Corn cob	100-500	0.038	[27]
Dual chamber MFC	Rice straw	450	NA	[28]

The penicillin removal was monitored every 3 hr. The results showed the maximal penicillin removal of the CMFC with WHB electrode was slightly higher than the AC electrode. The maximal penicillin removal of  $65.12 \pm 0.02\%$  was gained from the WHB electrode when the initial penicillin concentration was  $100 \mu\text{g/mL}$ .

The low-cost biochar electrode has been developed for a decade. The coconut shell biochar has been mixed with the metal and used for MFC electrodes. The maximal PD of  $0.038 \text{ W/m}^2$  was reached [22]. Chakraborty et al. displayed the biochar prepared from the microalgae by pyrolysis at  $900^\circ\text{C}$  can use as an MFC electrode. The maximal PD of  $12.86 \text{ W/m}^3$  was produced from the MFC system with a microalgae biochar electrode [23]. Besides, the biochar electrode has been prepared from the olive mill waste and pistachio nutshell. The results indicated that the maximal PD of  $0.27 \text{ W/m}^2$  has been found [24]. A comparison of biochar-based MFC was shown in Table 1. No previous study has been used the WHB integrated with CMFC for electricity generation.

Moreover, the MFC has been used for antibiotics, sulfamethoxazole, sulfadiazine, and sulfamethazine removal from the swine waste. The maximal OCV of  $0.536 \text{ V}$  was reached [29]. Wen et al. indicated that the constructed wetland-microbial fuel cell (CW-MFC) plated with *Canna indica* can generate the maximal OCV of  $0.464 \text{ V}$  whereas the maximal PD of  $0.074 \text{ W/m}^3$  was gained [30]. Furthermore, the MFC with metal cathodic electrode showed that the maximal PD of  $0.446 \text{ W/m}^2$  was gained where  $61\%$  of  $10 \text{ mg/L}$  sulfamethoxazole was removed [31]. In Jiang et al., the MFC showed high performance for sulfamethoxazole removal of  $87.52\%$  where the initial antibiotic concentration of  $20 \text{ mg/L}$  was used. In this study, the maximal PD of  $1.18 \text{ W/m}^2$  was generated [32].

## Conclusions

In conclusion, the WHB supercapacitor electrode integrated with the CMFC was considered for the low-cost electricity generation and pharmaceutical wastewater treatment system. The results showed the maximal power output of  $0.032 \pm 0.001 \text{ W/m}^2$ . While the penicillin removal of  $65.12 \pm 0.02\%$  was reached. The WHB showed a high potential for use in the MFC electrode.

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## Conflict of Interest

The authors declare no conflict of interest.

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