Improved the coconut shell biochar properties for bio-electricity generation of microbial fuel cells from synthetic wastewater

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Abstract

A microbial fuel cell (MFC) is a green device that utilizes chemical energy in organic materials to generate electricity. The low-cost electrode used in this study was made from agricultural waste, coconut shells. The electrochemical properties were improved by combining oxidizing agents and microwave heating processes. The modified coconut shell electrode outperformed virgin biochar by 30.89-fold (230.13±10.11 m²/g). The maximum open-circuit voltage, current density, and power density are respectively 995.00±5.00 mV, 841.67±14.43 mA/m², and 283.42±9.67 mW/m². This study demonstrated that modified coconut shell biochar could be used as a low-cost alternative electrode for electricity generation.

Keywords:
biochar
cocnut shell
electrode
microbial fuel cell

Introduction

Nowadays, global energy demand is rapidly increasing due to the depletion of conventional or renewable energy sources such as fossil fuels and coal (Nepal et al., 2021; Prabha et al., 2021). As a result, there is a high demand for environmentally friendly, universally applicable renewable energy sources (Ananthi et al., 2021). The search for alternative clean energy production to meet future energy needs is a major challenge due to the emission of greenhouse gasses (GHGs) into the environment (Mishra et al., 2021), as well as other limitations in the development and adaptation of new processes for green renewable energy production (Kurmar et al., 2021).

Microbial fuel cell (MFC) is a new technology that uses microbial metabolism to convert chemical energy from organic matter to electrical energy. The MFC is regarded as a more environmentally friendly wastewater treatment technology that also generates bioelectrical energy (Maddalwar et al., 2021). However, due to its electrode and membrane, this technology has been found to have some bottlenecks, such as high operational costs (Tan et al., 2021). MFC anode electrode materials should be biocompatible, high conductivity, chemically resistant, and cost-effective (Sonawane et al., 2020). As an MFC anode, various carbon electrodes such as graphite plate, fibrous carbon cloth, carbon granules, and carbon rods are recommended (Salehmin et al., 2021). The high surface area electrode is suggested because it provides more surface area for microbial attachment and biofilm formation. The electrode porous also allows the proton (H⁺) to reach the cathode electrode, resulting in the completion of a system circuit and the maintenance of the redox gradient (Li et al., 2021).

Unmodified electrodes typically have a low surface area and are not biocompatible. Clogging issues have become a barrier, resulting in decreased electricity generation and wastewater treatment efficiencies resulting in system failure (Rabaey et al., 2009). To address these issues, a modified porous electrode was developed (Kim et al., 2021). Strong oxidizing chemicals, such as potassium permanganate and strong acid, have been used to change the physicochemical properties of electrodes by increasing
porous and electrical conductivity (Lee and Shin, 2021). Biochar (BC) is a carbon-rich material that is resistant to degradation in the environment and is derived from the oxygen-limited pyrolysis of organic matter (Zhang et al., 2013; Sizmur et al., 2017). Because of its high cation exchange capacity, large surface area, stable structure, and low cost, the BC has received increased attention in recent decades (Li et al., 2017; Jung et al., 2018; Ni et al., 2019). In this study, the expandable coconut shell biochar prepared by a combination of oxidizing agents treatment and microwave heating process was compared with untreated coconut shell biochar. The conductivity of the treated electrodes was determined. The high conductivity electrode was used as an anode electrode of MFC for the generation of electrical energy compared with untreated coconut shell biochar.

Materials and Methods

Preparation of modified biochar

A commercial coconut shell BC used in this experiment is an available product of Southern Thailand. The BC was produced under pyrolysis conditions at approximately 400 °C. For the pre-treated process, the BC was autoclaved at 121 ºC for 15 minutes under the pressure of 1.5 atm and was modified following post-pyrolysis methods with the oxidizing agent. All chemical activated BC was expanded by microwave heating process (modified from Kim et al. (2021) and Lee and Shin (2021)); a schematic diagram of BC activation is shown in Figure 1. All electrodes were kept in the dried container until used.

Electrical conductivity of the electrode

The specific surface area of the modified BC was determined iodine adsorption method (Mianowshi et al., 2007), and calculated the following:

\[ S_{BET} = (0.9946 \times IN) - 4.91 \]  

where \( S_{BET} \) is the specific surface area, and \( IN \) is the iodine adsorption number gives an adsorbed iodine amount (mg) per 1 g modified electrode. The resistance (R) of the modified electrode was determined. The electrical conductivity (\( \sigma \)) was calculated following:

\[ \rho = \frac{R \times A}{L} \]  

\[ \sigma = \frac{1}{\rho} \]

where \( \rho \) is the resistivity (Ωm), R is the resistance (Ω), A is the surface area (m²), L is the electrode length (m), and \( \sigma \) is the electrode conductivity (S/m).

Surface morphology

The surface morphology of treated BC and untreated BC was analyzed by scanning electron microscopy (Quanta 450 FEG, FEI) at an acceleration voltage of 10 kV.

MFC design and operation

The 135 mL of synthetic wastewater was prepared according to the previous report (Jadhav et al., 2009). The composition includes 1.0 g/L glucose, 0.03 g/L CaCl₂, 0.08 g/L MgCl₂ · 6H₂O, 0.05 g/L KH₂PO₄, 0.11 g/L (NH₄)₂SO₄, 0.08 g/L (NH₄)₂Fe(SO₄)₂ · 6H₂O and 0.01 g/L NaHCO₃. It was sterilized before being used.

A schematic of two-chamber MFC is shown in Figure 2. The 150 mL plastic bottles were used as the anode and cathode chamber. The 4 cm² of the graphite plate was used as a cathode electrode. The 4 cm² of treated BC was used as an anode electrode. Two electrodes were connected with the copper wire. The 40 mL of catholyte solution (400 μM KMnO₄) was
prepared according to Eliato et al. (2016). The 1% (w/v) KCl agar was filled in a silicon tube (0.5 cm diameter) and used as a salt bridge. The 10% (v/v) of *Bacillus subtilis* (1 x 10^9 cell/mL) was used for electricity generation in an anode chamber. The open-circuit voltage (OCV) was monitored every 10 minutes for 500 minutes. The 1,000 Ω of external resistance was connected between the electrodes. The closed-circuit voltage (CCV), power (P), current (I), current density (CD), power density (PD), and internal resistance were calculated following:

\[ I = \frac{V}{R} \]  
(4)

\[ CD = \frac{I}{A} \]  
(5)

\[ P = \frac{I \times V}{A} \]  
(6)

\[ PD = \frac{P}{A} \]  
(7)

\[ R_{int} = \left( \frac{V_s \times R_L}{V_o} \right) - R_L \]  
(8)

where I is the current (mA), V is the voltage (mV), R is the resistance (Ω), P is the power (mW), the CD is the current density (mA/m^2), A is the electrode area (m^2), PD is the power density (mW/m^2), R_{int} is the internal resistance (Ω), V_s is the open-circuit voltage (V), V_o is the closed-circuit voltage (V), and R_L is the load external resistance (Ω).

![Figure 2. The schematic of the two-chamber MFC was used in this experiment.](image)

**Results and Discussion**

**Surface area and morphology**

The surface area of coconut shell biochar was (CS-BC) determined using a specific surface area (S\textsubscript{BET}) by the iodine adsorption method. The S\textsubscript{BET} of the untreated CS-BC was 7.45±3.47 m\textsuperscript{2}/g, whereas the S\textsubscript{BET} of combined oxidizing agent-microwave heating treated CS-BC was 230.13±10.11 m\textsuperscript{2}/g. The treated CS-BC presented the increase of surface area with untreated CS-BC (30.89 fold), which indicated the amount of iodine volume adsorption. Table 1 shows the surface area of modified biochar in this experiment compared with other studies. The morphology of treated CS-BC and virgin CS-BC were examined by SEM (Figure 3).

**Table 1. The surface area of modified biochar.**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Modified method</th>
<th>Surface area (m\textsuperscript{2}/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>Combined oxidizing agent-microwave</td>
<td>230.13±10.11</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>modification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Magnetic particle modification</td>
<td>5.71</td>
<td>Hao et al. (2018)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Mechanical modification</td>
<td>378.30</td>
<td>Gong et al. (2021)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Microwave-assisted pyrolysis</td>
<td>0.46</td>
<td>Nuryana et al. (2020)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Acid-base modification</td>
<td>246.90</td>
<td>Hasana et al. (2020)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Pickling-iron modification</td>
<td>814.62</td>
<td>You et al. (2019)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Chemical modification</td>
<td>400.00</td>
<td>Baharum et al. (2020)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Oxidizing agent modification</td>
<td>89.80</td>
<td>Adorna et al. (2020)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Iron modification</td>
<td>547.00</td>
<td>Zhang et al. (2019)</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>Calcite modification</td>
<td>9.32</td>
<td>Wang et al. (2021)</td>
</tr>
</tbody>
</table>
According to Table 1, the combined oxidizing agent-microwave modified CS-BC showed a higher surface area than oxidizing agent modified CS-BC, magnetic particle modified CS-BC, microwave-assisted modified CS-BC, and calcite modified CS-BC. Whereas this process still provides a lower surface area than mechanical modification, pickling-iron modification, and chemical modification.

Electrochemical properties

The electrode conductivity is one of the most important factors that affect electricity generation in a fuel cell. Low conductivity electrodes can limit electricity production by fuel cells (Halfon et al., 2019). Biochar is produced by biomass pyrolysis and generally gains low conductivity. The previous study exposed the biochar prepared from sodium lignin sulfonate possesses a conductivity of 7,800 µS/m (Zhang et al., 2019). On the other hand, the modified pine wood biochar with graphene oxide gains a conductivity of 580 µS/m (Rui et al., 2020). In this study, the oxidizing agent modified CS-BC has a conductivity of 31.23±3.10 µS/m. It achieves a 45.26 fold conductivity higher than virgin coconut shell electrode (0.69±0.06 µS/m). In Wang et al., the activated carbon was prepared from the wastewater sludge for the improvement of electron transfer in a microbial fuel cell. The result showed the modified activated carbon provided 23.29 µS/m of conductivity (Wang et al., 2018). The OCV of dual-chamber MFC with modified CS-BC and control was monitored every 10 minutes for 3 hours. For replication, the fresh synthetic wastewater was replaced every 3 hours for 3 times. The maximum OCV of 995±5 mV was achieved from the dual-chamber MFC with modified CS-BC that was higher 1.87-fold than the control (530±10 mV) shown in Figure 4. The CCV of dual-chamber MFC with modified CS-BC was studied at 1,000 Ω external resistance.

Figure 4. The OCV of dual-chamber MFC with modified CS-BC compared with control (untreated CS-BC).
The electrochemical properties were calculated according to Ohm’s law. The electrochemical properties in this experiment are displayed in Table 2. The results showed the dual-chamber MFC with the modified CS-MFC gained the higher CCV, CD, and PD with 67.82%, 67.92%, and 89.61%, respectively. Whereas the dual-chamber MFC with the modified CS-BC showed a lower internal resistance of 16.84% than the control. The MFC with biochar electrode has interested owing to its low cost for operation and scale-up. The study by Huggins et al. (2014) had shown the maximal PD of 532±18 mW/m² when the modified wood-based biochar (specific area of 469.9 m²/g) was used as an electrode (Huggins et al., 2014). Moreover, the sewage sludge biochar prepared from the carbonization at a high temperature of approximately 900 °C exhibits the maximum PD of 500 ±17 mW/m² where the 0.5 mg/cm² of platinum was used as a cathode catalyst (Yuan et al., 2013). The PD achieved from biochar-MFC is shown in Table 3.

Table 2. The electrochemical properties of the dual-chamber MFC with the modified CS-BC in this experiment.

<table>
<thead>
<tr>
<th>Electrochemical properties</th>
<th>Modified CS-BC</th>
<th>Untreated CS-BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV (mV)</td>
<td>995.00±5.00</td>
<td>530.00±10.00</td>
</tr>
<tr>
<td>CCV at 1,000 Ω (mV)</td>
<td>336.67±5.77</td>
<td>108.33±7.64</td>
</tr>
<tr>
<td>Current (mA)</td>
<td>0.34±0.01</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>Current density (mA/m²)</td>
<td>841.67±14.43</td>
<td>270.83±19.09</td>
</tr>
<tr>
<td>Power (mW)</td>
<td>0.11±0.00</td>
<td>0.01±0.00</td>
</tr>
<tr>
<td>Power density (mW/m²)</td>
<td>283.42±9.67</td>
<td>29.44±4.09</td>
</tr>
<tr>
<td>Internal resistance (Ω)</td>
<td>661.64±5.80</td>
<td>795.60±14.41</td>
</tr>
</tbody>
</table>

Table 3. The power output is achieved from the biochar-based MFC.

<table>
<thead>
<tr>
<th>Anolyte</th>
<th>Biochar</th>
<th>Surface area (m²/g)</th>
<th>PD (mW/m²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic wastewater</td>
<td>Coconut shell</td>
<td>230.13±10.11</td>
<td>283.42±9.67</td>
<td>This study</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Sewage sludge</td>
<td>NA</td>
<td>500±17</td>
<td>Yuan et al. (2013)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Water hyacinth</td>
<td>NA</td>
<td>24.70</td>
<td>Allam et al. (2020)</td>
</tr>
<tr>
<td>Tannery wastewater</td>
<td>Coconut shell</td>
<td>0.21</td>
<td>38.72</td>
<td>Naveenkumar et al. (2021)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Rice husk</td>
<td>1,809.00</td>
<td>317.70</td>
<td>Jiao et al. (2020)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Olive mill waste</td>
<td>742.00</td>
<td>271.00</td>
<td>Scarriar et al. (2020)</td>
</tr>
<tr>
<td>Hoagland nutrient solution</td>
<td>Mable wood</td>
<td>NA</td>
<td>11.11</td>
<td>Khudzari et al. (2019)</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>Watermelon rind</td>
<td>657.60</td>
<td>3,993.00</td>
<td>Jiang et al. (2022)</td>
</tr>
<tr>
<td>Rubber wastewater</td>
<td>Bamboo</td>
<td>NA</td>
<td>3.26</td>
<td>Chaijak et al. (2020)</td>
</tr>
</tbody>
</table>

Conclusion

The alternative low-cost electrode for use in a microbial fuel cell was developed in this study. The modified coconut shell biochar produced by combining an oxidizing agent with microwave heating had a porous structure, a high specific surface area, and electrochemical properties superior to virgin coconut biochar. The maximum PD of 283.42±9.67 mW/m² was obtained without the use of a costly metal catalyst on the cathodic surface. This study proposes a low-cost, easily prepared electrode that can be scaled up for microbial fuel cells, thereby replacing the costly chemical electrode.

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References


