Journal of Advanced Engineering Trends
ISSN : 2682 - 2091

Vol. 44, No. 1, January 2025

Sustainable Energy Generation and Wastewater Treatment Using CuO Nanoparticles-decorated Activated Carbon and Biomass-Derived Electrodes in Microbial Fuel Cells

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ARTICLE INFO

Article history:
Received: 31 August 2024
Accepted: 22 October 2024
Online: 21 February 2025

Keywords:
Microbial fuel cells
Sewage wastewater
Non-precious cathode
Biomass-derived anode
Power generation.

ABSTRACT

Synthesis and application of copper oxide (CuO) nanoparticles-decorated activated carbon for use as a cathode material in microbial fuel cells (MFCs) is introduced. The CuO-decorated activated carbon was prepared by dissolving copper nitrate in ethanol, followed by the addition of activated carbon to the copper nitrate/ethanol solution. The resulting slurry was dried and thermally treated at 300°C for 3 hours. The copper nitrate was used at a concentration of 7 wt.% relative to the activated carbon. X-ray diffraction analysis confirmed the presence of CuO nanoparticles on the activated carbon. The modified activated carbon was then used to fabricate the cathode. This involved mixing the CuO-decorated activated carbon with polyvinylidene fluoride polymer and dimethyl formamide to form a paste, which was subsequently cast onto carbon cloth. The coated carbon cloth was then thermally treated at 280°C. The anode was prepared from graphitized corncob, treated under an inert atmosphere at 900°C. An air cathode, single-chamber MFC was assembled and operated using sewage wastewater. The power and current densities were monitored over a period of two weeks, with maximum current and power densities of 2.12 A/m² and 0.466 W/m² achieved after 7 and 9 days, respectively.

1. Introduction

Microbial fuel cells (MFCs) are an emerging technology that harnesses the metabolic processes of microorganisms to generate electricity from organic substrates[1]. MFCs have garnered significant interest due to their potential for sustainable energy production and wastewater treatment. In an MFC, microorganisms oxidize organic matter at the anode, releasing electrons that travel through an external circuit to the cathode, where they combine with oxygen and protons to form water. This process not only generates electrical power but also helps in the breakdown of pollutants, making MFCs a promising solution for wastewater treatment [2].

Despite their potential, the wide application of MFCs is hindered by several challenges. One of the major obstacles is the high cost of the conventional platinum (Pt)-based cathode materials. Pt is an efficient catalyst for the oxygen reduction reaction (ORR), but its scarcity and high cost limit the economic feasibility of large-scale MFC deployment. Additionally, conventional anode materials such as carbon cloth, carbon paper, and carbon felt often result in low power outputs. These materials have limited surface area and electrical conductivity, which restrict the efficiency of microbial electron transfer and, consequently, the overall power generation of MFCs [3,4].

Sewage wastewater treatment is a critical environmental concern, with conventional methods including physical, chemical, and biological processes. These methods can be energy-intensive, costly, and sometimes inefficient at removing certain contaminants [5,6]. MFCs offer a compelling alternative by providing simultaneous wastewater treatment and electricity generation. By utilizing organic compounds present in sewage as a fuel source, MFCs can reduce the chemical oxygen demand (COD) and other pollutants in the wastewater while producing renewable energy. This dual functionality can lead to significant environmental and economic benefits, making MFCs an attractive option for sustainable wastewater management [7, 8].

In this study, the challenges associated with conventional MFC components by developing a cost-effective and efficient electrode material were addressed. Copper oxide (CuO) nanoparticles-decorated activated carbon is proposed as an effective non-precious cathode material. Moreover, graphitized corncob was exploited as biomass-derived anode with high surface area.

An air cathode, single-chamber MFC using sewage wastewater as the substrate was assembled without addition of external microorganisms. Over a two-week period, we monitored the power and current densities, achieving maximum values of 2.12 A/m² and 0.466 W/m² after 7 and 9 days, respectively. These results demonstrate the effectiveness of the CuO-decorated activated carbon cathode and the biomass-derived anode in enhancing MFC

performance. This study highlights the potential of using non-precious metal catalysts and sustainable materials in MFCs to achieve efficient wastewater treatment and renewable energy generation.

2. Experimental Work

Activated carbon and copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) were purchased from Sigma-Aldrich. Ethanol (99.9% purity), polyvinylidene fluoride (PVDF) polymer, and dimethyl formamide (DMF) were obtained from Merck. Corncobs were sourced locally and used for anode preparation.

To prepare the CuO-decorated activated carbon, 0.07 grams of copper(II) nitrate trihydrate were dissolved in 10 mL of ethanol under constant stirring until a clear solution was obtained. Subsequently, 1 grams of activated carbon were added to the copper nitrate/ethanol solution. The mixture was stirred continuously for 1 hours to ensure uniform dispersion of the copper nitrate on the activated carbon. The resulting slurry was then dried in an oven at 110°C for 5 hours to remove the solvent. The dried powder was thermally treated in a muffle furnace at 300°C for 3 hours to decompose the copper nitrate into CuO nanoparticles, resulting in CuO-decorated activated carbon.

Corncobs were washed thoroughly with deionized water and dried at 80°C for 24 hours. The dried corncobs were then subjected to carbonization by heating in a tubular furnace under an inert nitrogen atmosphere. The temperature was raised to 1000 °C at a rate of 10 °C/min and held for 2 hours to achieve graphitization. The graphitized corncobs were allowed to cool to room temperature under nitrogen flow, ground into a fine powder, and sieved to obtain uniform particle size.

The air cathode, single-chamber MFC was assembled using a cylindrical glass reactor with a total volume of 80 mL. The cathode was prepared by mixing the CuO-decorated activated carbon with PVDF polymer and DMF to form a paste. The mixture comprised 0.5 gram CuO-decorated activated carbon and 1 gram of PVDF in 8 mL DMF. This paste was cast onto carbon cloth (3.5×3.5 cm) and dried at room temperature. The coated carbon cloth was then dried in an oven at 80°C for 2 hours then thermally treated at 280°C for 3 hour to enhance adhesion and electrical conductivity. The anode consisted of the prepared graphitized corncob, which was placed at the bottom of the reactor. Sewage wastewater was used as the substrate and inoculum, filling the reactor to immerse the anode completely. The cathode was positioned at the top, exposed to air to facilitate oxygen reduction. Dimethyl formmamide

A potentiostat (VersaStat 4.0, USA) was used to perform linear scan voltammetry (LSV) measurements to determine the power and current densities of the MFC. The voltage range for LSV was set from OCP to 0.0 V at a scan rate of 1 mV/s. The resulting current was recorded, and the power density was calculated using the formula ($P = IV$), where P is the power density, I is the current density, and V is the voltage.

The structural and morphological properties of the prepared cathode and anode materials were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns were recorded using a Bruker D8 Advance diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). The samples were scanned in the 2θ range of 10° to 80° to identify the crystalline phases present. The surface morphology and distribution of CuO nanoparticles on the activated carbon were examined using a JEOL JSM-6510LV scanning electron microscope. The samples were sputter-coated with a thin layer of gold to enhance conductivity before imaging.

3. Results and discussion

The X-ray diffraction (XRD) analysis provided critical insights into the crystalline structure and composition of the CuO-decorated activated carbon. Figure 1 displays the XRD pattern for the modified activated carbon, revealing distinct diffraction peaks that confirm the successful formation of copper oxide (CuO) nanoparticles on the activated carbon surface.

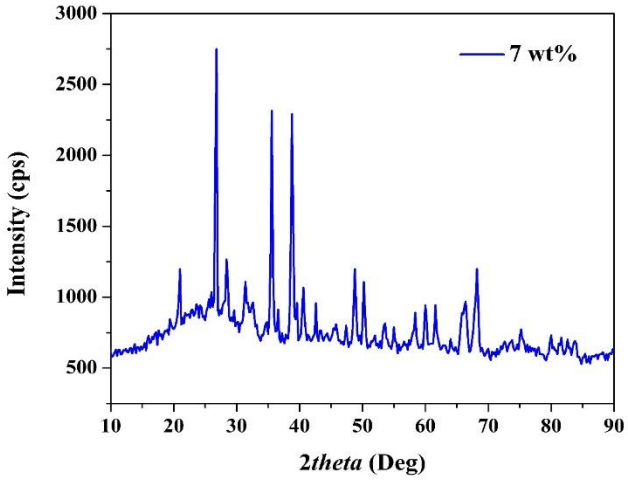


Figure 1: XRD pattern for the prepared CuO NPs-incorporated activated carbon

The characteristic diffraction peaks of CuO are observed at 2θ values of 35.3°, 38.7°, 44.2°, 46.1°, 48.6°, 51.2°, 53.3°, 58.1°, 59.2°, 61.3°, 65.8°, and 67.8°. These peaks correspond to the monoclinic structure of CuO, consistent with the standard reference data (ICDD card number 44-0706). The presence of these peaks in the XRD pattern confirms that the thermal treatment of the copper nitrate precursor at 300°C effectively decomposed it into CuO nanoparticles [9, 10].

In addition to the CuO peaks, the XRD pattern also exhibits diffraction peaks at 2θ values of 26.6°, 43.5°, and 46.4°. These peaks are characteristic of the activated carbon, matching the reference data (ICDD card number 26-1079). The peak at 26.6° is particularly indicative of the (002) plane of graphitic carbon, which suggests the presence of graphitic domains within the activated carbon matrix. The peaks at 43.5° and 46.4° correspond to the (100) and (101) planes, respectively, further confirming the crystalline structure of the activated carbon.

The formation of CuO nanoparticles on activated carbon can significantly impact the electrochemical performance of the cathode. CuO is known for its good catalytic activity in oxygen reduction reactions (ORR), which is crucial for the efficiency of MFCs. The improved catalytic activity can enhance the electron transfer processes at the cathode, leading to higher power and

current densities. This is particularly important given the challenges associated with the high cost and limited availability of conventional platinum-based catalysts.

The conversion of corncob biomass into a graphitized anode material through thermal treatment is illustrated in Fig. 2A, which shows photographic images of the corncob before and after the graphitization process. The significant reduction in size observed post-graphitization is a result of the high-temperature sintering at 1000°C. This process effectively converts the organic components of the biomass into carbon, leading to the formation of a more compact and structurally stable graphitized material. The size reduction indicates the removal of volatile substances and the consolidation of carbon structures, which is typical in the graphitization process. Fig. 2B presents the scanning electron microscopy (SEM) image of the surface of the graphitized corncob. The SEM image reveals a highly porous structure, characterized by numerous deep pores distributed across the surface. This porous architecture is a highly desirable attribute for an anode material in microbial fuel cells (MFCs) for several reasons [11, 12]:

- The presence of deep pores significantly increases the surface area of the anode. A higher surface area provides more sites for microbial attachment and colonization, which is crucial for the efficiency of MFCs. Microorganisms adhere to the anode surface and form biofilms, through which they transfer electrons generated during the oxidation of organic substrates. The increased surface area thus facilitates greater microbial loading and enhances the overall electron transfer process.
- The porous structure of the graphitized corncob enhances the mass transfer of nutrients and waste products to and from the microorganisms. Efficient mass transfer is essential for maintaining microbial activity and ensuring the sustained performance of the MFC. The interconnected pore network allows for better diffusion of substrates (e.g., organic compounds from wastewater) and removal of metabolic byproducts, supporting a stable and active biofilm.
- The graphitization process not only introduces porosity but also imparts structural stability to the corncob material. Graphitized carbon is known for its mechanical strength and resistance to corrosion, which are important properties for the durability and longevity of the anode in the harsh operating conditions of MFCs [13, 14].

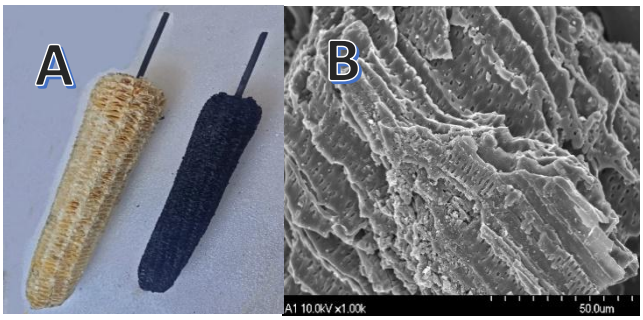


Figure 2: Photo image; (A) and SEM; (B) for the used graphitized corncob anode

The SEM image also suggests that the graphitized corncob retains some of the original fibrous structure of the biomass, which may contribute to its mechanical stability while providing a favorable environment for microbial attachment. This unique combination of high porosity and structural integrity makes the graphitized corncob an ideal anode material for MFCs. The use of a biomass-derived anode, such as graphitized corncob, aligns with the goals of sustainability and cost-effectiveness in MFC technology. Corncob, an agricultural waste product, is abundant and inexpensive, making it a viable alternative to conventional anode materials like carbon cloth, carbon paper, and carbon felt, which can be costly and less effective in promoting high microbial activity.

The obtained polarization curve obtained after 7 days of running time (data not shown) was used to draw the relationship between the power density and current density; Fig. 3. Overall, the polarization curve demonstrates the relationship between the cell voltage and the current density. The initial segment of the curve shows a steep decline in voltage with increasing current density, indicative of activation losses primarily associated with the kinetics of the electrochemical reactions at the electrodes. As the current density increases further, the curve exhibits a more gradual slope, reflecting ohmic losses due to the internal resistance of the MFC, including the resistance of the electrolyte, electrodes, and connectors. At higher current densities, the curve levels off, indicating mass transport limitations where the rate of substrate delivery and product removal becomes limiting.

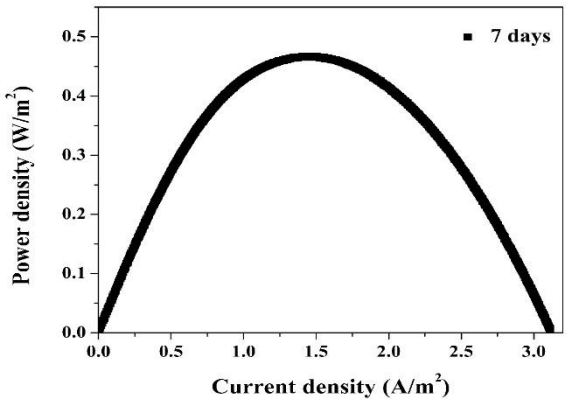
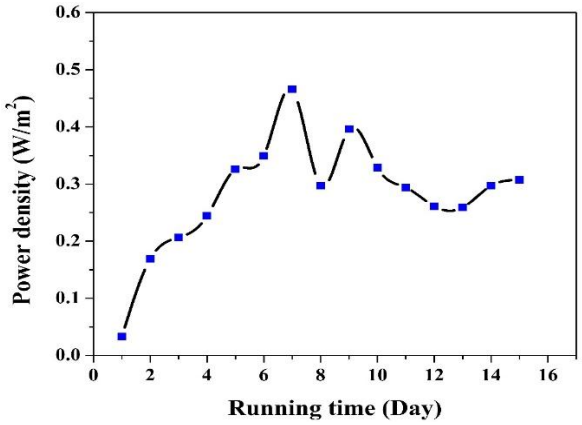
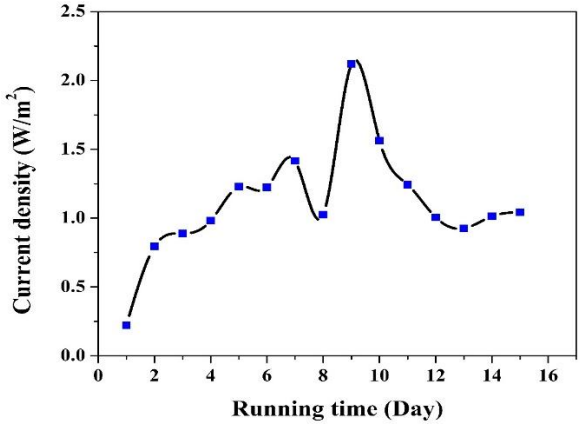


Figure 3: Polarization curve for an MFC assembled by corncob anode and Cu NPs-incorporated activated carbon cathode and driven by wastewater.

The temporal evolution of maximum power and current densities over a 15-day period is shown in Fig. 4. The power density (Fig. 4A) reached a peak of 0.48 W/m² after 7 days. This initial increase in power density can be attributed to the establishment of a mature and active biofilm on the anode surface, enhancing microbial electron transfer and overall MFC performance. However, after reaching this peak, the power density began to decline, likely due to the depletion of organic compounds in the batch mode operation. In batch mode, the substrate is consumed over time, and without replenishment, the concentration of available organic matter decreases, leading to reduced microbial activity and, consequently, lower power output [15, 16].



(A) and current density



(B) with running time for the assembled MFC.

Figure 4: Change of power density

Similarly, the current density (Fig. 4B) at the detected power density was observed after 9 days, reaching 2.23 A/m². The delay in reaching the peak current density compared to the power density suggests that while the biofilm was actively generating electrons, the system was initially more efficient in converting these electrons into power. Over time, as the organic substrate continued to deplete, the electron generation (current) also declined. This power density, further supporting the hypothesis that substrate depletion is a significant factor affecting the MFC performance in batch mode.

The observed trends in power and current densities highlight several key aspects of MFC operation:

- The initial increase in performance metrics underscores the importance of biofilm development on the anode. A well-established biofilm enhances microbial interactions and electron transfer rates, critical for maximizing MFC output.
- The subsequent decline in performance reflects the limitations of batch mode operation, where the finite amount of organic substrate leads to decreased microbial activity over time. This suggests that continuous or fed-batch operation might be more suitable for maintaining sustained MFC performance.
- The use of CuO-decorated activated carbon as the cathode and graphitized corncob as the anode likely contributed to the observed high initial power and current densities. The high surface area and favorable electrochemical properties of these materials support efficient microbial colonization and electron transfer, enhancing overall cell performance.

In conclusion, the polarization curve and the temporal variations in power and current densities provide a comprehensive understanding of the MFC's performance dynamics. The results demonstrate the potential of the developed electrode materials to achieve high power and current outputs, while also highlighting the challenges associated with substrate depletion in batch mode operation. These findings pave the way for further optimization of MFC configurations and operating conditions to achieve sustained and efficient energy generation from wastewater. Fig. 3 displays the polarization curve for the assembled MFC after 7 days running time. Fig. 4 shows the maximum power and current densities within a running time of 15 days. As shown in Fig. 4A, a maximum power density of 0.48 W/m2 was obtained after 7 days, then the power density decrease might be due to depletion of the organic compounds as the assembled MFC was working in a batch mode. On the other hand, the maximum current density was detected after 9 days reached to 2.23 A/m2 then, similar to power density, the maximum current density decreases with time.

4. Conclusions

In this study, copper oxide (CuO) nanoparticles-decorated activated carbon was synthesized and its application as an effective cathode material in microbial fuel cells (MFCs) was demonstrated. Moreover, a novel anode material was also developed by graphitizing corncob biomass under an inert atmosphere at 1000°C. The assembled single-chamber air cathode MFC, based on the prepared cathode and anode, using sewage wastewater as the substrate, demonstrated promising performance. The MFC achieved a maximum power density of 0.48 W/m² after 7 days and a a related current density of 2.23 A/m² after 9 days. However, the performance declined over time due to substrate depletion in batch mode operation. These findings highlight the potential of using non-precious metal catalysts and biomass-derived materials in MFCs for sustainable energy generation and wastewater treatment. The developed CuO-decorated activated carbon cathode and graphitized corncob anode provide a cost-effective and efficient alternative to conventional electrode materials, addressing key challenges in MFC technology. Future work will focus on optimizing the MFC configuration and exploring continuous operation modes to maintain sustained performance. In summary, this study introduces a viable approach to enhance MFC performance using innovative electrode materials, contributing to the advancement of renewable energy technologies and environmental sustainability.

Conflicts of Interest

The authors declare no conflict of interest.

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Abbreviation and symbols

CuO	**copper oxide**
MFCs	**microbial fuel cells**
XRD	**X-ray diffraction**
PVDF	**polyvinylidene fluoride**
DMF	**dimethyl formamide**
Pt	**platinum**
ORR	**oxygen reduction reaction**
COD	**chemical oxygen demand**
SEM	**scanning electron microscopy**
mL	**milliliter**
A/m^2	**Amber per square meter**
W/m^2	**Watt per square meter**