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Electrochemical Performance of Microbial Fuel Cells with Silverskin-Derived Biochar Cathodes

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Microbial fuel cells (MFCs) are used in this work to treat wastewater and remove pollutants. The biochar, which is based on silverskin, is synthesized and characterized. The pyrolysis of silverskin resulted in the production of biochar, a substance rich in carbon. Two different cathodes, one made from commercially available carbon and one from silverskin, were used in the design of the MFCs. Using non-pasteurized beer as a substrate, the MFCs were cycled while filled with a bacterial inoculum. Also, X-ray diffraction confirmed that hydroxyapatite (HAP) was formed in the wet deposition process used to create biochar composites with HAP. In static batch testing, the adsorption ability of the composites for heavy metals was assessed. The results showed that the composite significantly improved ion removal, especially for Cd(II). Within 24 hours, the residual concentration was less than 10 ppb. The findings show that silverskin biochar and its HAP composites may be used as cathodic materials in MFCs to treat wastewater that has both organic and inorganic contaminants. As a whole, they are promising for hybrid remediation of wastewater.
Keywords: Biochar, Electrodes, Pyrolysis, Silverskin, Adsorption.

1. Introduction

A promising environmentally friendly technology, microbial fuel cells (MFCs) harness the metabolic activities of microbes to produce energy from organic materials. Choosing the right cathode material is critical for boosting energy efficiency in metal-hydride fuel cells (MFCs), because this component is responsible for the electrochemical performance. Making MFCs more efficient might be as simple as using biochar as a cathode material. One eco-friendly and inexpensive substitute for conventional cathode materials like platinum is biochar made from silverskin, a waste product of the coffee industry. Reusing silverskin to make biochar is a great way to improve MFC performance and solves problems with waste management.

The disposal of silverskin, a byproduct of coffee bean processing, has been a source of environmental concern. We can get a useful substance with a lot of surface area and porosity by pyrolyzing this agricultural waste into biochar. Electron transfer mechanisms in MFCs, especially at the cathode, are greatly enhanced by these structural features of silverskin-

derived biochar (SDBC). An important mechanism in microbial fuel cells, the oxygen reduction reaction (ORR) affects the overall efficiency of power production; biochar supplies active sites for this reaction. The porous structure of SDBC makes it a great choice for cathodes because it improves the contact between the microorganisms and the surface of the cathode, which in turn increases the power output and the efficiency of the electrochemical processes.

Biochar cathodes made from silverskin may improve the electrochemical efficiency of microbial fuel cells in a number of ways. These include surface area, conductivity, porosity, and the presence of oxygen reduction catalytic sites. According to studies, SDBC has beneficial properties that improve ORR kinetics, including high porosity and functional surface groups. Because of these characteristics, electrons are able to flow more easily, leading to more efficient energy production. As far as current density is concerned, SDBC has shown to be on par with or even better than traditional cathodes. Its increased power density is a result of its porous structure, which allows for better electron transport between the cathode and anode.

In real-world scenarios, MFCs that use biochar cathodes made of silverskin show remarkable durability and very little performance deterioration with time. For practical applications, where the system's lifespan is as vital as its initial power production, this resilience is crucial. The usage of SDBC also drastically reduces the price of MFCs, which makes the technology more accessible and ideal for widespread adoption. Because of its lower production costs, greater sustainability, and comparable electrochemical performance, biochar is a great alternative to more conventional materials like platinum.

There are many processes that contribute to the improved performance of microbial fuel cells when biochar cathodes made from silverskin are used. The biochar's surface functional groups that include oxygen are a key component. The electrocatalytic activity for the oxygen reduction process is enhanced by functional groups like hydroxyl and carbonyl, which promote oxygen adsorption and facilitate its reduction at the cathode. Power densities and generating efficiency are both improved as a result. Oxygen and electrolyte may diffuse more effectively into the cathode because to SDBC's hierarchical pore structure, which also helps with mass transfer. Not only does this make the ORR process better, but it also makes the MFC run more efficiently by lowering its internal resistance.

The increased efficiency is due in large part to the fact that biochar made from silverskin is electrically conductive. In spite of biochar's lower conductivity compared to metals, SDBC has sufficient conductivity to enable electron transport from the anode to the cathode. Thanks to this, in addition to its big surface area and porous structure, SDBC cathodes may attain power outputs and current densities that are on par with those of traditional materials. With their enhanced electrochemical performance, MFCs with SDBC cathodes are now a practical choice for a range of uses, such as decentralized energy production and wastewater treatment.

Using biochar cathodes made from silverskin has significant environmental and economic benefits in addition to the electrochemical ones. As a low-cost and renewable substitute for costly minerals like platinum, the recycling of silverskin trash into a valuable product lessens the ecological footprint of coffee manufacturing. A sustainable material for biochar production, silverskin is plentiful and readily available. By repurposing trash into a useful commodity, biochar's usage in MFCs is in line with the concepts of a circular economy, which

aim to decrease waste and dependence on non-renewable resources. The electrochemical performance of microbial fuel cells using cathodes made of silverskin biochar is quite good, mostly because of the biochar's beneficial characteristics, which include a high porosity, surface functionality, and conductivity. With these improvements, oxygen reduction and electron transport become more efficient, which in turn leads to better power densities and consistent performance over time. In addition to being a potential material for expanding microbial fuel cell technology, SDBC has substantial economic and environmental advantages when used. Microbial fuel cells may benefit greatly from biochar made from silverskin instead of more conventional cathode materials due to its enhanced performance, low environmental impact, and low cost.

2. REVIEW OF LITERATURE

Stufano, Paolo et al., (2022). Even though coffee is one of the most consumed beverages in the world, it produces massive amounts of waste when used. In fact, these wastes may be a fantastic supplementary raw material for a variety of circular economy concepts In this article, we summarize the most important results from the last decade of this useful approach for recycling coffee grounds in order to provide a new and eco-friendly way to recycle coffee grounds. This might contribute to the ongoing effort to create a coffee-drinking community that is more sustainable, energetic, and pleasant.

Vakros, John et al., (2021) Scientists are now investigating the possibility of using activated carbon, which is made from biomass waste, as a means of storing energy. To create a simple three-electrode system that could function with a single alkaline electrolyte, a photocatalytic fuel cell and a supercapacitor electrode were combined. By enabling the simultaneous conversion and storage of solar energy, this device promotes the use of biomass wastes for energy purposes.

Zhao, Lei et al., (2021) Research has shown that RCA-biochar, which is formed from cornstalk residue during anaerobic bio-hydrogen production, effectively increases the yields of bio-hydrogen produced from cornstalk hydrolysate. How RCA-biochar aids in bio-hydrogen production from maize stalks during SSF (simultaneous saccharification and fermentation) remains a mystery. Therefore, filling this knowledge gap is the driving force for our study. Under various pH levels (5.5, 6.0, 6.5, 7.0) The increasing bio-hydrogen production was shown to be correlated with both the initial pH and the quantity of RCA-biochar. Batch experiments showed that the beginning pH clearly affected saccharification, whereas RCA-biochar significantly affected anaerobic fermentation.

Santos Andrade, Tatiana et al., (2020) Biochar, created by carbonizing spent coffee grounds without activation, has the right combination of micro, meso, and macroporosity. This trait has been exhibited in many ways. The pure substance included 96% carbon, oxygen, 2.2% potassium, and 1% unknown minerals. Biochar was used to make a supercapacitor electrode and photocatalytic fuel cell. End product: an electrical generator. Recent research suggests that biochar may be used in supercapacitors with capacitance values up to 200 Fg^{-1}. This basic arrangement uses solar energy conversion and photocatalytic fuel cells to degrade organic molecules and store electric energy in a supercapacitor.

3. MATERIALS AND METHODS

Biochar Production and characterization

Two days of drying at 85°C followed by five seconds of a knife mill set at 10,000 RPM to smash the silverskin into powder. Prior to pyrolysis, it was passed through a nitrogen flow of 0.5 L/h in a quartz reactor for two hours to remove oxygen. Then, it was lowered to a temperature below 50°C using a nitrogen flow. Then, it was raised to 900°C from room temperature at a rate of 10°C per minute. One hour was spent keeping the temperature at 900°C.

MFC components and set-up

Cathodes: The carbon fabric circle of each cathode was 9 cm in diameter and had a 5 cm lateral strip for a thin titanium wire. Hand-mixed conductive ink was applied to the center region using 1.00 g of carbon source (biochar or activated carbon Timcal-ENSACO), 4.56 mL of Milli-Q water, 0.95 mL of 60% PTFE solution, and 0.41 mL of Triton. Baked at 340°C for 30 minutes, this ink covered a 38 cm^2 carbon fabric. Three ink coatings were applied. Each cathode has a 1.5 cm thick, 9 cm external diameter, 7 cm internal void diameter polystyrene ring floater attached with inert sealing glue.

MFC Set up: Run two MFCs with different cathodic materials to create four MFCs:

CTRL-MFCs used commercial carbon cathodes, whereas SK-MFCs used silverskin biochar.

Each microbial fuel cell (MFC) was in a 12 cm-tall, 10-cm-diameter polypropylene cylindrical container. A 10x10 cm carbon fabric current collector attached to a thin titanium wire was in the 175 g of graphite granules that made up one-third of the height and covered the bottom. The cathode floated on wastewater while Milli-Q water was introduced as required. The anode and cathode were connected to a 100 Ω external load using insulated copper wires. During MFC acclimation, 400 mL of a 300:7:693 solution of bacterial inoculum, non-pasteurized beer, and tap water was introduced. Two cycles of 14 mg/L and 30 mg/L diluted non-pasteurized beer in tap water were done following the four-hour acclimatization period.

Monitoring Of MFC

Chemical parameters: The COD was measured frequently using spectrophotometry. Lange HT 200 S heated each MFC's solution to 175 °C for 15 minutes, then digested it using the HT-COD cuvette test (Hach Lange Gmbh). Spectrophotometers (Lange DR 3900) detected COD after cooling.

Electrochemical parameters: A multichannel Data Logger (Graphtech midi Logger GL820) was utilized to monitor device cell potential (Ecell) by detecting potential decrease across a 100 Ω resistance (R), serving as both electrical load and shunt resistance. The measurement was done every 20 minutes. The produced current (I) was computed using Ohm's law equation $I = Ecell\ R{-}1$.

Hydroxyapatite/biochar composite production

The composites were made by wet deposition at 80°C with increased phosphate. To begin, 1.00 g of silverskin-based biochar was mixed with 250 mL of 0.07 M $(NH_4)_2HPO_4$ solution in a five-necked round flask. The mixture was swirled for 30 minutes in a nitrogen-free

environment. A pH of roughly 10 was achieved by adding 10 mL of a 28-30 wt% NH_4OH solution. After that, a peristaltic pump was used to gently add 100 mL of 0.11 M $Ca(NO_t)_2 \bullet 4H_2O$ solution at 1.65 mL/min. Ammonia solution was regularly added to maintain a basic pH. Vacuum filtration followed 5 minutes of suspension whirling after insertion. Washing powders with Milli-Q water after the operation neutralized them. After that, they were vacuum-dried at 50°C for 16 hours. Finally, the powders were thermally treated for 8 hours at 120°C in air. A 1.18 g composite was produced. X-ray diffraction data was compared to reference pattern JCPDS 00-064-0738 to demonstrate hydroxyapatite (HAP) formation.

Adsorption tests on composite

Static batch adsorption tests assessed biochar and composite sorption capability. Solid material (approximately 100 mg) was mixed with magnetic stirrers in test tubes before being immersed in 1 mg L^{-1} Cd(II) and 5 mg L^{-1} Zn(II) water solutions. Experiments were conducted at 30.0 ± 0.1 °C with a constant solid-to-liquid ratio of 4 gsorbent L^{-1}. The adsorption kinetics of binary Cd(II)-Zn(II) mixtures were studied using an ICP-AES (Perkin-Elmer, Optical Emission Spectrofotometer, Model Optima 8000 DV). Researchers measured Cd(II) and Zn(II) in the supernatant at regular contact times for four days.

4. RESULTS AND DISCUSSION

MFC operation

Every MFC had its wastewater replenished at the start of the first operational period cycle and again in the second. The first cycle current densities for SK-MFC and CTRL-MFC were 150 and 95 mA m-2, respectively. Cycle 2 showed average currents for both cell types rise. SK-MFC surpassed CTRL-MFC in current output throughout the monitoring period. Silverskin biochar improved cathodic performance.

At cycle 2, when both cells had the greatest current, the polarization curves were taken to further examine any electrochemical performance differences between the two devices. Table 1 illustrates the power curves. SK-MFC had a maximum power density of 27.9 mW m-2, about three times that of CTRL-MFC. Silverskin-based cathode MFCs can operate at higher current densities than control MFCs. Faster electrode kinetics, better mass transfer, and lower overpotentials reduce energy dissipation and improve performance. Silverskin MFCs improved somewhat over control MFCs but couldn't compete with literature-specific systems. By monitoring COD levels before and after each operational stage, this study sought to establish each system's organics remediation capabilities.

Table 1 illustrates each cycle's COD removal for both cells. After 10 days, all cycles consumed organic substrate effectively. After cycle 2, the systems removed COD similarly, but their electrochemical essential properties differed. SK-MFC and CTRL-MFC attained a parallel pathway, leads to bulk microbial degradation processes and almost completely eliminates organic matter.

Table 1: Analysis of Monitored Chemical and Electrochemical Parameters

MFC	COD Removal (%)			Power Density (mW m-2)
	Acclimation	Cycle 1	Cycle 2	
SK-MFC	101.1±1.8	79±6	98.2±3.2	27.9
CTRL-MFC	101.1±3.3	71±2	93.9±3.3	10.7

HAP/biochar composites production

An early investigation suggested a biochar/hydroxyapatite composite with 10 wt.% HAP for second-generation MFC organics removal and inorganics remediation. Silverskin would be used. A charcoal suspension precipitated hydroxyapatite from a calcium-phosphorus precursor-containing water solution. Hydroxyapatite attached and grew on charcoal, according to XRPD research. The composite material's XRPD pattern (Figure 1) showed crystalline HAP reflections (JCPDS 00-064-0738). Additionally, biochar created a noticeable signal in the 20˚-30˚ 2theta region.

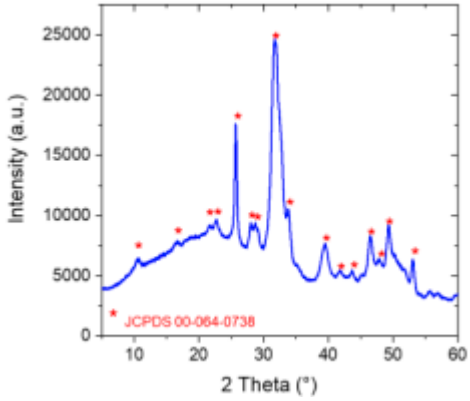

Figure 1: XRPD Analysis of HAP/Biochar Composite

The composite's sorption capacity toward Cd(II) and Zn(II) ions was measured ex situ using static batch adsorption studies as a function of time before using it as a cathode in MFCs for hybrid wastewater treatment. We independently researched silverskin-biochar's sorption properties to learn about HAP's potential benefits in the composite. Figures 2 and 3 show that adding HAP to the composite material improves the solution's residual element concentration. Since the composite absorbed all heavy metal cations in one day, Cd(II) contamination is difficult to manage.

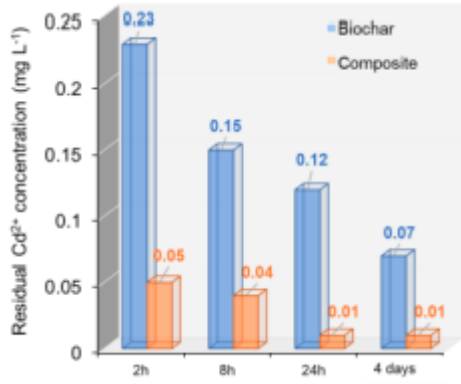

Figure 2: Adsorption Test Results for Cd(II) on Biochar and Composite Sorbents

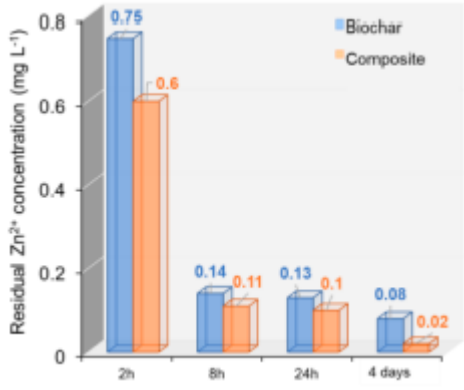

Figure 3: Adsorption Test Results for Zn(II) on Biochar and Composite Sorbents

Ca(II) cation, a component of HAP, has an ion radius of 0.1 nm, which is close to Cd(II)'s 0.095 nm. Adsorption is thermodynamically favored by Ca(II) and Cd(II) ions' similar ionic radii, which allow them to interchange more readily. After four days, the composite material absorbed more ions than charcoal for both ions. Biochar adsorption was 98.4% for Zn(II) and 93% for Cd(II) after four days, compared to 99.6% and 99.9% for the HAP-containing composite. These findings support future investigation into hydroxyapatite and silverskin biochar composites as cathodic materials for microbial fuel cells. This applies to wastewater treatment with inorganic and organic contaminants.

5. CONCLUSION

Finally, a groundbreaking development in renewable energy is the use of silverskin-derived biochar (SDBC) cathodes in microbial fuel cells (MFCs). In addition to improving the electrochemical performance of MFCs, using SDBC as a cathode material helps the environment by finding a new application for coffee processing waste. Power densities are increased and stability is enhanced due to functional groups, a wide surface area, and high porosity in SDBC, which allow for efficient electron transfer and improve the oxygen reduction process (ORR). For all these reasons, SDBC is a great substitute for conventional

materials like platinum that doesn't hurt the environment. It would be a mistake to ignore the financial benefits of employing biochar made from silverskin. The use of a plentiful and inexpensive byproduct drastically lowers the total cost of MFCs, opening up a world of possibilities for this technology in fields such as decentralized energy generation and wastewater treatment. The economic feasibility of MFCs is further enhanced by the durability and long-term stability of SDBC cathodes. Using biochar made from silverskin as a cathode material in MFCs is a great way to make these systems more efficient and longer-lasting. Green energy solutions will greatly benefit from SDBC's scalability and environmental advantages in the future.

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