**PhD Theses**

# Air-cathode ML-MFC reactor configuration using wood as container and separator to prevent deterioration and biofilm formation on cathode surface

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## Problem area

In the past few decades, a strong emphasis on sustainability has driven the scientific community to address issues harming the ecosystem (Nastro, 2014). Simultaneously, concerns about depleting crude oil and the growing push for alternative energy sources have gained momentum. In light of these challenges, microbial fuel cells (MFCs) have garnered global interest as a sustainable technology with the potential to generate electricity from organic matter in wastewaters, simultaneously treating the wastewaters and contributing to environmental remediation (Feng et al., 2008). The MFC technology holds promise to fulfill at least a part of future energy needs (Logan, 2010). Additionally, it is self-sustaining, affordable, and in some cases, does not require substantial capital investments.

Among researchers, membrane-less microbial fuel cells (ML-MFCs) outperform membrane MFCs; an air-cathode is preferred over an aqueous-cathode for not requiring an air supply. However, cathode deterioration is a common issue with all membrane-less air-cathode designs, inevitable due to contact with the anolyte leading to biofilm formation on the cathode's surface. This issue causes the cell's efficiency to decline over time. The cost of constructing and maintaining an MFC unit at high efficiency, compared to the bioelectric output, renders MFC commercially unviable. Despite these challenges, selecting the appropriate design and materials for an MFC unit is crucial.

The conventional construction of ML-MFC units is laborious, time-consuming, environmentally unfriendly, and costly in most cases. However, these drawbacks can be overcome by employing eco-friendly and readily available materials, such as wood, in the MFC unit structure. For example, wood has been tested to address challenges in ML-MFC. Its appealing characteristics, such as biodegradability, porosity, accessibility, treatability, ability to withstand microbial attacks, and long lifespan, make wood a particularly attractive choice for constructing ML-MFCs..

## Objectives

In light of the previously mentioned problem, the research objectives are as follows:

- ✓ Build and test wooden ML-MFCs using three types of wood species, measure water loss through moisture diffusion, and determine the optimal resistor.
- ✓ Evaluate the substrate to assess the water treatment capability of the wooden ML-MFCs using COD tests, pH, and conductivity. Additionally, analyze water loss through moisture diffusion.
- ✓ Study the bioelectric production of WML-MFCs with different wood species, employing OCV, MPD, and MCD measurements under varying experimental conditions.
- ✓ Test and compare three different wall thicknesses of WML-MFCs (2 mm, 3 mm, and 4 mm) for two species.
- ✓ Characterize the wooden wall of the containers using advanced analytical techniques such as EDX, SEM, and AFM.

## Research methodology

*Preparation of Electrodes:*

To construct the anode electrode, carbon felt with a surface area of 114 $cm^2$ was utilized, while the cathode electrode was fashioned from carbon cloth with a surface area of 162 $cm^2$. Both electrodes underwent a thorough cleaning process with deionized water and were subsequently dried at 80 °C for 24 hours. A 24-hour soak in 1M HCl was employed to eliminate surface impurities. Following this, another round of washing with deionized water and drying at 80 °C for 24 hours ensued. Connecting four pieces of carbon felt as the anode electrode with a copper wire, they were then placed inside each WML-MFC container, occupying a total volume of 24 $cm^3$. The cathode electrode, connected with a copper wire, was positioned outside the container and secured with a fabric thread. No catalyst was loaded on the cathode, and no pre-treatment was applied to the anode and wood plates. Prior to current and power measurements, various external resistors between 400 Ω – 1 MΩ were tested to ascertain the optimal external resistor for WML-MFC.

*Fabrication of WML-MFC Container Using Wood:*

Untreated wooden plates sourced from oak (Quercus robur), Scots pine (Pinus silvestris), and black locust (Robinia pseudoacacia) were cut into plates with thicknesses of 2 mm, 3 mm, and 4 mm using a wood cutting machine. Assembled with silicone adhesive, the container's dimensions were 37 × 37 × 59 mm (±1 mm), with an inner volume of 55 ± 5 ml. After placing the anode inside the container, the internal volume reduced to 25 ± 5 ml. Two holes were drilled on each box—one (9 mm diameter) for influent and effluent, and another (2 mm diameter) for the copper wire from the anode electrode.

*Inoculation and Operation of WML-MFC:*

Each WML-MFC unit was inoculated with 20 ± 5 ml of substrate, a mixture of 200 ml anaerobic digestion sludge, 300 ml distilled water, outdoor mud, and sucrose. After an hour of settling, the substrate was injected into the container. Experiments ran in batch mode with varying hydraulic retention times (HRTs). Initially, 25 ml of substrate was fed into each container. Operating under an open circuit (OC) for a week established a stable microbial community in the anode compartment. Due to high moisture diffusion through wooden walls, daily substrate additions were necessary to keep the anode electrode immersed. All experiments occurred at room temperature (15°C to 25°C).

*Analysis:*

Electric productivity was monitored and calculated using data analog (open circuit voltage, maximum current density, and maximum power density). Morphological analysis employed scanning electron microscopy (SEM), while energy-dispersive X-ray spectroscopy (EDX) determined elements and chemical composition for wood plates and the cathode. Viscoelastic behavior analysis was conducted through dynamic mechanical analysis (DMA) for the wood plates.

## Results

*Cell Voltage with Open-Circuit and Start-Up Progress to Acclimation Time:*

To evaluate the success of the WML-MFC concept, OCV, MCD, and MPD were crucial metrics. Under uniform experimental conditions, including temperature and influent, OCV, CD, and PD were assessed for various species. The experiment initiated with an open circuit until reaching the maximum OCV after 351 hours. WP4-MFC-1, among 4 mm wall thickness prototypes, exhibited the highest OCV of 0.551 V with a 42% COD reduction efficiency. WP4-MFC-3 reached 321 mV after 371 hours, and WP4-MFC-2 achieved 269 mV after 412 hours. Among oak containers, WO4-MFC-2 demonstrated the best performance, touching an OCV of 141 mV within 343 hours. Notably, Scots pine outperformed oak in OCV by 78-81%, while black locust showed significantly lower values than oak.

After each replacement of effluent with freshly seeded substrate, the voltage rose until peaking. The voltage took approximately 25 – 30 hours to stabilize. Small voltage jumps during biofilm development, especially for WP4-MFC-2 and WP4-MFC-3, were observed due to ambient temperature changes between day and night (15°C to 25°C). The rise in ambient temperature influenced substrate temperature in softwood (WP4-MFC-2 and WP4-MFC-3), while oak was less affected due to its lower thermal conductivity compared to Scots pine.

*External Resistor Selection:*

MPD for WP4-MFC, WO3-MFC, WP3-MFC, WO2-MFC, and WP2-MFC was achieved with resistances of 330 kΩ, 51 kΩ, 20 kΩ, 820 kΩ, and 81 kΩ, respectively.

*Bioelectricity Generation of WML-MFC as a Closed Circuit:*

Switching from OC to CC (with 330 kΩ resistors), WP4-MFC-3 demonstrated the highest MPD and MCD of 35 $mW/m^2$ and 0.09 $mA/m^2$, respectively, after 397 hours. Meanwhile, WO4-MFC-2 reached MPD and MCD of 4 $mW/m^2$ and 0.03 $mA/m^2$, respectively, after 404 hours. During closed circuit operation (with resistors of 820 kΩ for oak and 467 kΩ for Scots pine), 2 mm and 3 mm wall thickness WML-MFCs demonstrated the highest MPD and MCD of 5.14 $mW/m^2$ and 0.023 $mA/m^2$, and 4.7 $mW/m^2$ with 0.0029 $mA/m^2$ during 1000 hours of the experiment, respectively. WP3-MFC produced higher current and power density compared to WO3-MFC by nearly 500%, while WO2-MFC surpassed WP2-MFC by almost 200%. WP2-MFC exhibited negative voltage for more than 300 hours, and 2 mm MWL-MFCs showed sharper peaks and valleys compared to 3 mm wall thickness MWL-MFCs. The peaks and valleys of 3 mm wall thickness MWL-MFCs were sharper than 4 mm MWL-MFCs.

*Effluent Condition and Wastewater Treatment Performance of WML-MFC:*

In all 4 mm wall thickness cases, effluent conductivity almost doubled in Scots pine and was 27 - 100% higher in oak than in the influent. The drop in pH occurred at different rates for 4 mm wall thickness oak and Scots pine containers. For 3 mm and 2 mm wall thickness oak and Scots pine containers, the pH increased from 4 to 5 ± 0.8. Scots pine containers demonstrated better water treatment performance between 0-48 hours. After three days of HRT, slow progress in water treatment occurred in all 4 mm wall thickness containers. The COD of effluent for WO2-MFC, WP2-MFC, WO3-MFC, and WP3-MFC increased from initial COD of 5071 to 7663, 7792, 7964, and 6871, respectively, while with 4 mm wall thickness WML-MFCs, it decreased. This suggests that 4 mm is a critical wall thickness for preparing WML-MFC regarding water loss with moisture diffusion and the speed of water treatment, especially with Scots pine.

*Effect of HRT on Bioelectricity Production:*

WP4-MFC-1 displayed the highest OCV of 0.551 V with an HRT of 2 days and a high COD substrate, while WP4-MFC-3 showed the highest bioelectricity production with MPD and MCD of 35 $mW/m^2$ and 0.09 $mA/m^2$, respectively, with an HRT of 2 days.

*Cathode Condition During the Experiment:*

One primary objective was to find a solution for preventing cathode electrode microbial attack and deterioration. After three months of continuous operation, the WML-MFC cathode showed no trace of biofilm or microbial attack visually. The SEM image of oak and Scots pine cathode electrodes exhibited a remarkably similar morphology with no traces of microbial degradation or biofilm formation for all containers, except for some debris and remnants due to getting wet during the experiment.

*Mechanical Properties and Morphological Structure of Wood Plates of WML-MFCs:*

Significant mechanical loss was observed in oak, while Scots pine exhibited only slight changes. SEM investigation of used oak samples revealed cracks, whereas used Scots pine showed a smooth surface with no cracks. These cracks significantly affect wood strength and durability, especially with low wall thickness. Debris settlement was observed on both samples' surfaces. Oak presented higher color absorbance from wastewater compared to Scots pine. From DMA and SEM tests, it is clear that Scots pine performed better than oak in terms of durability against wastewater microbial attack and the impacts of moisture diffusion. EDX analysis of WML-MFCs showed absorption of copper and some other chemicals like fluorine, aluminum, and iron but not in highly significant volumes. Similar findings were seen in oak 3 mm and 4 mm wall thickness. For 4 mm wall thickness of oak and Scots pine, 2.47% and 3.80% of nitrogen were observed, which was not found for 2 mm and 3 mm wall thickness.

**Main conclusions of the research**

*Findings:*

*The research findings are summarized below, highlighting achievements and implications:*

- *The WML-MFC prototype demonstrated potential in safeguarding the cathode from biofouling, preventing cathode deterioration. This suggests that wood, as a separator and container, offers a cost-effective solution to enhance cathode performance and durability for bioelectricity generation in WML-MFCs* ***(CT-CP4) (CT-PA)****.*
- *The cost reduction in building and maintaining ML-MFCs, coupled with the prevention of cathode deterioration, raises hope for future commercialization. The wooden membrane-less microbial fuel cell system proves to be a cost-effective and environmentally friendly approach* ***(CT-BC2)****.*
- *Scots pine 4 mm containers exhibited the highest COD reduction percentage at 48%, while oak containers achieved 39% within a hydraulic retention time of 48 hours. Black locust showed the lowest bioelectricity production, with the least stability in OCV. The MPD and OCV reached 35 $mW/m^2$, 551 mV, and 4 $mW/m^2$, 269 mV (with a 330 kΩ resistor) for Scots pine and oak, respectively. Black locust achieved a maximum OCV of 51 mV, sustained for a maximum of 2 hours* ***(CT-JP1-submitted)****.*
- *Water loss in WML-MFCs occured due to moisture diffusion in wood, and the amount of water loss is influenced by wall thickness and wood species* ***(CT-JP1-submitted) (CT-CP4)****.*
- *.*
- *Wood, as an insulating material, protects microbial activity against low ambient temperatures, ensuring performance efficiency even in cold weather* ***(CT-BC2)****.*
- *The bioelectricity and water treatment efficiency of WML-MFC were most effective with an HRT of 2 days and a 4 mm wall thickness* ***(CT-JP1-submitted)****.*
- *Successful WML-MFCs are achievable with 2 mm and 3 mm wall thicknesses, demonstrating viability for various purposes. The highest MPD and MCD for 2 mm and 3 mm wall thickness were*

*5.14 mW/m$^2$ at 0.023 mA/m$^2$ and 4.7 mW/m2 at 0.0029 mA/m$^2$, respectively, during 1000 hours of experimentation **(CT-PA)**.*

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- *For effective water treatment, a minimum wall thickness of 4 mm is required to fabricate WML-MFC **(CT-PA)**.*
- *The highest electric production occurs with a 3 mm wall thickness of WML-MFC when utilizing the right resistor. The 3 mm wall thickness yielded the maximum power density (without water treatment) **(CT-PA) (CT-JP1-submitted)**.*
- *Containers with a wall thickness less than 3 mm must be fabricated from dense wood species or include a PEM in the system. Compared to 3 mm wall thickness MWL-MFCs, 2 mm Scots pine MWL-MFCs exhibited negative voltage for more than 300 hours, with highly sharp peaks and rapid decreases. Additionally, the peaks and valleys of 3 mm MWL-MFCs were sharper than those of 4 mm MWL-MFCs **(CT-PA) (CT-JP1-submitted)**.*
- *Wooden walls have a significant impact on pH, normalizing the influent pH around 5 ± 0.4**(CT-PA) (CT-JP1-submitted)**.*

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## List of publications

***Patent Application:***

**CT-PA:** P2300280, A wooden membrane-less microbial fuel cell reactor configuration.

***Journal Publication:***

**CT-JP1:** Tahir, C.A., Agarwal, C.A., Pásztory, Z., Csóka, L., 2024. A novel membrane-less microbial fuel cell reactor using wood as container and separator to prevent air–cathode deterioration and biofouling. *Discover WATER*, 15–29. https://doi.org/10.1007/s43832-024-00085-x

***Book Chapters:***

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**CT-BC1**: Tahir, C.A., Agarwal, C.A., Csóka, L., 2020. Advances in Green Ion-Batteries using Aqueous Electrolytes, in: Boddula, R., Inamuddin, I., Pothu, R., Asiri, A.M. (Eds.), Rechargeable Batteries: History, Progress, and Applications. *Scrivener Publishing LLC, Beverly (MA)*, pp. 379–402.

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