

Research Paper

Received: 30 July 2023, Accepted: 25 September 2023, Published online: 30 September 2023

DOI: 10.21625/resourceedings.v3i2.979

Chemical Oxygen Demand Sensor Based on Microbial Fuel Cell Using Low-Cost Electrodes Fabricated from Waste Rice Husks

Soichiro Hirose¹, Trang Nakamoto², Kozo Taguchi³

¹*Department of Electrical and Electronic Engineering, Ritsumeikan University, Kusatsu, Japan.*

²*Assistant Professor, Department of Electrical and Electronic Engineering, Ritsumeikan University, Kusatsu, Japan*

³*Professor, Department of Electrical and Electronic Engineering, Ritsumeikan University, Kusatsu, Japan*

taguchi@se.ritsumei.ac.jp

Abstract

Environmental pollution is one of the problems that humankind must solve for a sustainable future. Monitoring of Chemical Oxygen Demand (COD) is an important indicator for monitoring the status of organic pollution in water. However, conventional methods for monitoring COD face high costs and complicated design issues. In this study, the use of microbial fuel cells (MFC) composed of low-cost and easy-to-fabricate electrodes using smoked charcoal from rice husks and Japanese ink was investigated for use in COD sensors. Rice husks are an industrial waste product. Therefore, they can be used at a low cost, and using them can help solve the waste problem, which is one of the causes of environmental pollution. With these materials, the electrodes were fabricated for the cost of \$0.022/cm³. In addition, floating MFC was used for the sake of sensing COD in rivers, waterways, and lakes. The high physical stability of the block-shaped electrode used in this study allowed a biofilm to form on the anode surface by inserting the anode into the soil. The block-shaped electrodes were physically stable in solution. The results showed that there was a correlation between COD concentration (30~150 mg/L) and MFC voltage for more than eight months. Block-shaped electrodes fabricated with rice husk smoked charcoal and Japanese ink would be a promising electrode for MFC to monitor COD in solution in real-time.

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Keywords

Microbial fuel cell; COD; Sensor; Rice husk

1. Introduction

Environmental pollution is one of the problems that humanity must solve for a sustainable future. Among them, water pollution is a major threat to ecosystems and human health around the world (Boelee et al., 2019). Water pollution can be chronic, caused by heavy metals and organic compounds, or sudden, caused by artificial accidents or illegal incidents (Zamora-Ledezma et al., 2021, David & Niculescu, 2021, Liang et al., 2022, Wang et al., 2021). Sudden water pollution seriously threatens the safety of industrial and domestic water supplies and can cause social panic (Long et al., 2019). In recent years, sudden water pollution has become more frequent (Li et al., 2019).

To reduce the damage caused by sudden water pollution, it is important to detect the occurrence of water pollution and identify its source (Wu et al., 2020). This requires frequent measurement of water quality at many points.

Chemical Oxygen Demand (COD), one of the indicators of water pollution, is generally measured by collecting samples in the field and using reagents and spectrometers, which require high measuring and human costs to perform many measurements (Wang et al., 2019). To reduce labor costs, sensors for monitoring COD have been studied (Mohammadi et al., 2020, Sun et al., 2022). However, many of them use electrical devices that require external energy, which poses a measuring cost problem.

Microbial Fuel Cells (MFC) are systems that convert organic matter in water into electrical energy (Nguyen et al., 2022). Recently, the use of MFCs for monitoring COD has been considered (Xiao et al., 2020). This is based on the fact that the amount of electricity generated by an MFC is affected by the COD level in the water. Furthermore, since monitoring of COD is performed by generating electrical energy, it is expected to reduce the cost of measurement.

In this study, a COD sensor was fabricated using a block-shaped electrode made from rice husks to reduce the cost significantly. Since rice husks are industrial waste, they not only reduce costs but also promote solutions to the waste problem, which is one of the factors contributing to environmental pollution. Furthermore, by utilizing a block-shaped electrode with high physical strength, microbes were attached to the anode surface using a simple method, such as simply inserting the anode into the soil. In addition, a floating MFC was adopted to facilitate the placement and maintenance of the sensor in rivers and lakes. Since the reduced cost and simplified placement of the sensors make it feasible to set them up at many locations, they are expected to be used to detect outbreaks of sudden water pollution and to identify the source of the pollution. Therefore, the purpose of this COD monitoring experiment was to provide alerts for sudden increases in COD. Furthermore, the experiment was run for 230 days without maintenance, assuming that the system would be operated for an extended period of time.

2. Materials and methods

2.1. Fabrication of MFC for COD sensor

Block-shaped electrodes were fabricated using rice husk smoked charcoal (Tokorozawa Ueki Bachi Center, Ltd., Saitama, Japan), Japanese ink (Boku-Eki, Daiso Industries Co., Ltd., Hiroshima, Japan), and stainless steel mesh (304–100 mesh) as materials for the electrodes. Japanese ink was used as a binder because it is a conductive colloidal solution that hardens after drying. The block-shaped electrodes were fabricated using the same method as in the previous study (Hirose et al., 2023). The method is simple and easy to mass-produce: mix the above electrode materials, pour them into a mold, and let them harden by drying. The detailed composition of the electrode materials is shown in Table 1. In single-chamber MFCs, microbial deposition on the cathode surfaces can lead to excess electron backflow, which is a cause of poor MFC performance (Li et al., 2023). Therefore, the copper powder was added only to the cathode for bactericidal properties. In MFC, electrons are received from microorganisms at the anode, so if microbes adhere to the cathode, the electrons flow back.

Table 1 Amount of anode and cathode material.

Material	Anode (0.8 cm ³)	Cathode (2.4 cm ³)
Rice husk smoked charcoal	0.2 g	0.6 g
Japanese ink	0.7 ml	3 ml
Copper powder	-	0.1 g

As shown in Figure 1, the fabricated MFC consists of an anode, a cathode, and a float. The cathode surface was exposed to the air using a float to accelerate the reduction reaction at the cathode. There are two advantages to using floats. First, the MFC can maintain its position on the water surface even when the water level changes. Second, since the MFC is floated on the water's surface, it is simple to set it up. These two advantages make the MFC suitable for

setting up at many points in rivers and lakes. The material cost of the electrodes fabricated in this experiment was \$0.022 per 1 cm³.

2.2. Adjustment of COD level

In this experiment, the Luria–Bertani (LB) medium was used as the organic matter source. The COD of the LB medium is 18,600 mg/L. Specific COD values were obtained by diluting the LB medium with tap water. LB medium was prepared by the following method. Tryptone 5 g, yeast extract 2.5 g, and sodium chloride 5 g were dissolved in 500 ml of purified water. 2.5 ml of sodium hydroxide solution (0.025 mol/l) was added to adjust pH. The prepared LB medium was sterilized by autoclave.

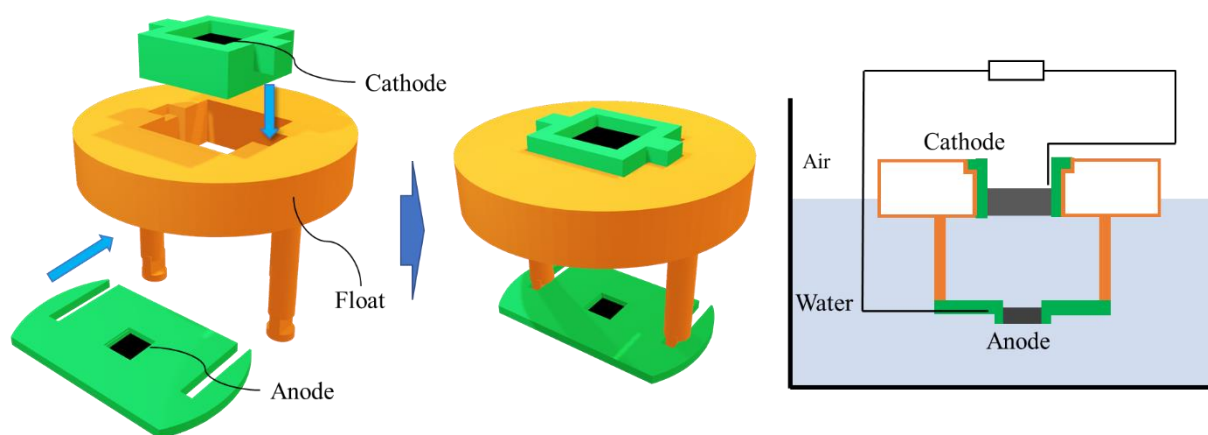


Figure 1. Schematic diagram of MFC configuration.



Figure 2. Method of biofilm formation on anode surfaces.

2.2. Biofilm formation on the anode surface

For an MFC to generate electricity, microorganisms biofilms must be formed on the anodes. However, rivers and lakes have low COD under normal conditions, making it difficult to ensure biofilm formation on the anode. Therefore, to ensure the formation of a biofilm on the surface of the anode, the anode was inserted into the soil for five days (Figure 2). The soil was collected from land on the campus of Ritsumeikan University. The soil has not been characterized due to the lack of soil characterization systems. The surface of the anodes removed from the soil was rinsed with tap water to remove any excess soil.

2.3. COD sensing effectiveness measurement

First, MFC was floated in a solution with a COD of 5 mg/L, assuming normal conditions in rivers and lakes. Immediately after the MFC was floated, electricity was generated by the decomposition of organic matter obtained from the soil, so the sensing experiment was started after this electricity generation was finished. COD was switched between 30 and 150, and the load (10 k Ω) voltage was monitored at each COD level. The 10 k Ω load was chosen to

ensure the MFC was not over-discharged, so the voltage response to the COD change was in a differentiable range. Taking China as an example, the maximum COD for surface water environmental standards (GB3838-2002) is 40 mg/L, so it is necessary to be alert to levels above that. When switching COD levels in the range of 30 mg/L to 150 mg/L, the COD level was set to 5 mg/L from each COD level each time and waited until the MFC was not generating power. The automatic voltage measurement system (NI USB-3210, National Instruments Corp., USA) was used to monitor voltage.

3. Results and discussion

3.1. Observation of biofilm on the anode surface

The surface of the anodes was observed by SEM (S-4300, Hitachi, Ltd., Japan) after removal from the soil, and the attached soil was washed off by water. Samples were dehydrated by ethanol and coated with gold for SEM observation. The SEM image shown in Figure 3 confirms that good biofilm was formed on the anode surface. Thus, it was found that biofilms are formed on the surface by a simple method, such as inserting anodes into soil that can be easily obtained.

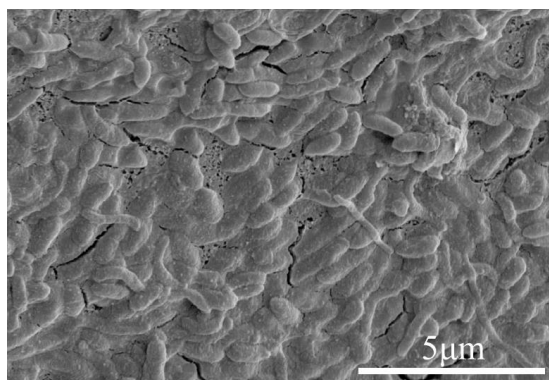


Figure 3 SEM image of the anode surface after being plugged into the soil for five days.

3.2. MFC Power Characteristics

The power density curve of the MFC was measured at COD 150 mg/L and 40 mg/L. Measurements were taken when the voltage reached a steady state after switching COD. The power density and current density were calculated by measuring the voltage with a multimeter when the external resistance was varied from 14 kΩ to 2 kΩ. At a COD level of 150 mg/L, the maximum power density of the MFC was $3.39 \mu\text{W}/\text{cm}^2$ at a current density of $0.015 \text{ mA}/\text{cm}^2$ (Figure 4). This indicates that the biofilm formed by plugging the anodes into the soil for five days contributed to the operation of the MFC. In addition, a significant difference in MFC output was observed between COD of 40 mg/L ($0.196 \mu\text{W}/\text{cm}^2$, $0.0035 \text{ mA}/\text{cm}^2$) and 150 mg/L from Figure 4. Obviously, the power density was much lower when COD concentration was low. A linear relationship between the MFC output and the COD concentration of the water is expected to be obtained.

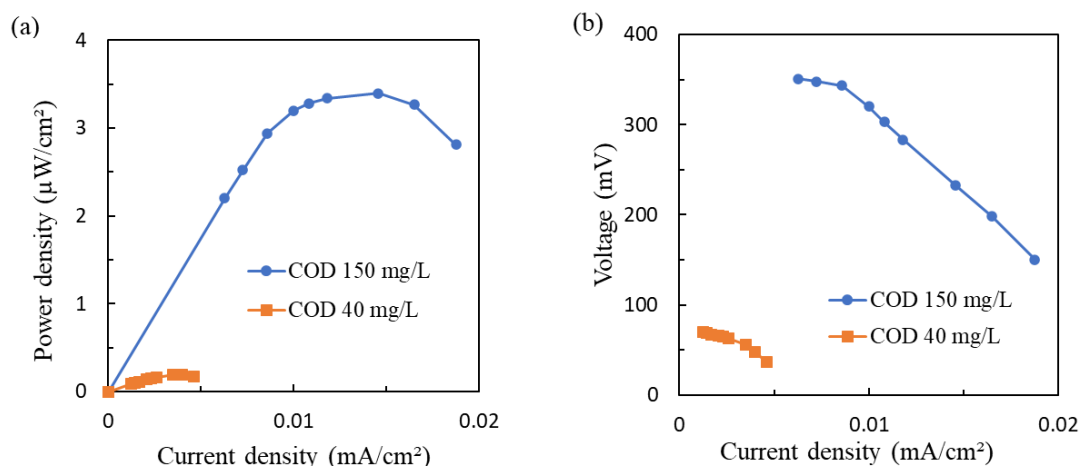


Figure 4 (a) Power density and (b) polarization curves at COD of 40 mg/L and 150 mg/L.

3.3. Correlation between COD level and MFC voltage

Figure 5 shows the maximum voltage of the MFC at each COD level in the range of 30 mg/L to 150 mg/L. Very little voltage was generated at COD values of 30 mg/L (0.008 V). It can be considered that up to a COD of 30 mg/L, there was not enough organic matter for the microbes to produce enough electrons to generate electricity in the MFC. The voltage was obtained when COD was 40 mg/L and higher, and a good linear relationship between COD and voltage was observed up to 100 mg/L. This may be because of two factors: (i) the increased amount of organic matter affected the metabolic activity of the microbes, and (ii) the increased number of microbes in contact with the anodes.

When COD was higher than 125 mg/L, the MFC was saturated with power generation. There is a correlation between COD levels and MFC voltage at levels above 40 mg/L, which is the environmental standard for water quality. Moreover, the voltage was 0.3 V at 125 mg/L and above. Thus, it is expected that the generated voltage of the MFC could perform the role of an alert signal for early detecting water pollution.

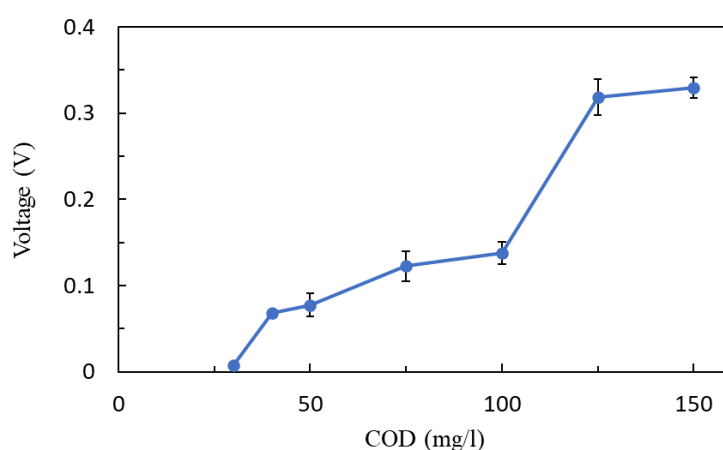


Figure 5 Voltage of MFC at each COD level.

3.4. Response characteristics of MFC for COD sensors

The response time of the MFC was measured when COD levels changed. The horizontal axis of Figure 6 represents the time elapsed since the COD level was changed. At a COD of 150 mg/L, the voltage of the MFC began to increase at 1.25 hours. After 12 and 24 hours, 194 mV and 270 mV voltages were obtained, respectively.

Comparing COD of 50 mg/L, 100 mg/L, and 150 mg/L, it was found that the higher the COD level, the shorter the MFC response time (50 mg/L: 8.25 hours, 100 mg/L: 3.25 hours, 150 mg/L: 1.25 hours). The higher the amount of organic matter, the more likely the microbes were transferred from the starved state to the active state in a shorter time. Depending on the level of organic matter, the marked difference in time to start the response could help locate the source of contamination with a simple electrical system.

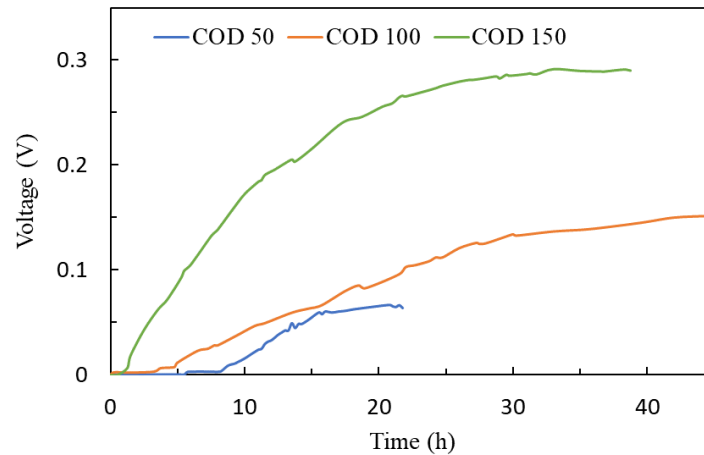


Figure 6 Voltage change in MFC when switching COD levels to 50 mg/L, 100 mg/L, and 150 mg/L.

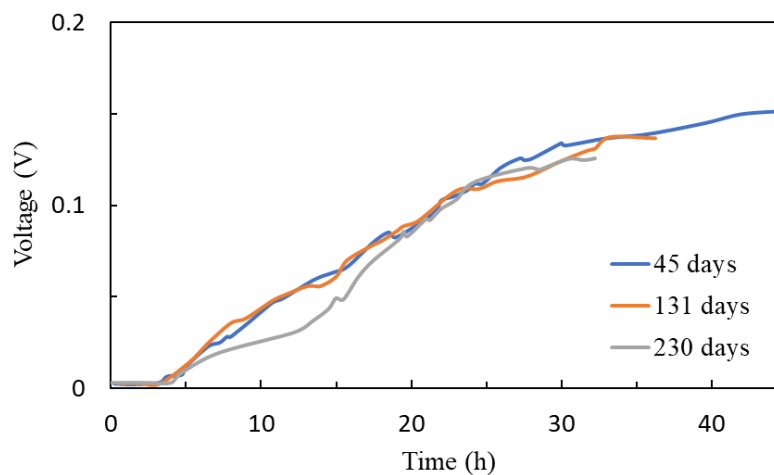


Figure 7 Voltage characteristics for COD 100 mg/L at 45, 131, and 230 days after setting up the MFC.

3.3. Long-term stability evaluation of COD sensor

The voltage response of the MFC to COD 100 mg/L was selected and shown in Figure 7. The voltage response of the MFC to COD of 50 mg/L and 150 mg/L were similar to what is shown in Figure 6. The response times on days 45, 131, and 230 were 3.25, 3.25, and 4.25 hours, respectively, with no significant change over time. For the steady-state voltage, the voltage at day 230 (126 mV) was 16.5% less than that at day 45 (151 mV). Since the sensors were kept in an environment below COD 5 mg/L for about three months, the activity level of the biofilm on the anode surface was affected, and the sensing performance was considered to have deteriorated slightly. However, it can be expected to perform the function of alerting the user to the occurrence of sudden water pollution.

4. Conclusion

In this study, we investigated the application of MFC using electrodes made of smoked charcoal from rice husks, an industrial waste, as a COD sensor to alert sudden water pollution. Using rice husk smoked charcoal and Japanese ink as the electrode material, and the electrode was fabricated at a low material cost of \$0.022 per cm³. Because the electrodes are in block shape, biofilms were formed on the surface simply by inserting the anode into the soil for five days. The biofilm was maintained for at least 230 days on a block-shaped electrode with excellent physical stability. Furthermore, the MFC was made to float on the water surface so that it could be easily set up without specialized knowledge. A correlation was observed between the voltage and COD level of the produced MFC. There was also a correlation between COD level and sensor response speed; the higher the COD level, the faster the sensor began to respond. This difference in reaction rate could be used to identify the source location of the pollution. A limitation of

this research was that the soil used for pre-biofilm formation on the anode surface had not been characterized to find out the bacterial community in the soil. This limitation will be taken into account in future studies.

Acknowledgments

The abstract of this paper was presented in Climate Change and Environmental Sustainability (CCES) - 3rd Edition which was held on the 17th and 18th of September 2023.

Funding declaration:

This research did not receive any specific grants from funding agencies in the public, commercial, or not-for-profit sectors/individuals.

Ethics approval:

Not applicable.

Conflict of interest:

The authors declare that there is no competing interest.

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