ISSN: 2710-0588

Treatment of Shipboard Oily Wastewater Using Modified-Anode Microbial Fuel Cells

Weijie Yang, Yuwen Tao, Chun Zhao and Shaojun Zhang*

School of Shandong Jiaotong University, Weihai 264200, China

*Corresponding author

Abstract

With the rapid development of the shipping industry, pollution caused by shipboard oily wastewater has become an increasingly serious threat to marine ecosystems. Conventional physical, chemical, and biological treatment methods have limitations such as high energy consumption, unstable treatment performance, and potential secondary pollution when treating highly emulsified oily wastewater. To improve the electricity-generation and oily-wastewater-treatment performance of microbial fuel cells (MFCs), three anodes, namely CF, CeO_2/CF, and CeO_2-β-CD/CF, were prepared using carbon felt as the substrate and applied in dual-chamber MFCs. The effects of different anode materials on electricity generation and oil degradation were comparatively investigated. The water contact angles of CF, CeO_2/CF, and CeO_2-β-CD/CF were 101.632°, 86.845°, and 66.877°, respectively, indicating that the combined modification with CeO_2 and β-CD significantly improved the surface wettability of carbon felt. SEM observations showed that the modification increased the surface roughness of the carbon fibers without noticeably damaging their original three-dimensional fibrous structure. The maximum output voltages of the MFCs equipped with the three anodes were 0.5313 V, 0.6300 V, and 0.6785 V, respectively, and the maximum voltage of the CeO_2-β-CD/CF-based MFC was 27.71% higher than that of the CF-based MFC. After 7 days of continuous operation, the corresponding oil degradation rates were 58.23%, 71.48%, and 77.16%, respectively. These results demonstrate that the CeO_2-β-CD composite modification provides favorable conditions for microbial attachment, biofilm formation, and sufficient contact between the electrode and anolyte by improving the surface wettability and morphology of carbon felt, thereby enhancing both electricity generation and oil-pollutant degradation. This study provides a promising technical approach for the efficient treatment of shipboard oily wastewater.

Keywords

Microbial fuel cell; Shipboard oily wastewater; Carbon felt; Cerium oxide; β-Cyclodextrin.

1. Introduction

In recent years, environmental pollution and energy shortages have become two major challenges affecting sustainable social and economic development. Although fossil fuels remain an important part of the global energy system, their continuous consumption accelerates the depletion of non-renewable resources and releases considerable amounts of pollutants into the environment. Therefore, the development of technologies capable of simultaneously achieving wastewater treatment and energy recovery has attracted increasing attention. Microbial fuel cells (MFCs) are bioelectrochemical systems that directly convert the chemical energy stored in organic matter into electrical energy through microbial metabolism, providing a promising approach for environmental remediation and renewable-energy recovery [1].

ISSN: 2710-0588

Ship oily wastewater is an important source of marine pollution generated during ship operation, maintenance, and cargo transportation. According to its source, ship oily wastewater can generally be divided into oily tank-washing wastewater, oily ballast water, and engine-room bilge water. Oily tank-washing wastewater is mainly generated during the cleaning and maintenance of cargo tanks or oil tanks. Oily ballast water is formed when ballast water comes into contact with residual oil in cargo tanks. Engine-room bilge water is produced by the accumulation of leaked fuel oil, lubricating oil, hydraulic oil, cooling water, and cleaning wastewater in the lower part of the engine room. Due to ship motion, mechanical vibration, and the presence of surfactants, oil pollutants may exist as free oil, dispersed oil, and stable emulsified oil, resulting in complex wastewater composition and considerable treatment difficulty [2].

If untreated ship oily wastewater is discharged directly into the marine environment, oil pollutants may spread over the water surface and form an oil film. This film can restrict oxygen exchange between water and air, reduce the dissolved oxygen concentration, and interfere with the photosynthesis, respiration, growth, and reproduction of aquatic organisms. In addition, some petroleum hydrocarbons can accumulate through the aquatic food chain and pose potential risks to marine ecosystems and human health. Therefore, the effective treatment of ship oily wastewater is essential for marine environmental protection and the sustainable development of the shipping industry [3].

Conventional treatment methods for ship oily wastewater mainly include physical separation, chemical treatment, and biological treatment. Physical methods are generally simple to operate, but their removal efficiency is limited for finely dispersed and stable emulsified oil. Chemical methods can improve oil removal by oxidation, coagulation, or flocculation, but they often require additional chemical reagents and may generate secondary pollutants. Biological treatment methods are relatively environmentally friendly, but their performance can be affected by salinity, oil concentration, wastewater composition, and microbial activity. Consequently, developing a low-energy, environmentally friendly, and efficient technology for treating complex ship oily wastewater remains an important research objective [4].

A typical dual-chamber MFC consists of an anode chamber, a cathode chamber, an anode, a cathode, an external circuit, and a proton exchange membrane or ion exchange membrane separating the two chambers. In the anaerobic anode chamber, electrogenic microorganisms oxidize organic matter and release electrons and protons. The electrons are transferred to the anode and subsequently flow through the external circuit to the cathode, thereby generating an electric current. Meanwhile, the protons migrate through the membrane into the cathode chamber and participate in the cathodic reduction reaction. Through this process, MFCs can remove organic pollutants while recovering part of their chemical energy in the form of electricity [5].

The operating performance of an MFC is affected by reactor configuration, microbial community, substrate characteristics, temperature, pH, external resistance, and electrode materials. Among these factors, the anode is the primary site for microbial attachment, biofilm formation, organic-matter oxidation, and extracellular electron transfer. Its surface morphology, electrical conductivity, chemical stability, wettability, and biocompatibility directly influence MFC start-up, internal resistance, electricity generation, and pollutant-removal efficiency. Therefore, the selection of an appropriate anode material is essential for improving the overall performance of an MFC [6].

Carbon-based materials are widely used as MFC anodes because of their relatively low cost, good electrical conductivity, chemical stability, and biocompatibility. Carbon felt, in particular, possesses a three-dimensional fibrous structure and a relatively large surface area, which can provide space for microbial colonization and biofilm development. However, untreated carbon felt still has limitations, including insufficient surface activity and restricted interfacial

ISSN: 2710-0588

interaction between the electrode and microorganisms. These limitations may reduce microbial attachment and electron-transfer efficiency, thereby restricting electricity generation and wastewater-treatment performance [7].

In recent years, different functional materials have been introduced into carbon-based electrodes to improve the electrochemical and wastewater-treatment performance of MFCs. CeO_2-containing electrodes have been investigated in MFC systems because of their potential application in electrode-interface regulation and electrochemical reactions [8]. β-Cyclodextrin-containing electrodes have also been applied in MFCs and have demonstrated feasibility in improving electrode performance and organic-wastewater treatment [9]. However, comparative studies of CF, CeO_2/CF, and CeO_2-β-CD/CF anodes for the treatment of saline and highly emulsified ship oily wastewater remain limited.

Therefore, in this study, conventional carbon felt (CF), cerium oxide-loaded carbon felt (CeO_2/CF), and cerium oxide–β-cyclodextrin composite carbon felt (CeO_2-β-CD/CF) were used as anode materials to construct three dual-chamber microbial fuel cells under identical operating conditions. The output voltage and oil degradation performance of the MFCs equipped with different anode materials were comparatively investigated. Through comparison of the maximum output voltage and the oil degradation rate after continuous operation, the influence of different anode materials on the electricity-generation and oily-wastewater-treatment performance of the MFC was evaluated. This study is expected to provide an experimental basis for the selection of MFC anode materials and the efficient treatment of ship oily wastewater.

2. Experimental Preparation and Characterization

2.1. Preparation of MFC Anodes

Carbon felt was used as the substrate to prepare three types of anodes: untreated carbon felt (CF), CeO_2-modified carbon felt (CeO_2/CF), and CeO_2-β-cyclodextrin composite-modified carbon felt (CeO_2-β-CD/CF).

During production, transportation, and storage, dust, oil, and other impurities may adhere to the surface of carbon felt, occupy active sites, and interfere with subsequent material loading and microbial attachment. Therefore, the carbon felt was pretreated before modification.

The carbon felt was cut into square pieces with dimensions of 1.5 cm × 1.5 cm. The samples were successively ultrasonically cleaned in absolute ethanol and deionized water for 30 min to remove surface organic contaminants and soluble impurities. After cleaning, the carbon felt was dried in an electric blast drying oven at 60 °C for 2 h. The obtained electrode was denoted as CF.

A total of 0.3 g of nano-CeO_2 powder was added to 100 mL of deionized water. The mixture was magnetically stirred and ultrasonically dispersed to obtain a homogeneous CeO_2 suspension.

The pretreated CF electrode was completely immersed in the CeO_2 suspension and ultrasonically treated for 30 min, allowing the CeO_2 particles to fully contact the carbon-felt fibers and enter the internal pore structure. The electrode was then statically immersed for 12 h to improve the loading of CeO_2 on the carbon-felt surface. Afterward, the electrode was removed, gently rinsed with deionized water to eliminate loosely attached particles, and dried at 60 °C for 2 h. The resulting electrode was denoted as CeO_2/CF.

A total of 0.4 g of β-cyclodextrin (β-CD) was dissolved in 100 mL of deionized water under magnetic stirring for 1 h to obtain a β-CD solution. The solution was then mixed with the prepared CeO_2 suspension, followed by stirring and ultrasonic treatment to form a uniformly dispersed CeO_2-β-CD composite suspension.

ISSN: 2710-0588

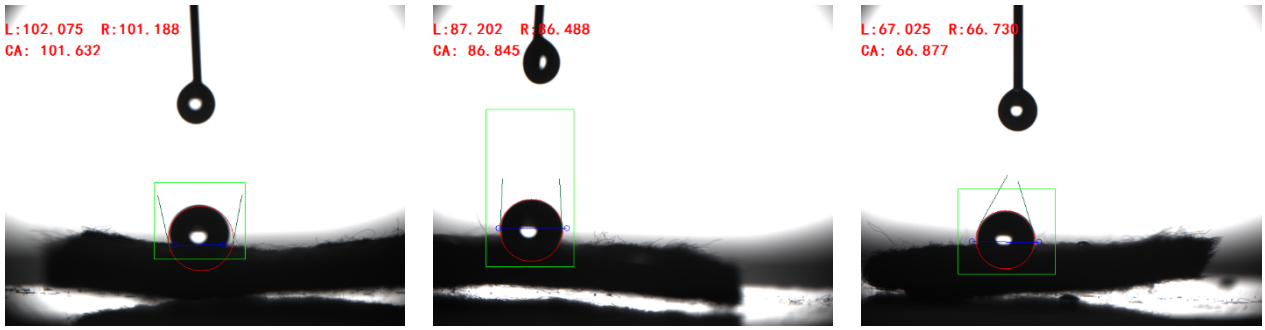
The pretreated CF electrode was immersed in the composite suspension and ultrasonically treated for 30 min to promote the uniform dispersion and loading of CeO_2 and β-CD on the carbon-felt fibers. The electrode was then statically immersed for 12 h. After immersion, it was rinsed with deionized water and dried at 60 °C for 2 h. The obtained composite anode was denoted as CeO_2-β-CD/CF.

2.2. Contact Angle Analysis of Anode Materials

Static water contact angle measurements were conducted to characterize the surface wettability of the electrodes. During the test, each electrode sample was horizontally fixed on the sample stage. A water droplet was deposited onto the electrode surface using a microsyringe, and the droplet profile was recorded with an optical imaging system. The contact angle was obtained by fitting the solid–liquid–gas three-phase interface according to the Young–Laplace equation.

The water contact angle reflects the hydrophilicity of the electrode material. When the contact angle is lower than 90°, the material surface is considered hydrophilic, and a smaller contact angle indicates stronger hydrophilicity. In contrast, a contact angle greater than 90° indicates hydrophobicity. Improved surface hydrophilicity facilitates the penetration of the anolyte into the internal structure of the carbon felt and provides favorable conditions for microbial attachment and biofilm formation. Therefore, the contact angles of CF, CeO_2/CF, and CeO_2-β-CD/CF were compared to evaluate the effect of electrode modification on surface wettability.

As shown in Fig. 1, the water contact angles of CF, CeO_2/CF, and CeO_2-β-CD/CF were 101.632°, 86.845°, and 66.877°, respectively. The contact angle of the unmodified CF electrode was greater than 90°, indicating a hydrophobic surface. After CeO_2 loading, the contact angle of CeO_2/CF decreased to 86.845°, showing that the surface wettability of the carbon felt was significantly improved and changed from hydrophobic to hydrophilic. With the further introduction of β-CD, the contact angle of CeO_2-β-CD/CF decreased to 66.877°, exhibiting the strongest hydrophilicity among the three electrodes. These results indicate that the combined loading of CeO_2 and β-CD effectively improves the surface wettability of carbon felt, promotes sufficient contact between the electrode and the anolyte, and provides a more favorable interfacial environment for microbial attachment and biofilm formation.



(a) CF (b) CeO_2/CF (c) CeO_2-β-CD/CF

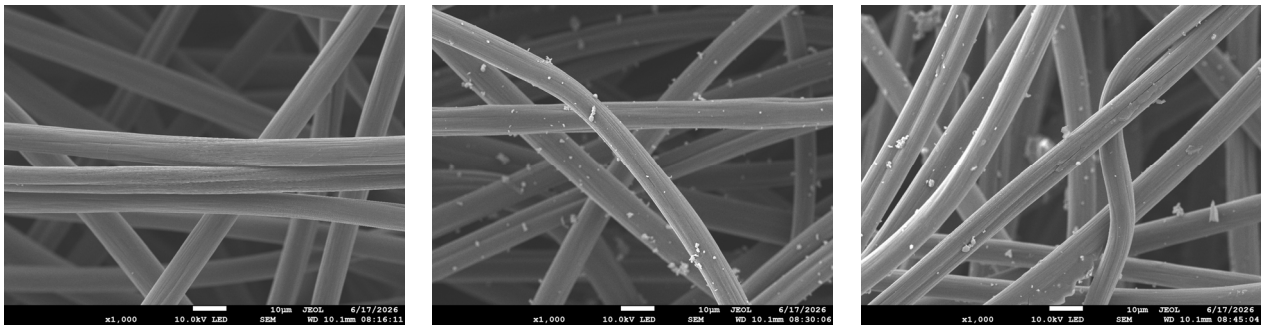
Figure 1. Water contact angles of different anode materials

2.3. SEM Analysis of Anode Materials

Scanning electron microscopy (SEM) characterizes the microstructure and surface morphology of materials based on electron beam–sample interactions. Before observation, the samples were fixed on conductive adhesive and coated with an Au–Pd alloy to improve surface conductivity. The surface morphologies of CF, CeO_2/CF, and CeO_2-β-CD/CF were then observed under vacuum conditions at an accelerating voltage of 10.0 kV and a magnification of ×1000.

ISSN: 2710-0588

As shown in Fig. 2(a), untreated CF exhibited an interlaced three-dimensional fibrous structure with a relatively smooth surface. After CeO_2 loading, numerous granular deposits appeared on the carbon fibers, resulting in increased surface roughness, as shown in Fig. 2(b). In Fig. 2(c), granular and irregular deposits were observed on the surface of CeO_2-β-CD/CF, showing a relatively continuous coating structure. The modification did not noticeably damage the original fibrous framework of carbon felt, while the increased surface roughness provided more potential sites for microbial attachment and biofilm formation.



(a) CF (b) CeO_2/CF (c) CeO_2-β-CD/CF

Figure 2. SEM images of different anode materials

2.4. Cultivation of Electrogenic Microorganisms and Preparation of Electrolytes

The mixed microbial community used in the anode chamber consisted of *Clostridium butyricum*, *Shewanella* sp., *Rhodopseudomonas palustris*, *Bacillus subtilis*, and *Saccharomyces cerevisiae*. Each strain was first activated separately and subsequently inoculated into an inorganic salt medium for mixed cultivation. The culture was incubated at 35 °C and 180 r/min for 24 h to obtain a stable microbial inoculum.

The inorganic salt medium contained 0.01 g/L disodium ethylenediaminetetraacetate, 3.0 g/L KH_2PO_4, 1.5 g/L K_2HPO_4, 2.0 g/L NH_4NO_3, 0.01 g/L anhydrous $CaCl_2$, and 0.1 g/L $MgSO_4 \cdot 7H_2O$. The medium was prepared with distilled water, and its initial pH was adjusted to 7.5.

The anolyte was prepared using emulsified diesel as the organic substrate. The inorganic salt medium was sterilized at 121 °C for 15 min and cooled to room temperature. Subsequently, 2.0 g of No. 0 diesel and an appropriate amount of Span 80 were added, and the total volume was adjusted to 1 L. The mixture was magnetically stirred until a uniform emulsified diesel solution with an oil concentration of 2.0 g/L was obtained.

Potassium ferricyanide can act as an effective electron acceptor in the cathode chamber of a dual-chamber MFC [10]. Therefore, potassium ferricyanide was completely dissolved in deionized water to prepare a 30 mM solution, which was used as the catholyte. Before the MFC was assembled and started, the prepared mixed microbial culture was inoculated into the anolyte.

2.5. Construction and Startup of MFC Devices

Three dual-chamber MFC devices were constructed under aseptic conditions to compare the performance of CF, CeO_2/CF, and CeO_2-β-CD/CF anodes. Before assembly, the MFC chambers were sterilized by ultraviolet irradiation for 2 h. Subsequently, 50 mL of anolyte and 50 mL of catholyte were added to the anode and cathode chambers, respectively, and 1 mL of the prepared mixed microbial culture was inoculated into the anolyte.

The CF, CeO_2/CF, and CeO_2-β-CD/CF electrodes with dimensions of 1.5 cm × 1.5 cm were separately immersed in the anolyte as anodes. A carbon rod with a diameter of 0.5 cm and a

ISSN: 2710-0588

length of 15 cm was used as the cathode. The anode and cathode were connected through an external circuit, and all MFC devices were operated under the same conditions.

The anode chamber was sealed with a silicone plug to maintain an anaerobic environment suitable for microbial growth and metabolism. The cathode chamber was exposed to air to facilitate the cathodic reduction reaction. After assembly, the devices were operated continuously to promote microbial attachment and biofilm formation on the anode surfaces. The construction procedure was adapted from the dual-chamber system described in the reference study.

3. Performance of MFC Devices for Treating Shipboard Oily Wastewater

3.1. Output Voltage Performance Analysis of MFC Devices

The output voltage is an important parameter for evaluating the electricity-generation performance of MFCs. During the test, a CT4008 battery testing system was used, and a 1000 Ω external resistor was connected to each MFC device. The output voltage was recorded at intervals of 1 min during continuous operation, and the collected data were automatically stored by the system.

As shown in Fig. 3, the output voltages of the three MFCs initially increased and subsequently decreased. During the initial stage, the microorganisms gradually adapted to the anolyte and attached to the anode surfaces, leading to an increase in voltage output. The maximum output voltages of the CF, CeO_2/CF, and CeO_2-β-CD/CF MFCs were 0.5313 V, 0.6300 V, and 0.6785 V, respectively. Compared with the CF anode, the maximum output voltages of CeO_2/CF and CeO_2-β-CD/CF increased by approximately 18.58% and 27.71%, respectively.

After reaching the maximum values, the output voltages gradually decreased, which may be attributed to the continuous consumption of available substrates and the weakening of microbial metabolic activity. During the later stage, the voltage curves gradually stabilized. Throughout the operation period, the MFC equipped with the CeO_2-β-CD/CF anode exhibited the highest voltage output, followed by CeO_2/CF and CF. The improved electricity-generation performance may be related to the enhanced surface wettability and roughness of the modified anodes, which facilitated electrode–anolyte contact and provided more favorable conditions for microbial attachment and biofilm formation.

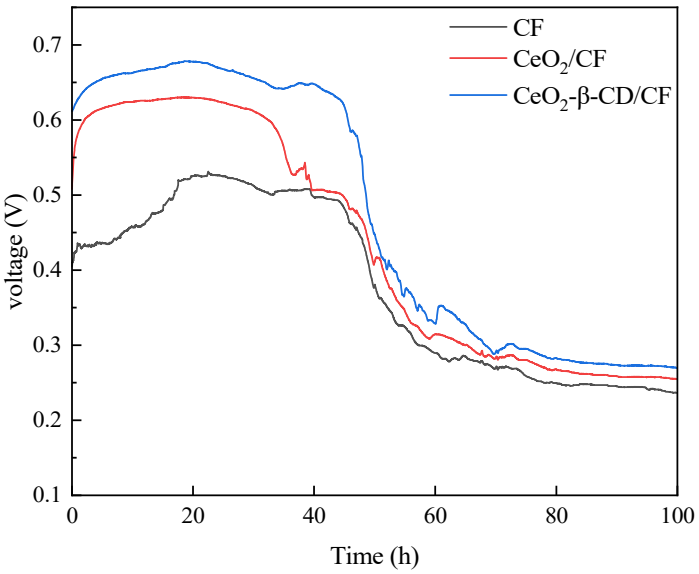


Figure 3. Output voltage curves of MFCs equipped with different anodes

ISSN: 2710-0588

3.2. Degradation Performance of MFC Devices for Shipboard Oily Wastewater

In this experiment, the oil degradation rate refers to the change in oil content in shipboard oily wastewater before and after treatment by the MFC devices under specified conditions. It is an important parameter for evaluating the oily wastewater treatment performance of the MFCs. The oil content was determined using a UV-1800 ultraviolet spectrophotometer.

Before determining the oil degradation rate, a standard curve of emulsified diesel was established. Emulsified diesel was used as the solute and petroleum ether as the solvent to prepare standard solutions with different oil concentrations. The absorbance of each standard solution was measured using an ultraviolet spectrophotometer. As shown in Fig. 4, the linear regression equation of the standard curve was: $y = 0.01862x - 0.00143$, $R^2 = 0.99945$

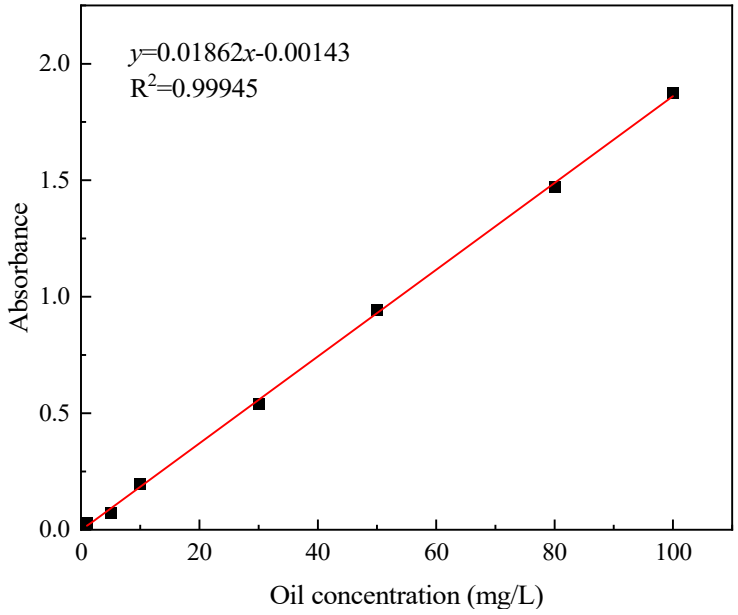


Figure 4. Standard curve of oil concentration

where x represents the oil concentration in the standard solution and y represents the corresponding absorbance. The high coefficient of determination indicates a good linear relationship between oil concentration and absorbance.

For oil-content determination, 10 mL of anolyte was collected, followed by the addition of 0.6 g of NaCl and 5 mL of petroleum ether. The mixture was vortexed for 10 min, ultrasonically extracted for 30 min, and centrifuged at 5670 r/min for 10 min. After phase separation, the upper petroleum ether phase was collected, dried with anhydrous sodium sulfate, and filtered. The volume was then adjusted to 1 mL with petroleum ether, and the absorbance was measured using a UV-1800 ultraviolet spectrophotometer.

The oil degradation rate of the MFC device was calculated according to Equation (1):

$$\eta = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where η is the oil degradation rate, C_0 is the initial oil concentration in the oily wastewater, and C is the oil concentration after MFC treatment.

ISSN: 2710-0588

The MFC devices equipped with CF, CeO_2/CF, and CeO_2-β-CD/CF anodes were subjected to a continuous 7-day degradation test. As shown in Fig. 5, the oil degradation rates of the three systems were 58.23%, 71.48%, and 77.16%, respectively. Compared with the CF-based MFC, the degradation rates of the CeO_2/CF and CeO_2-β-CD/CF systems increased by 13.25 and 18.93 percentage points, respectively.

Among the three systems, the CeO_2-β-CD/CF-based MFC exhibited the highest oil degradation rate. This may be attributed to the improved surface wettability and roughness of the composite anode, which enhanced contact among the electrode, microorganisms, and oily wastewater. The introduction of β-CD may also promote the adsorption and enrichment of oil pollutants on the anode surface, thereby providing favorable conditions for microbial metabolism and oil degradation.

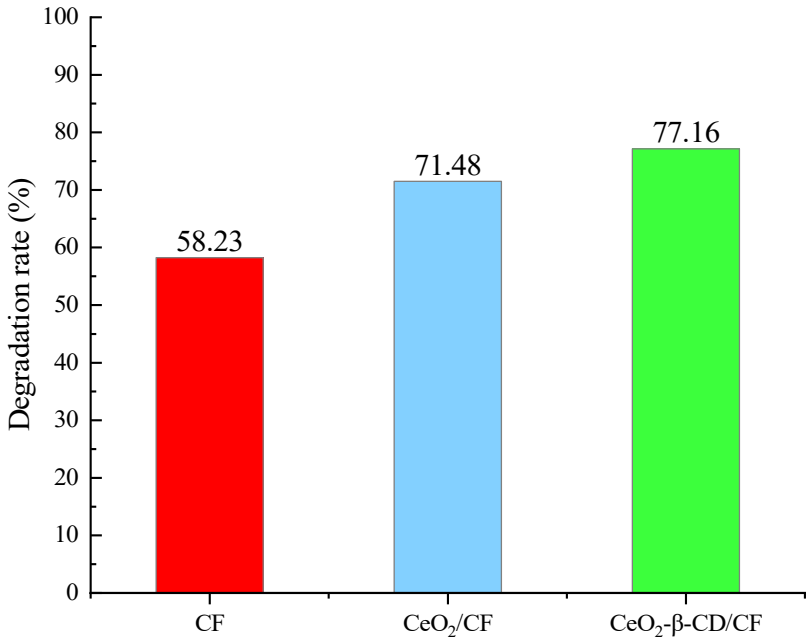


Figure 5. Oil degradation rates of MFC devices equipped with different anodes

4. Conclusion

In this study, CF, CeO_2/CF, and CeO_2-β-CD/CF anodes were prepared and applied in dual-chamber MFCs for the treatment of shipboard oily wastewater. Contact angle measurements showed that the water contact angle decreased from 101.632° for CF to 86.845° for CeO_2/CF and 66.877° for CeO_2-β-CD/CF, demonstrating that the loading of CeO_2 and β-CD effectively improved the surface wettability of carbon felt. SEM observations showed that granular and irregular deposits formed on the modified carbon fibers, increasing the surface roughness without noticeably damaging the original three-dimensional fibrous framework. The maximum output voltages of the CF-, CeO_2/CF-, and CeO_2-β-CD/CF-based MFCs were 0.5313 V, 0.6300 V, and 0.6785 V, respectively. Compared with CF, the maximum output voltages of CeO_2/CF and CeO_2-β-CD/CF increased by 18.58% and 27.71%, respectively. After continuous operation for 7 days, the oil degradation rates of the three MFCs were 58.23%, 71.48%, and 77.16%, respectively. The CeO_2-β-CD/CF-based MFC exhibited the highest electricity-generation and oil-degradation performance. These results demonstrate that the composite modification of carbon felt with CeO_2 and β-CD can improve the overall performance of MFCs, potentially by enhancing surface wettability, increasing available attachment sites, and promoting contact

ISSN: 2710-0588

among the electrode, microorganisms, and oil pollutants. Therefore, CeO_2-β-CD/CF is a promising anode material for the efficient treatment and energy recovery of shipboard oily wastewater.

References

[1] Jalili, P., Ala, A., Nazari, P., et al. (2024). A comprehensive review of microbial fuel cells considering materials, methods, structures, and microorganisms. *Heliyon*, *10*(3). https://doi.org/10.1016/j.heliyon.2024.e19283.

[2] Kári-Horváth, A. (2024). Overview of the utilization and disposal of waste from maritime shipping and examination of possible solutions. *Hungarian Agricultural Engineering*, *43*, 37–52. https://doi.org/10.17676/HAE.2024.43.37

[3] Pinar, O., & Rodríguez-Couto, S. (2024). Advancements in bilge wastewater treatment: A review for current and future trends. *Science of The Total Environment*, *951*, 175587. https://doi.org/10.1016/j.scitotenv.2024.175587

[4] Mohyudin, S., Farooq, R., Jubeen, F., et al. (2022). Microbial fuel cells a state-of-the-art technology for wastewater treatment and bioelectricity generation. *Environmental Research*, *204*, 112387. https://doi.org/10.1016/j.envres.2021.112387

[5] Ma, J., Zhang, J., Zhang, Y., et al. (2023). Progress on anodic modification materials and future development directions in microbial fuel cells. *Journal of Power Sources*, *556*, 232486. https://doi.org/10.1016/j.jpowsour.2023.232486

[6] Agrahari, R., Bayar, B., Abubackar, H. N., et al. (2022). Advances in the development of electrode materials for improving the reactor kinetics in microbial fuel cells. *Chemosphere*, *290*, 133184. https://doi.org/10.1016/j.chemosphere.2021.133184

[7] Fan, X., Zhou, Y., Jin, X., et al. (2021). Carbon material-based anodes in the microbial fuel cells. *Carbon Energy*, *3*(3), 449–472. https://doi.org/10.1002/cey2.112

[8] Pandey, K., Gupta, P., Verma, N., et al. (2021). A CeO_2 sprinkled graphitic novel packed bed anode-based single-chamber MFC for the treatment of high organic-loaded industrial effluent in upflow continuous mode. *Journal of Materials Chemistry A*, *9*(40), 23106–23116. https://doi.org/10.1039/D1TA05636A

[9] Fan, L., & Xi, Y. (2022). Effect of β-cyclodextrin/polydopamine composite modified anode on the performance of microbial fuel cell. *Bioprocess and Biosystems Engineering*, *45*(5), 855–864. https://doi.org/10.1007/s00449-022-02732-1

[10] Varnava, C. K., Persianis, P., Ieropoulos, I., et al. (2024). Electricity generation and real oily wastewater treatment by Pseudomonas citronellolis 620C in a microbial fuel cell: pyocyanin production as electron shuttle. *Bioprocess and Biosystems Engineering*, *47*(6), 903–917. https://doi.org/10.1007/s00449-024-02997-1