

# Preparation of New MFC Anode and Degradation Performance of Ship's Oily Waste Water

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**Abstract:** Microbial fuel cells (MFCs) have emerged as a promising technology for sustainable energy production and environmental remediation, particularly in treating oily wastewater in the maritime industry. However, their practical application has been limited by low power output and energy conversion efficiency. Research has explored enhancing MFC power output through anode modification and electrode material optimization, with biochar showing potential as an alternative anode material. Our study developed pine cone biochar as an anode for MFCs, demonstrating excellent biocompatibility and significantly improved power generation and degradation performance. FT-IR, contact angle measurements, and electrochemical techniques characterized the MFC performance, with biochar-based MFCs achieving higher voltage, power output, and current density compared to carbon felt. Additionally, biochar MFCs exhibited a higher oil wastewater degradation rate and COD removal efficiency. These findings suggest that biochar is a promising anode material for MFCs, warranting further research to optimize MFC design and operational conditions for effective wastewater treatment and energy recovery.

**Keywords:** MFC, Biochar anode, Electrochemical property, Ship oily-waste water.

## 1. Introduction

Microbial fuel cell (MFC) has received much attention in recent years due to its potential in sustainable energy production[1] and environmental remediation[2,3]. Microbial fuel cells are a promising technology for the treatment of oily wastewater in the maritime industry, offering a sustainable solution that combines environmental remediation with energy production[4]. However, its low power output and energy conversion efficiency have significantly limited its use in practical applications. Research on enhancing the power output of microbial fuel cells has shown promise, integrating supercapacitive features and optimizing electrode materials have been used to strengthen the power output of MFC[5,6], there are not appropriate for industry use. One way to enhance the power output and degradation performance of microbial fuel cells is through anode modification. For example, Y. Hindatu[7] showed that carbon nanotubes, stainless steel, conductive polymers, metal oxides, and electrolytes for anode modification can enhanced efficiency in energy generation and organic matter degradation. However, the widespread application of microbial fuel cell technology is constrained by technical challenges and economic limitations. The selection of anode materials remains a barrier that needs to be overcome for further advancements in MFC technology. We have developed pine cone biochar as an anode material for microbial fuel cells, which demonstrates excellent biocompatibility, significantly enhancing the power generation and degradation performance of MFCs. The performance of the MFCs was characterized using FT-IR, contact angle measurements, and electrochemical techniques, revealing that pine cone biochar effectively improves the operational efficiency of MFCs.

## 2. Experimental

### 2.1. Preparation of anode materials

Depending on the needs of the experiment, the anode will be experimented with carbon felt and biochar, respectively. For the cathode, the more common carbon rods will be used as electrodes.

**Biochar Preparation:** Biochar needs to be carbonized in a box resistor box for a certain time and temperature before it can be formed. Carbonization experiments will be carried out by selecting pine cone slices that have been carbonized for 30 min at 100°C, 200°C, 250°C, 300°C, 350°C, 400°C, and 450°C, respectively. After the pine cone blades are carbonized, the appropriate carbonized pine cones will be selected by comparison of appearance and hardness. The pine cone leaf pieces obtained by carbonizing at 300°C for 30 min will be selected as the anode electrode in this experiment.

### 2.2. MFC construction

The microbial fuel cell test can be divided into three parts according to the research order: substrate preparation, electrode fabrication, and characterization and analysis. The substrate is divided into two kinds: anode substrate and cathode substrate. The anode substrate solution consists of microbial culture medium, oil sewage water, and bacterial strains. The cathode solution was composed of potassium ferricyanide solution.

A two-chamber MFC reactor was used, separated by a proton exchange membrane, with an external load resistance of 1 kΩ. The anode was carbonized natural biomass electrode material, and the cathode was a carbon rod. The dual-chamber type fuel cell reaction chamber parts (Fig. 1) fabricated from poly(methyl methacrylate) by 3D printing were assembled according to the biomass membrane, the main body of the chamber, the outer cover of the chamber, and the fixtures.

The conical flask, anode material, cathode material, each

solution, and the microbial fuel cell shell used in the experiment were sterilized in a sterile bench for 30 min.

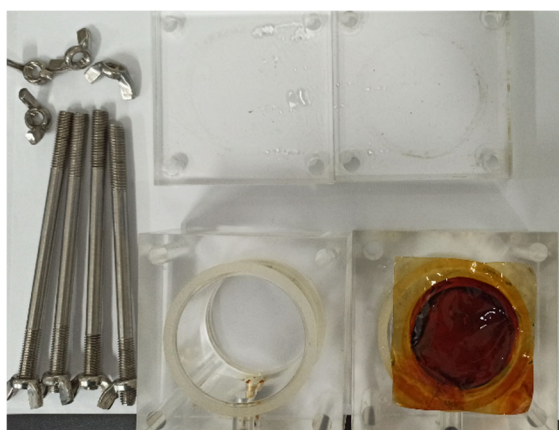


Figure 1. Microbial Fuel Cell Parts

## 2.3. Electrode primer preparation

### 2.3.1. Preparation of Oily Sewage:

Oily sewage can be two kinds of oily sewage collected from the bilge of the ship or synthetic oily sewage. In order to ensure that there is an obvious experimental effect, this test was carried out using 2000 ppm synthetic oil sewage. Use a pipette gun to suck up 0# diesel fuel, adjust the scale and then drop 0.2 ml into the prepared 100 ml of deionized water to form a mixture of oil and water. The beaker containing the oil-water mixture was placed in a magnetic stirrer for 20 min to fully agitate and emulsify the oil-water mixture. The emulsified oil-water mixture should be sterilized for 24 h on a sterile bench using ultraviolet sterilizing lamps.

### 2.3.2. Preparation of microbial media

The media involved in the thesis was carried out using nutrient broth, which needs to be autoclaved at 120°C for 20 min before use. The main components are shown in Table 1

Table 1. Nutrient broth medium and its components

Number	Ingredient	Dose g/L
1	peptone	10.0
2	Beef infusion powder	3.0
3	Sodium chloride	5.0
4	pH value	7.3
5	Deionized water	100

### 2.3.3. Bacterial strain selection

the role of the strain is to degrade the oil wastewater and produce electric current. After the preparation of strains, 5 ml of strains should be taken out and added to 100 ml of nutrient broth and put into 30°C constant temperature shaker for 24 h for strain activation. The main strains are shown in Table 2.

Table 2. Strain Name and Manufacturer

Number	Strain Name	Manufacturer
1	Yeasts	Angie's Yeast Co.
2	Pseudomonas aeruginosa Type III	Fontainebleau Biotechnology Co.
3	Clostridium butyricum type I	Fontainebleau Biotechnology Co.

### 2.3.4. Cathodic primer preparation

The cathodic substrate used in the experiments was

prepared using potassium ferricyanide ( $K_3[Fe(CN)_6]$ ) and deionized water to form a solution as the cathodic substrate. Potassium ferricyanide was weighed by a balance of 5 g and put into 500 ml of deionized water to form a potassium ferricyanide solution with a concentration of 120 mM. It was also stirred with a glass rod until it was completely dissolved and then put into a sterile operating table for sterilization.

## 3. Results and Discussion

### 3.1. Material characterization

#### 3.1.1. Analysis of the contact angle of water droplets

Before the start of the experiment, the selected biochar material and carbon felt were placed into an angular contactmeter for hydrophilicity testing. The test results of carbon felt are shown in Figure 2 (a), and the test results of biochar materials are shown in Figure 2 (b). Through the test, it can be found that the hydrophilicity of pine cone leaf biochar material is higher than that of carbon felt. The level of hydrophilicity indicates the level of microbial aggregation during the experiment. The higher the hydrophilicity, the superior microbial biocompatibility, and the higher the efficiency of electricity generation and decontamination.

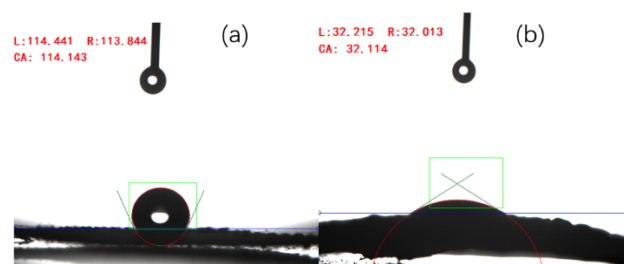


Figure 2. Results of Angular Contact Experiments on Different Materials

The contact angle gauge can assist in the comparison of the wettability and hydrophilicity of the electrode surface. The contact angle  $\alpha$  of the basic carbon felt electrode is 114.143°, but the contact angle of the biochar electrode after carbide  $\alpha$  is 32.114°.

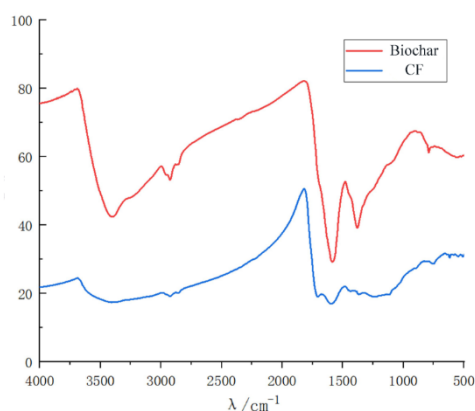
Through the contact angle data of various electrodes, it can be found that the contact angle of biochar anode is low, indicating that it has good surface wettability and hydrophilicity. Good hydrophilicity can promote the adsorption of strains on the electrode, and form the phenomenon of microbial colony covering the electrode, thereby improving the power production performance of MFC.

#### 3.1.2. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is an effective method for analyzing functional groups. The sample to be tested is put into the spectrometer, when the infrared light passes through, different functional groups absorb the infrared light differently, and the instrument plots the spectral distribution according to the transmittance of different frequencies, and different substances represent different functional groups or chemical bonds. Using infrared spectroscopy to characterize the pine cone leaf biochar material, and by consulting the functional group comparison table, we can analyze the changes of functional groups, chemical structures and isomers before and after the modification of the material.

Specific experimental method: the electrode material of

pine cone leaf, which was finished carbonization, was minus a small piece with scissors, and ground into a fine powder with an agate mortar and pestle for spare use. Potassium bromide powder was mixed with the electrode material powder in the ratio of 100:1 and fully ground and sliced for infrared spectroscopy scanning.



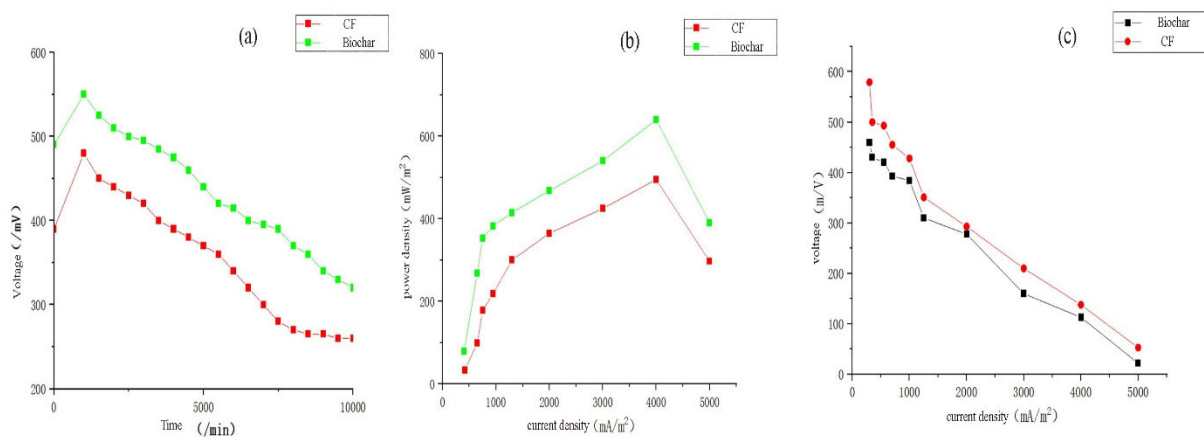
**Figure 3.** Fourier transform infrared spectroscopy analysis

The results of infrared spectroscopy (FT-IR) test of biochar from pine cone leaves are shown in Fig. 3. Among them, in the range of 4000~500  $\text{cm}^{-1}$ , both the traditional carbon felt material and the biochar anode material showed broad and strong absorption peaks at 3400  $\text{cm}^{-1}$ , and 3400  $\text{cm}^{-1}$  was the absorption peak of -OH, and the hydroxyl group, as a hydrophilic group, existed in the two anode materials, which

proved that both materials had hydrophilicity, and compared with the two, the peak intensity of the biochar anode material was greater, which could be deduced that the The biochar anode material selected in this study has good hydrophilicity, which is suitable for the survival of the electrode-producing degrading bacteria and has good biocompatibility. It is more conducive to the transfer of electrons and generates higher voltage and power density, which can be verified from the power density curve and voltage curve analyzed above. 2924  $\text{cm}^{-1}$  is the absorption vibration peak of C-H, 1581.2  $\text{cm}^{-1}$  is the absorption vibration peak of COO-M, and 1369  $\text{cm}^{-1}$  is the absorption vibration peak of  $\text{CH}_3$ .

### 3.2. Electrochemical performance analysis

After testing the hydrophilicity, the microbial fuel cell was assembled in the order of proton exchange membrane, reaction chamber, and fixation device from the inside to the outside by using the aseptic operating table. After the fuel cell was assembled sequentially, the prepared anode substrate was added to the left reaction chamber of the microbial fuel cell using a pipette gun, and the cathode substrate was added to the right reaction chamber of the cell. Both sides of the anode primer were added 25 ml. After each use of the pipette gun, the barrel needed to be changed when the aspirated solution was replaced. After the primer has been added, place biochar or carbon felt on the anode side and secure it with a clamped wire. On the cathode side, carbon rods are placed and fixed with clamped wires. The assembled microbial fuel cell was connected to the electrochemical workstation to measure and record the current-voltage using the BTSDA Version software.



**Figure 4.** (a) Time and voltage curves.(b) Current density and power density curves. (c) Current density and voltage curve.

As shown in Fig. 4(a), when using biochar material as anode electrode, its voltage is much higher than other electrodes, and the maximum output voltage is as high as 560 mV. When the MFC startup is finished and the stabilization period is reached, the MFC voltage of biochar as anode is stabilized at 550 mV, and the MFCs of the anode materials of the carbon felts are all lower than this concentration. As shown in Fig. 4(b), the power densities of the MFC of the anode electrodes of different materials are obviously different, and the maximum power and current density of the MFC can reach 472  $\text{mW}/\text{m}^2$  and 4972  $\text{mA}/\text{m}^2$ , respectively, when the biochar material is elected as the anode electrode. From Fig. 4(c), it can be seen that the polarization curves of the MFC built up in this experiment are close to a straight line and show a certain linear relationship with the voltage. shows a certain linear relationship.

### 3.3. Degradation rate of oily water

Experimentally, the rate of chemical reactions can be quantified. To determine the oil content in water samples, the detection standard “Detection of Oil - Ultraviolet Spectrophotometric Method SL93-1994” was employed. Pure petroleum ether was selected as the extraction agent, and the oil pollution concentration was calculated by measuring the absorbance at a wavelength of 256 nm.

The ultraviolet absorption standard curve for emulsified diesel was established. Firstly, standard oil solutions were prepared by extracting emulsified diesel from simulated ship oil wastewater using petroleum ether and diluting it to 1000  $\text{mg}\cdot\text{L}^{-1}$ . The oil solution was then further diluted to concentrations of 5, 15, 25, 35, 50, 60, 70, 80, 90, and 100  $\text{mg}\cdot\text{L}^{-1}$ . Secondly, the absorbance of these solutions was

measured using a UV spectrophotometer, and the standard curve was fitted as  $y = 0.0189x - 0.0188$ , with a high degree of fit as indicated by  $R^2 = 0.9998 > 0.99$ .

The degradation rate of emulsified diesel was calculated. In a 10 mL water sample that had already been decomposed, 5 mL of petroleum ether and 0.6 g of sodium chloride were added, and the mixture was vibrated at  $120 \text{ r}\cdot\text{min}^{-1}$  for 30 minutes. This was followed by 20 minutes of ultrasonic vibration and a 10-minute centrifugation to remove bacteria and floccules. The residual oil was then extracted. The organic phase was added to an appropriate amount of anhydrous  $\text{Na}_2\text{SO}_4$ , allowed to stand for 1 hour, filtered, and the filtrate collected into a 10 mL volumetric flask. Petroleum ether was added to the flask to reach the mark, and the oil content was determined by measuring the absorbance at 256 nm using the emulsified diesel standard curve.

The degradation rate is calculated as:

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

Under identical conditions, except for the choice of anode materials, carbon felt (CF) and BD-300 biochar of equal surface area were employed as the anode materials in microbial fuel cell (MFC) systems. Each MFC was externally connected to a  $1\text{k}\Omega$  resistor. After 7 days, the oil content in the MFC systems was measured using a UV spectrophotometer, and the oil concentration was calculated using the standard curve equation obtained from the fitting. The degradation rates of oil-contaminated water by the two different anode materials were determined. The 7-day degradation rates of the MFC systems loaded with carbon felt and biochar were 40% and 55.25%, respectively. The biochar-loaded MFC exhibited a 15.25% higher degradation rate than the carbon felt-loaded MFC. This demonstrates that biochar, as an anode material for MFC systems, enhances the degradation rate of oil-contaminated water. Therefore, the use of biochar as the anode material in MFC systems can further increase the 7-day degradation rate of oil-contaminated water in ship engine rooms.

### 3.4. COD removal efficiency

The removal efficiency of chemical oxygen demand (COD) from emulsified crude oil by microbial fuel cells with different electrode materials is depicted in Figure 5. The trend of the COD removal rate curve for the biochar-electrode MFC is similar to that of the carbon felt-electrode MFC. Initially, the COD removal rate rapidly increases and then gradually decreases, eventually stabilizing. The biochar-electrode MFC exhibits a COD removal rate of 73.13%, which is more than 20% higher than the 52.27% achieved by the carbon felt-electrode MFC. This suggests that the high hydrophilicity and compatibility of the biochar material are the reasons for the significant increase in degradation capability. The rapid increase in the number and activity of microorganisms produces specific enzymes and surfactants, leading to a substantial increase in the demand for organic matter, thereby effectively enhancing the COD removal efficiency of the MFC for oil-contaminated water. This indicates that the biochar electrode material has superior conductivity, adsorption performance, and biocompatibility.

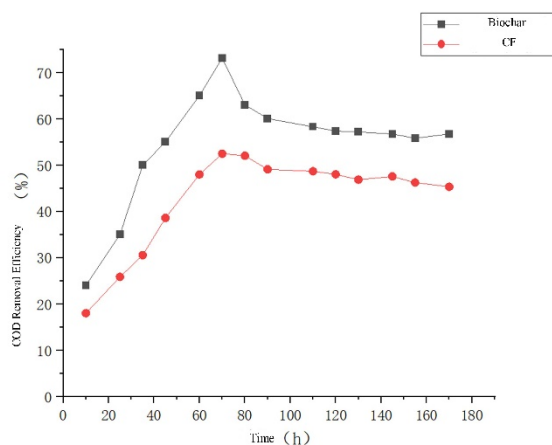


Figure 5. COD removal rate curve

## 4. Conclusion

In this study, a complete microbial fuel cell system was constructed by preparing the anode electrode, anode solution, and cathode solution of the MFC. The performance of the MFC was evaluated through electrochemical analysis, oil pollution degradation rate analysis, and COD degradation rate analysis, yielding the following conclusions:

**Output Voltage Curve:** After the MFC reached the steady state at the end of the startup phase, the voltage of the MFC with biochar as the anode stabilized at 550 mV. The power density curve revealed that the MFC with biochar anode material achieved a maximum power output of  $472 \text{ mW}/\text{m}^2$ . The current density curve indicated that the current density reached  $4972 \text{ mA}/\text{m}^2$ . These results indicate that biochar material outperforms carbon felt material in terms of electrochemical performance for the degradation of oily wastewater.

**Oil Pollution Degradation Test:** The biochar electrode demonstrated a degradation rate of 55.25% in 7-day oil wastewater degradation. The COD removal rate was 73.13%. These findings suggest that the biochar material exhibits superior performance in degrading oily wastewater compared to carbon felt material.

These results provide evidence that biochar is a promising anode material for MFCs due to its enhanced electrochemical performance and superior degradation efficiency of oily wastewater. Further research is warranted to optimize the MFC design and operational conditions for practical applications in wastewater treatment and energy recovery.

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