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Investigation on the Treatment of Marine Oily Wastewater Using Stacked Microbial Fuel Cell Configurations

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Abstract

In the process of microbial fuel cell (MFC) scale-up, the collection of clean energy is an important part of the application. However, due to the limitations of the structure and performance of the MFC itself, the power generation capacity of the device is weak and the output voltage is low, so it is difficult to achieve commercial application of microbial fuel cell technology. In order to obtain a higher voltage output capacity and further study the performance characteristics of amplified MFC, this paper uses the existing equipment in the laboratory to construct two stack schemes of double MFC and three MFC through the stacking design of single cells, and explores the effects of different modes on the power production performance and oil degradation performance of series MFC devices. The advantage of this design is that the MFC structure is simplified, making the device more compact, and saving investment space for industrial applications. The battery series technology is used to expand the power production performance of the device and improve the efficiency of energy recovery.

Keywords

MFC; Oil Degradation Performance; Electricity Production Performance.

1. Introduction

A microbial fuel cell is a bioelectrochemical system that converts chemical energy into electricity through a catalytic reaction by microorganisms[1]. The MFC consists of an anode and cathode electrode, a proton exchange membrane, an electrolyte, microorganisms, and an external circuit[2]. The main functions of the MFC system are power generation and pollutant removal.

In terms of battery power production, the MFC consists of two electrodes, the anode of the fuel electrode, which is made of a substance that easily oxidizes and releases electrons, and the cathode, which is made of a material that is easily reduced and accepts electrons. Together, these two electrodes form the core of the MFC, which converts chemical energy into electrical energy through a redox-reduction reaction[3]. The electronegative terminal releases electrons into the electropositive terminal. When the anode and cathode are very close together, a redox reaction takes place between them, and the energy released is converted into heat. As a result, the two electrodes are able to separate while electrons can flow from the anode to the cathode with an external load while still in contact, allowing the reaction to proceed smoothly and thus to obtain energy recovery[4].

In order for the MFC unit to achieve good power generation, an electrolyte is required to separate the anode and cathode. Electrolytes contain ions, but these ions do not conduct electricity, so they are effective against short circuits between the anode and cathode[5]. At the anode, bacteria release electrons by oxidizing organic matter, while H ions are transferred to the cathode through the proton exchange membrane. Protons passing through the exchange

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membrane and electrons passing through the circuit combine with each other in the presence of oxygen at the cathode, thus completing the current loop[6].

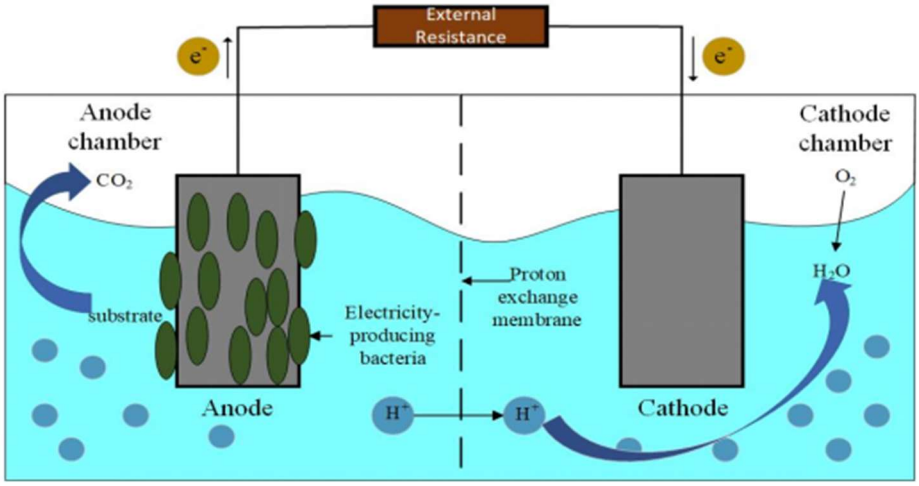

Fig. 1 Principle diagram of dual chamber MFC purification and power generation

2. Experiment Preparation

2.1. Preparation of MFC Anodes

Compared with conventional carbon felt anode materials, biochar exhibits distinct advantages. The high-temperature pyrolysis process endows biochar with an abundant porous architecture and numerous surface functional groups, thereby enabling a large specific surface area and robust adsorption capacity, which facilitate efficient substrate adsorption and electron transport. The natural biomass skeleton of biochar ensures excellent biocompatibility, promoting microbial attachment and growth, while inherent minerals provide energy sources for microorganisms. Through process optimization, biochar demonstrates superior mechanical strength, corrosion resistance, and structural stability, making it suitable for complex environmental applications. Moreover, its natural degradability after disposal highlights its green and eco-friendly characteristics. Therefore, this study employs agricultural waste corn cobs as raw materials, which are widely available and cost-effective, aligning with the principles of sustainable development.

For the preparation of corn cob biochar, the raw material was first cut into thin flakes with a thickness of 3 mm and dimensions of 1 cm × 1 cm. The flakes were then immersed in absolute ethanol and subjected to ultrasonic treatment with shaking for 30 min to remove surface impurities, followed by ultrasonic cleaning with deionized water for an additional 30 min. After cleaning, the flakes were dried in an electric blast oven at 90°C for 2 h. The dried samples were placed in a muffle furnace for vacuum carbonization at 350°C for 30 min, and subsequently cooled to room temperature within the furnace to prevent biochar oxidation due to high-temperature exposure to air.

To enhance the specific surface area of biochar, acid-base modification was performed using KOH, NaOH, and HCl solutions. The specific procedure was as follows: 2 g of corn cob biochar was added to 40 g/L solutions of KOH, NaOH, and HCl, followed by ultrasonic shaking for 30 min and static incubation for 12 h. Thereafter, the samples were washed to neutrality using 1 M H_3PO_4 or $NaHCO_3$ solutions in combination with deionized water, accompanied by an additional 30 min of ultrasonication before filtration. The filtered samples were dried in an oven at 90°C for 2 h to obtain the modified materials, designated as HCl-modified, KOH-modified, and NaOH-modified corn cob biochar.

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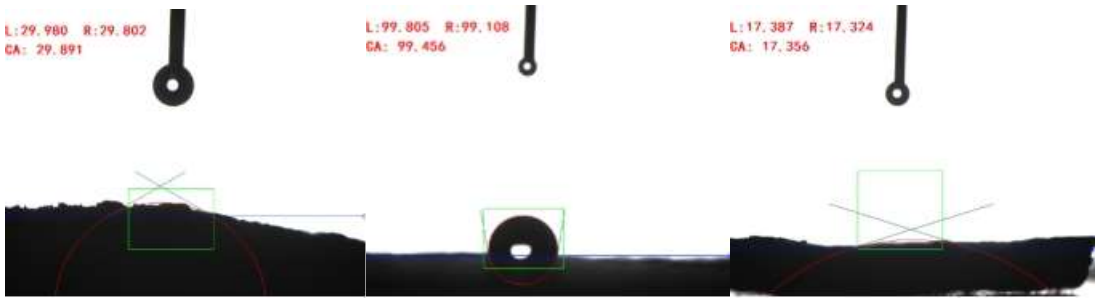
2.2. Characterization and Analysis of Modified Anodes

Acid-base modification can alter the structural properties of biochar materials, and higher porosity is beneficial for microbial attachment to electrode materials. However, the performance differences of acid and alkali substances affect the formation of biochar surface roughness. Therefore, selecting an appropriate modifier is crucial for enhancing the performance of microbial fuel cell (MFC) devices. The selection of modifiers for corn cob anode materials can be conducted through the following characterization methods:

(1) Water Drop Contact Angle Analysis of Modified Corn Cob Biochar

The water drop contact angle is a characterization method for determining the hydrophilic/hydrophobic properties of materials. Using a camera for continuous capture, the slide glass with the material was horizontally placed on the workbench, and water droplets were titrated onto the material surface using a syringe. A triple-phase contact point is formed among the solid material, liquid water drop, and gaseous environment. The Young-Laplace equation fitting algorithm was used to calculate the contact angle θ between the solid and liquid phases. Specifically, θ = 90° was defined as the critical point: when θ < 90°, a smaller θ indicates better wettability and stronger hydrophilicity; when θ > 90°, a larger θ indicates poorer wettability and stronger hydrophobicity.

The water drop contact angle of biochar reflects its hydrophilicity. As shown in Fig. 2, the contact angles of traditional anode material carbon felt, unmodified corn cob biochar, and corn cob biochar modified by different acid/alkali solutions were measured. The results showed that the carbon felt (Fig. (a)) had a contact angle of 99°, exhibiting hydrophobic characteristics. The unmodified corn cob biochar (Fig. (b)) had a contact angle of 29°, demonstrating good hydrophilicity. With the modification, the contact angles of biochar decreased: the contact angles of corn cob biochar modified by KOH, NaOH, and HCl solutions (Figs (c)-(e)) were 17°, 8°, and 22°, respectively. This indicates that NaOH-modified biochar had a more rough surface and ultra-strong hydrophilicity. Compared with carbon felt, the porous structure of corn cob biochar itself improved wettability, and acid-base modification optimized the surface roughness. Notably, NaOH-modified biochar with a smaller contact angle was more conducive to microbial attachment, thereby facilitating the formation of a well-developed microbial biofilm in microbial fuel cells.



(a) CF (b) Unmodified corn cob (c) KOH modified corn cob

(d) NaOH modified corn cob (e) HCl modified corn cob

Fig. 2 Water droplet contact angles of different anode materials

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(2) Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Modified Corn Cob Biochar

Fourier transform infrared (FTIR) spectroscopy is a physical characterization method that identifies the internal structure and chemical composition of materials by utilizing the absorption of specific infrared wavelengths by chemical bonds or functional groups. The procedure was as follows: first, potassium bromide (KBr) was pressed into a thin pellet under a constant pressure of 15 MPa for 90 s using a tablet press as the background scan. Subsequently, a small amount of the sample was mixed with KBr and tableted using the same method. Finally, the sample was scanned by an FTIR spectrometer with a resolution of 5 cm^{-1} over a wavelength range of 4000–400 cm^{-1} to determine the internal functional groups, enabling qualitative and quantitative analysis of the material.

To investigate the effect of different modifiers on the chemical composition of corn cob biochar, FTIR tests were conducted on the samples before and after modification, and the results are shown in Fig. 3. As indicated in Fig. 3, the unmodified corn cob biochar exhibited distinct characteristic absorption peaks at 3400 cm^{-1}, 1579.7 cm^{-1}, and 1255.5 cm^{-1}, confirming the presence of -OH, -COO, and C-N groups. Notably, the NaOH-modified biochar displayed the strongest -OH absorption peak compared to other modified samples, suggesting that NaOH modification introduced more -OH hydrophilic groups to the biochar. This enhancement in hydrophilicity facilitates the attachment, growth, and reproduction of electrogenic bacteria, which is consistent with the results of the water contact angle experiments for different biochars.

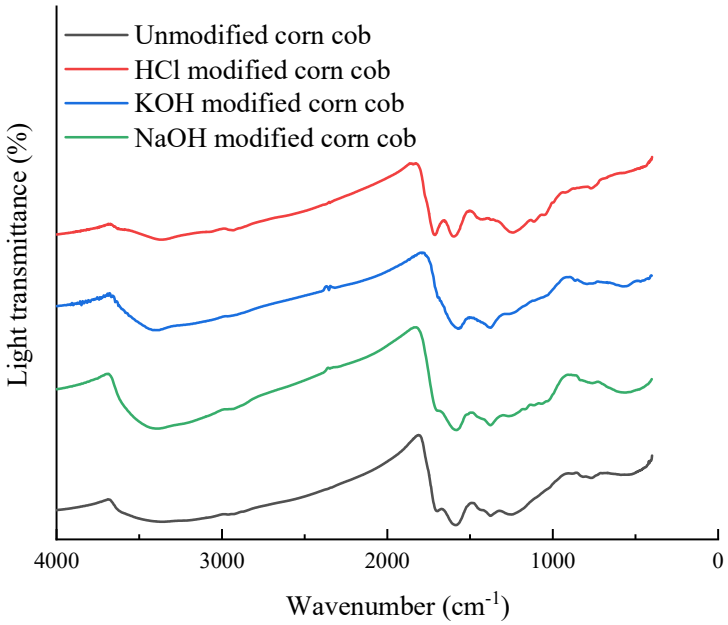

Fig. 3 Fourier transform infrared spectroscopy of corn cob biochar before and after modification

2.3. Cultivation of Electrogenesis Strains and Configuration of Electrode Solutions

First, single-strain activation was performed for Clostridium butyricum, Shewanella, Rhodopseudomonas palustris, Bacillus subtilis, and active yeast. Subsequently, combined cultivation of the five strains was conducted in an inorganic salt medium, which was cultured in a constant-temperature shaker at 35°C and 180 r/min for 24 h to promote rapid reproduction and growth of microorganisms, thereby constructing a composite microbial community as the anode microorganisms of the MFC. The components and contents of the

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inorganic salt medium were as follows: disodium ethylenediaminetetraacetate 0.01 g/L, potassium dihydrogen phosphate 3 g/L, dipotassium hydrogen phosphate 1.5 g/L, ammonium nitrate 2 g/L, anhydrous calcium chloride 0.01 g/L, distilled water 100 g/L, magnesium sulfate heptahydrate 0.1 g/L, and the pH value of the medium was 7.5.

The anode electrolyte used in the experiment was an emulsified diesel solution prepared with the inorganic salt medium. The specific preparation method of the anode solution in this chapter was as follows: on a sterile workbench, the inorganic salt medium was prepared according to the reagent ratio in Table 1. The medium was placed in a pressure steam sterilizer and operated at 121°C for 15 min to kill miscellaneous bacteria. Then, 2 g of 0# diesel and an appropriate amount of Span 80 emulsifier were injected into the medium, and the solution was made up to 1 L. A magnetic stirrer was used for sufficient stirring to achieve the emulsification of diesel, thereby obtaining an anode electrolyte with an oil concentration of 2 g/L. Potassium ferricyanide, as an excellent electron acceptor, can significantly enhance the electrochemical performance of the cathode[7]. Therefore, in this experiment, potassium ferricyanide was fully mixed and dissolved with deionized water to prepare a 30 millimolar potassium ferricyanide solution as the cathode solution of the MFC.

2.4. Construction and Start-up of Stacked MFC Units

The traditional dual-chamber MFC setup was conducted under aseptic conditions on a sterile workbench. After UV sterilization of the MFC cell housing for 2 hours, 50 mL of anode electrolyte (supplemented with 1 mL of the composite microbial culture) and 50 mL of cathode electrolyte were separately injected into the anode and cathode chambers. The prepared 1 cm × 1 cm modified biochar was immersed in the anode electrolyte as the anode electrode, while a carbon rod (0.5 cm diameter, 15 cm length) served as the cathode electrode. In the anode chamber, one upper aperture was dedicated to electrode insertion, and the other was sealed with a silicone plug to maintain anaerobic conditions. Conversely, the cathode chamber featured one aperture for the carbon rod and another vented to the atmosphere, facilitating efficient combination of electrons, protons, and ambient oxygen to sustain the cathodic oxidation reaction.

Leveraging existing square MFC components in the laboratory, two stacked configurations were designed and assembled using SolidWorks: a 2-MFC system comprising two dual-chamber units connected in series and a 3-MFC system with three units. The 2-MFC stack adopted an alternating arrangement of anode and cathode chambers, with adjacent units separated by partition plates. A Nation-117 proton exchange membrane was inserted between the anode and cathode chambers of each unit. End caps were installed at both extremities to seal the electrolytes and isolate air. Structural integrity was ensured by four M8 × 20 stainless steel fully threaded rods traversing all chambers and end caps, secured with M8 wing nuts.

For the 2-MFC system, two independent single-cell batteries were externally connected with 1000 Ω resistors respectively, forming a series closed circuit with a total external resistance of 2000 Ω. In the stacked configuration of the two-unit battery device, the single dual-chamber MFCs are sequentially named 2-MFC1 and 2-MFC2 from left to right.

The construction principle of the stacked 3-MFC is based on the structure of 2-MFC, with an additional set of bipolar chamber fuel cells connected to one end of the device. A proton exchange membrane is similarly used to separate the anode and cathode chambers, and the outermost sides are sealed by end caps. The fuel cell device is fixed with four M8×30 stainless steel fully threaded rods and M8 wing nuts.

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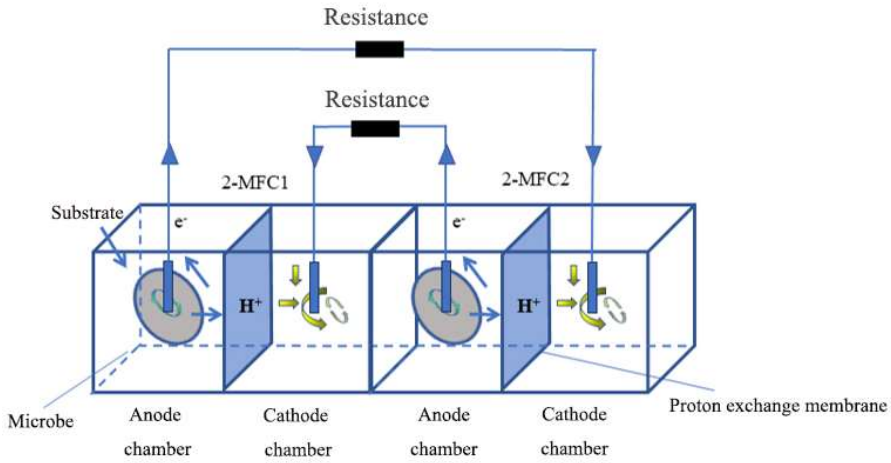

Fig. 4 Schematic Diagram of 2-MFC

For the 3-MFC system, three independent single-cell battery units were each externally connected with a 1000 Ω resistor, forming a series closed circuit with a total external resistance of 3000 Ω. In the stacked configuration of the three-unit battery device, the single dual-chamber MFCs are sequentially named 3-MFC1, 3-MFC2, and 3-MFC3 from left to right. The output voltage of the circuit was detected using a CT4008 Neware battery testing system, and operational data of the MFC devices were collected continuously for 7 days to analyze the differences in power generation performance of microbial fuel cells under different stacked modules.

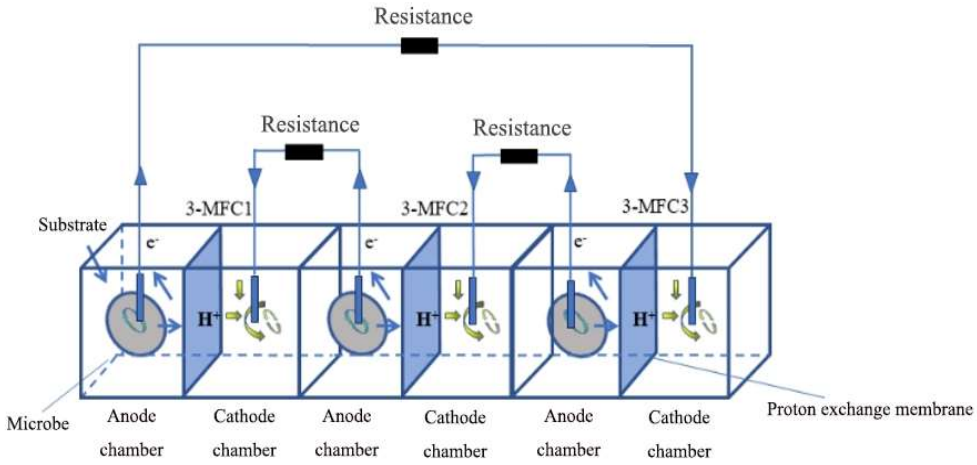

Fig. 5 Schematic Diagram of 3-MFC

3. Treatment of Ship Oily Wastewater by Stacked MFC Device

3.1. Power Generation Performance Analysis of Stacked Series-MFC

The output voltage trends of 2-MFC and 3-MFC under series connection tests are shown in Figure 6. The results indicate that both stacked systems maintained stable voltage outputs initially, but experienced abrupt declines at different degrees in the later stage, primarily due to voltage reversal in single-cell units of the series circuit. Although multi-unit stacking enhances power generation capacity, extreme operational anomalies occur in the mid-late stage, attributed to insufficient cathode oxygen, anode substrate depletion, inter-unit impedance discrepancies, and catalyst deficiency[8]. This reveals a trade-off between power

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enhancement and operational stability, necessitating optimization of electrode materials, substrate supply, and cathode aeration to mitigate voltage reversal.

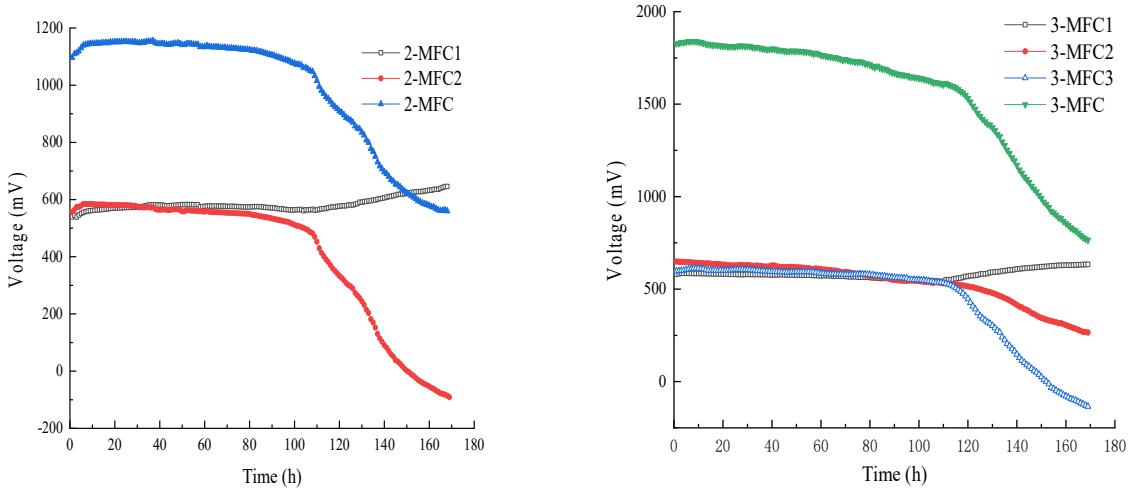

Fig. 6 Output voltage analysis of stacked series MFC

As shown in Fig. 6, the single-cell voltages and total circuit voltage of the 2-MFC system remained stable during the early and mid-test stages, with the total voltage maintaining ~1100 mV and the output voltages of 2-MFC1/2-MFC2 stabilizing at ~560 mV. However, after 108 h of operation, the voltage of 2-MFC2 dropped rapidly. Although 2-MFC1 showed a slight voltage increase, the total circuit voltage was more strongly affected by 2-MFC2, and the voltage growth of 2-MFC1 could not offset the overall decline. The voltage drop accelerated as operation prolonged, primarily due to voltage reversal in 2-MFC1 after 108 h-its voltage even turned negative at the end of operation, switching from a discharging to a charging state that absorbed electrons from other cells, causing the total voltage to drop rapidly. This trend aligns with Logan's[9] findings that in series-connected circuits, single cells with weak power generation capacity experience premature voltage decay in the later stage, creating a potential difference with other cells and leading to voltage reversal.

Fig. 6 shows that the 3-MFC system similarly exhibited stable voltage outputs during the early and mid-operation stages, with the total series voltage reaching 1800 mV and stabilizing, while each single-cell voltage remained at ~600 mV. After 114 h of stable operation, 3-MFC3 first showed a rapid voltage decline, dropping to -134 mV at 168 h. Although 3-MFC1 and 3-MFC2 showed minor voltage fluctuations in the later stage, their overall trends remained relatively stable. The total voltage of 3-MFC approximated the sum of the three single-cell voltages, but after 114 h, the total voltage also dropped rapidly due to the trend of 3-MFC3.

In practice, while the series design amplifies the battery voltage, voltage reversal in the later stage of stacked operation compromises the overall output voltage. Thus, addressing voltage reversal becomes critical for ensuring the stable operation of MFC devices.

3.2. Degradation Performance of Stacked MFC for Ship Oily Wastewater

Power generation performance and oil degradation efficiency are two critical metrics for evaluating the effectiveness of microbial fuel cell (MFC) devices in treating ship oily wastewater. Previous experiments on stacked MFC systems revealed that voltage reversal occurring in the late operation stage compromises the power amplification of MFCs. Whether this voltage reversal phenomenon also interferes with the normal oil degradation efficiency is another crucial factor to investigate in the treatment of ship oily wastewater.

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The oil degradation performance of single-unit MFC, 2-MFC, and 3-MFC devices was tested continuously for seven days. The obtained oil degradation rates of each battery group are shown in Fig. 7. Results indicate that the single-unit MFC achieved the highest degradation rate of 81.1%, while significant differences were observed in the degradation efficiencies of single cells within the other two stacked configurations. In the 2-MFC system, the degradation rates of 2-MFC1 and 2-MFC2 were 78.6% and 72.4%, respectively. In the 3-MFC system, 3-MFC3 exhibited the lowest degradation efficiency at 68.1%, whereas 3-MFC1 and 3-MFC2 achieved degradation rates of 76.5% and 73.8%, respectively.

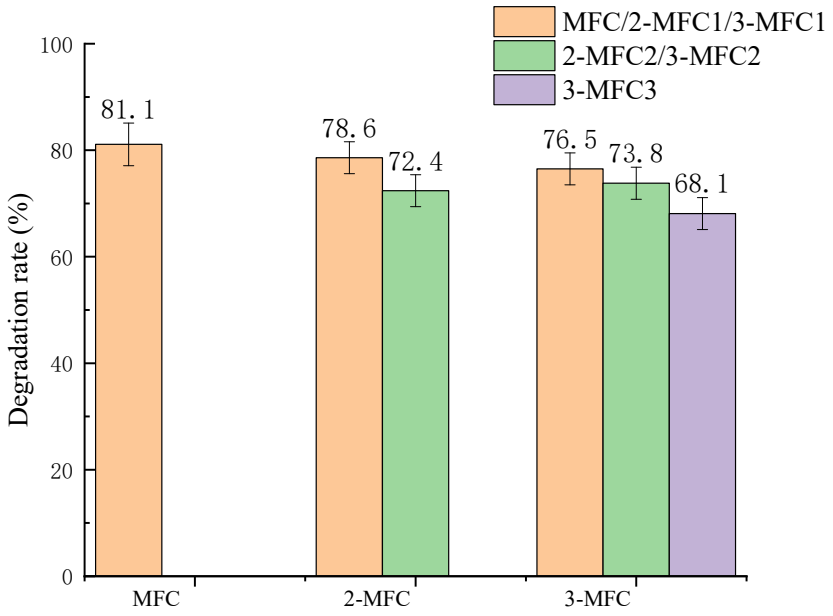

Fig. 7 Analysis of oil pollution degradation performance of stacked series MFC

Experimental results show that the degradation rate of single-unit MFC (81.1%) exceeds that of series-connected stacked systems, attributed to voltage reversal in series circuits affecting individual cell performance. In 2-MFC, the degradation rate of 2-MFC2 (72.4%) is significantly lower than 2-MFC1 (78.6%); in 3-MFC, 3-MFC3 (68.1%) shows the lowest efficiency compared to 3-MFC1 (76.5%) and 3-MFC2 (73.8%). This indicates that voltage reversal in series-connected cells reduces overall degradation efficiency, with reversed cells exhibiting the lowest rates.

Voltage reversal forces cells into a charging state, causing electron accumulation on anode surfaces. This charge buildup disrupts the microenvironment for attached microbes, reducing their activity and substrate decomposition capacity. Meanwhile, high-performance cells in the series circuit are unable to complete normal power generation and degradation cycles due to electrochemical interference from reversed cells, further compromising overall treatment efficiency.

Thus, voltage reversal not only decreases energy conversion efficiency during power generation but also impairs wastewater purification, limiting the practical application of stacked MFC series designs in simultaneous power production and oil pollution treatment.

4. Conclusion

To enhance energy recovery efficiency and address the low power generation capacity of MFC devices, this chapter designs and constructs 2-MFC and 3-MFC systems with multi-unit stacked series connections based on a square dual-chamber MFC, conducting voltage output and

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degradation performance tests. A continuous stacked MFC circulation system is further developed to suppress voltage reversal, investigating its impact on the treatment efficiency of ship oily wastewater. Key conclusions are as follows:

Seven-day continuous performance tests on 2-MFC and 3-MFC stacked series systems show stable voltage outputs from individual cells in the first half of the test. However, in the latter stage, both systems exhibit rapid voltage drops to negative values in one of the single cells, caused by voltage reversal. The total output voltages of 2-MFC and 3-MFC, initially maintaining at 1100 mV and 1800 mV (summing the voltages of individual cells), significantly decline due to voltage reversal in the later stage. Regarding oil degradation efficiency over 7 days, 2-MFC1 and 2-MFC2 achieve 78.6% and 72.4%, while 3-MFC1, 3-MFC2, and 3-MFC3 reach 76.5%, 73.8%, and 68.1%, respectively. Experiments reveal that single cells with voltage reversal exhibit the lowest degradation rates.

In conclusion, stacked series MFCs can enhance the total output voltage, but are constrained by voltage reversal, which simultaneously reduces oil degradation efficiency.

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