ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

Study on PTh/MWCNTs Modified Orange Peel Biochar Electrode to Improve The Degradation Performance of Microbial Fuel Cell Power Generation and Cutting Waste Liquid

Tongyu Yu[1, a], Chenglei Wang[1, b], Xiaomeng Fan[1, c], Xiaoshuang Qi[1, d]

[1]School of ShanDong JiaoTong University, Weihai 264200, China.

[a]750597417@qq.com, [b]1432220396@qq.com, [c]1243494069@qq.com, [d]2994148487@qq.com

Abstract

Microbial fuel cells (MFCs) have attracted widespread attention in the field of oily wastewater treatment as a device that can decompose organic matter by oxidation of electricity-producing flora and convert chemical energy into electricity. Among them, the anode material of MFC has a non-negligible influence on the voltage output of MFC and the adhesion of electrogenic flora. Therefore, a biocompatible orange peel biochar material was selected as the anode material for MFC, and then modified with polythiophene (PTh) with excellent electrical conductivity. Due to the low degree of conjugation and structural defects of PTh when acting alone, the conductivity is not obvious, so PTh is compounded with multi-walled carbon nanotubes (MWCNTs) that can change the pore size of the inner wall to make up for the shortcomings between the two, so as to obtain a more cost-effective PTh/MWCNTs composite electrode material. Compared with traditional MFC, MFC made of PTh/MWCNTs composite electrode material has more advantages in power generation and degradation of oily wastewater, and provides new ideas for the treatment of cutting waste liquid.

Keywords

Polythiophene; Multi-walled carbon nanotubes; Microbial fuel cells; Power density.

1. INTRODUCTION

In recent years, with the strong support of national policies, the development of China's industry has achieved remarkable results, with the increase of people's demand for related products, the demand for mechanical production equipment is also increasing, how to deal with a large number of cutting waste liquid generated in the industrial production process has become an urgent problem to be solved. Once the cutting waste liquid enters the river and lake, the alkanes will isolate the water body, resulting in the lack of oxygen and death of aquatic animals such as fish in the river; The pigments floating on the water surface will also isolate the light, causing the plants in the water to fail to obtain nutrients through photosynthesis and wither, and over time, pollute the water body, resulting in the self-purification capacity of the ecological cycle of the water body cannot be carried out normally, and the water quality gradually deteriorates.Microbial fuel cells (MFC) technology is an excellent way to treat cutting waste. MFC mainly decomposes waste pollutants such as waste liquid and alkanes through the cultivated electricity-producing microorganisms, and then outputs electrical energy as its own nutrients, and the entire degradation process is in a closed-loop state without external energy intervention. Microbial fuel cell technology has great potential in the field of waste liquid

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

treatment because of its advantages of high material adaptability, no repeated pollution, high energy conversion rate and easy operation.

2. EXPERIMENTAL INSTRUMENTS AND MATERIALS

The waste liquid stock solution selected in this experiment was taken from an airport equipment production company in Weihai, the appearance was light milky yellow, the surface had yellow-brown oil slick and black float, the formula was confidential, and there was a mixed pungent odor of metal and oil.

The instruments used in this section are shown in Table 1.

Table 1. Experimental instrument

Name	Model	Manufacturer
Fourier infrared spectrometer	IRAffinity-1S	Shimadzu (China) Co., Ltd
Thermostatic culture oscillator	ZWY-2102C	Shanghai Zhicheng Analytical Instrument Manufacturing Co., Ltd.
Box type resistance furnace	SX2-2.5-10A	Shaoxing Shangyu Daoxu Scientific Analysis Instrument Factory
Vertical pressure steam sterilizer	LS-751D	Jiangyin Binjiang Medical Equipment Co., Ltd.
One ten thousandth electronic balance	ES410D	Tianjin De Ante Sensing Technology Co., Ltd.
Battery detection system	CT4008	Shenzhen Xinwell Electronics Co., Ltd.
Multimeter	ZTW0111C	Zhejiang Chint Instrument Co., Ltd.
Contact angle measuring instrument	SDC-100	Dongguan Shengding Precision Instrument Co., Ltd.
Waterproof constant temperature Incubator	GNP-9050	Shanghai Jinghong Experimental Equipment Co., Ltd.
Electric blast drying oven	101-0	Shanghai Dengsheng Instrument Manufacturing Co., Ltd.

Table 2. Experimental material

Material	Source of production
Citrus	Chengdu, Sichuan Province
Graphite felt	Carbon energy technology joint stock company
Carbon cloth	Carbon energy technology joint stock company
Proton membrane	Suzhou Yilongsheng Energy Technology Co., Ltd.
Microbial fuel cell housing	Chuzhou Wente Instrument Technology Co., Ltd.

The main chemical reagents used in this chapter are shown in Table 3.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

Table 3. Experimental reagent

Reagent	Purity	Manufacturer
Absolute ethanol	Analytically pure	Yantai Far East Fine Chemical Co., Ltd.
Potassium ferricyanide	Analytically pure	Tianjin Guangfu Technology Development Co., Ltd.
Thiophene	Analytically pure	Shanghai Macklin Biochemical Technology Co., Ltd.
Deionized water	Analytically pure	Jinan Tianmu Chemical Technology Co., Ltd.
Multi-walled carbon nanotubes	Analytically pure	Shenzhen Suiheng Technology Co., Ltd.
Camphor sulfonic acid	Analytically pure	Wuhan Kemick Biomedical Technology Co., Ltd.
Ammonium persulfate	Analytically pure	Tianjin Yongda Chemical Reagent Co., Ltd.

The medium used in this experiment was sterilized by autoclave for 30 minutes and the temperature was set to 121°C.

Table 4. Inorganic salt medium composition and content

Ingredient	Content g/L
$C_{10}H_{14}N_2Na_2O_8$	0.01
KH_2PO_4	3
$CaCl_4$	0.01
K_2HPO_4	1.5
$MgSO_4$ \7H_2O	0.1
NH_4Cl	2
Deionized water	1000

3. CONSTRUCTION OF MICROBIAL FUEL CELL DEVICE

3.1. Device Design

The anode chambers of the MFC device are arranged in a cylindrical shape opposite the cathode chambers, separated by a proton membrane. PTh/MWCNTs modified orange peel biochar, ordinary biochar, carbon cloth (CC) and other electrode materials are selected for the anode, the thickness is 0.4 cm, the side length is 1 cm, and CC is selected as the cathode material of MFC. There are two symmetrical through-holes in the anode chamber and cathode chamber of MFC, and symmetrical distribution is presented through the proton exchange membrane, and the electrode materials of the cathode and anode are put into the interior of the electrode chamber through the small holes in the upper part of the MFC, so that the distance between the two electrodes and the proton exchange membrane is consistent. As shown in Figure 1, the other well is plugged through a rubber stopper depending on whether the experiment requires oxygen.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

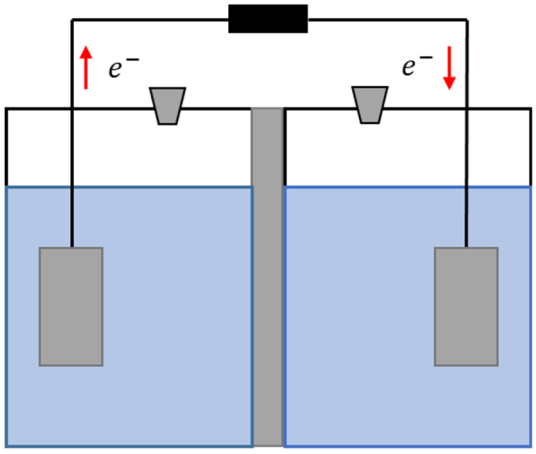


Figure 1. Design of dual-chamber MFC device

MFC cathode solution mainly uses 30 mmol/L potassium ferricyanide solution. The main components of the anode liquid are the basic medium and laboratory-grown microorganisms using cutting waste liquid as the carbon source.

3.2. Selection of Electrogenic Bacteria

In order to maximize the experimental effect, the degradation and power production effect of the constructed MFC device are more ideal. In this paper, a combination of microorganisms mixed with a variety of microorganisms was used for experiments, and the electrogenic bacteria were placed in a constant temperature shaker for activation, as shown in Figure 2. On the basis of the existing flora in the laboratory, according to the literature [1,2] the flora was added and configured, and ten strains including yeast, Pseudomonas swamp, lactic acid bacteria, Clostridium butyrate, Acinetobacter, nitrifying strains and denitrifying strains were selected to construct a composite flora.

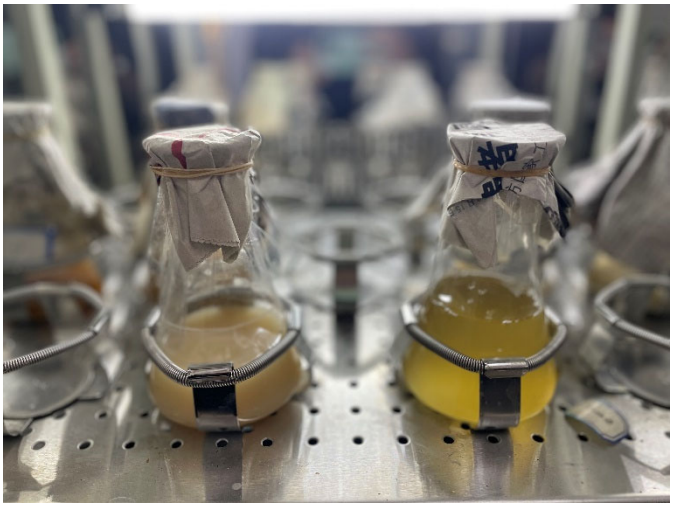


Figure 2. Strain activation

3.3. Test Platform

The output voltage of the MFC is one of the important indicators to judge the stability and sustainability of the battery. As shown in Figure 3, the CT4008 data detection system is used to acquire the MFC output voltage data of three sets of different anode materials with external resistance at (1000 Ω) every 5 minutes.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

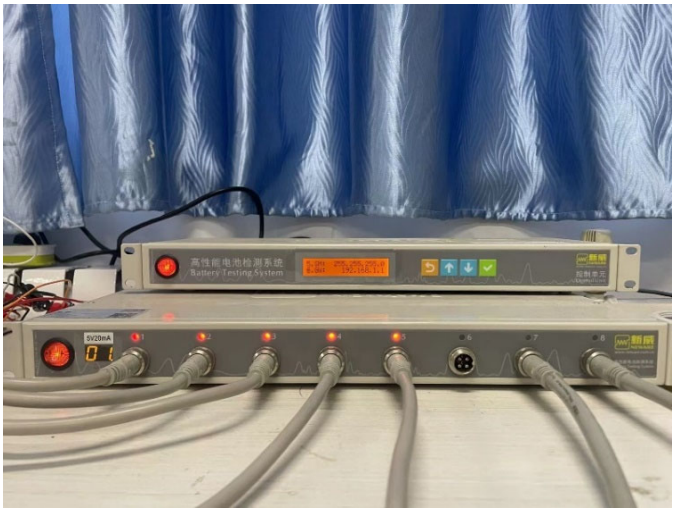


Figure 3. Test test device

A series of experiments on MFC are carried out according to a certain period. When conducting electrochemical performance-related experiments, the output voltage of the MFC device is less than 50 mV, which is regarded as the end of a period. Replace the internal materials of the MFC device and carry out a new period experiment [3], select the best data for sorting and analysis.

4. PREPARATION OF PTH/MWCNTS MODIFIED ELECTRODE

Preparation of orange peel biochar: Orange peel biochar was prepared by using citrus peel as raw material by using high temperature oxygen limited calcination technology. First, the citrus peel is cut into small pieces with a diameter of 3 cm and washed with deionized water to remove residual root whiskers and magazines from the surface; Then, the cut citrus peel was placed in an electric blast drying oven at 60°C to dry for 12 h; Finally, in order to improve the carbonization rate, the dried citrus peel is placed in the muffle furnace for high-temperature firing, the firing temperature of the resistance furnace is adjusted to 400 °C, and the muffle furnace is turned off after 20 min at this temperature, and the orange peel biochar [4] can be obtained after the temperature is reduced, as shown in Figure 4.

Figure 4. Orange peel biochar

Preparation of polythiophene: Weigh 0.1 mol/L thiophene (Th) monomer and 0.01 mol/L camphor sulfonic acid in a beaker, pour 30 mL of deionized water for ultrasonic shaking, and

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

place it in 85 ℃ after mixing uniformly. In a water bath, add 0.1 mol/L ammonium persulfate (APS) solution during the heating of the water bath. Then the mixed solution of the three is placed in a centrifuge by test tube loading. After centrifugation, it is washed with methanol and deionized water and then carried out a second centrifugation to obtain a mixture precipitation, and the precipitation is dried to obtain a reddish-brown polythiophene [5].

Polythiophene/multi-walled carbon nanotubes modified orange peel biochar: Weigh the multi-walled carbon nanotubes in a beaker, add $CHCl_3$ and perform ultrasonic shaking. After mixing the two, add a small amount of anhydrous ferric chloride, add the prepared polythiophene under nitrogen conditions, and then filter out large particles of impurities through a filter screen to obtain polythiophene/multi-walled carbon nanotubes (PTh/MWCNTs) composites. In order to reduce the experimental error and improve the experimental success rate, dilute hydrochloric acid (0.10mol/L), acetone, anhydrous ethanol and deionized water were washed in sequence. Then it was placed in a vacuum drying oven for drying, and the temperature was set to 50°C for 24 hours to obtain polythiophene/multi-walled carbon nanotubes (PTh/MWCNTs) composite samples. Finally, the polythiophene/multi-walled carbon nanotubes (PTh/MWCNTs) composite sample was added to deionized water and stirred for 40 minutes to prepare 0.15 mg/mL polythiophene/multi-walled carbon nanotubes (PTh/MWCNTs) composite sample solution [6].

The prepared orange peel biochar was soaked in the polythiophene/multi-walled carbon nanotubes (PTh/MWCNTs) composite solution prepared above. After soaking for 48 hours, take it out and place it in the refrigerator, and refrigerate it at 4°C for 18 hours. After refrigeration, wash it with absolute ethanol, and dry it in a drying oven to obtain the orange peel biochar electrode modified with PTh/MWCNTs.

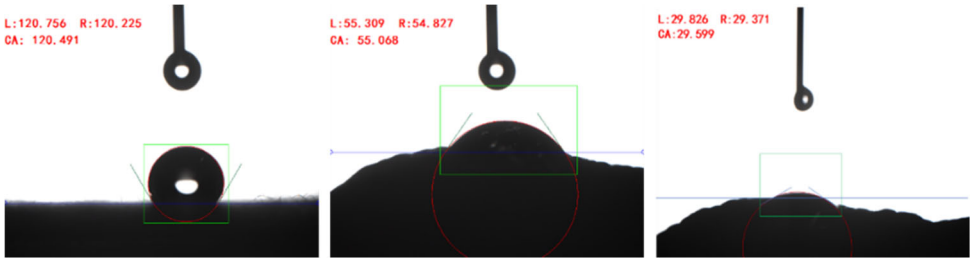
5. CHARACTERIZATION AND ANALYSIS OF MICROBIAL FUEL CELL ELECTRODE PERFORMANCE

5.1. CA Analysis

The electrode to be characterized is placed horizontally on the workbench, the deionized water droplets are placed on the surface of the electrode to be characterized by a syringe, and the state of the water droplets on the electrode surface is observed by light and shadow imaging in the host computer software to judge the hydrophobicity degree of the water droplets and the electrode surface. The size of the hydrophobic degree is expressed by the size of the contact angle, the contact angle range is between , the larger the contact angle, the worse the wetting performance of the electrode surface, the lower the hydrophilic degree, the worse the wetting degree of the anode liquid on the electrode surface. Conversely, the more prominent the wetting performance of the electrode surface and the higher the degree of hydrophilicity, the more likely the anode liquid to infiltrate the electrode surface, which is more conducive to the attachment of electrogenic microorganisms in the anode solution to the electrode surface [7].

The degree of wettability of the anode material can affect the amount of biological adhesion, and the contact angle size of the wetting and hydrophilic electrode surface can be shown by the water droplet experimental test, and the contact angle determination of three different anode materials is shown in Figure 5.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003



a.Carbon cloth b.Biochar c Modified biochar.

Figure 5. Hydrophilic and hydrophobic test diagram of different anode materials

Figure 5 shows the contact angle test results of different electrode materials, and the advantages and disadvantages of hydrophilicity and wetting degree of electrode surface are mainly presented by the size of the contact angle. In the state where the electrode surface is completely dried, the contact angle of the CC electrode (Figure 5-a), the contact angle of orange peel biochar (Figure 5-b), and the contact angle of the anode modified by PTh/MWCNTs (Figure 5-c).

Through the contact angle test of three different electrodes, it is found that the contact angle of CC electrode is the smallest, and the contact angle of the anode modified by PTh/MWCNTs is better than that of unmodified biochar electrode and CC electrode, and its hydrophilicity and wetting degree are greatly improved, mainly because there is a large number of hydrophilic -OH inside the composite electrode material, and the negative charge carried by the electrogenic microorganisms has a strong interaction with the hydroxyl group, which promotes a large number of electrogenic microorganisms to attach to the electrode surface. In addition, there is also the interaction between van der Waals forces and electrostatic electricity between electrogenic microorganisms and composite electrode materials, which is more favorable for electrode attachment of electrodes of electrogenic microorganisms under the above two effects [8]. After the wetting degree and hydrophilicity of the electrode are greatly improved after the modification of orange peel biochar by PTh/MWCNTs, the adsorption capacity of the electrode surface to microorganisms is also enhanced, and the electrons produced by the degradation of abundant electrogenic microorganisms are increased, thereby improving the power production performance of MFC.

5.2. FTIR Analysis

Weigh 1 mg of unmodified biochar sample and 100 mg of potassium bromide powder (KBr) in an agate mortar for repeated mixing and milling. Use a medicated spoon to weigh part of the mixture in a sheet mold. With tablet press compaction, set the pressure of the tablet press to 20 MPa and hold the pressurization process for 2 minutes. Then the sheet mold containing the sample is taken out and observed by light. Finally, the sheet mold with the sample is placed on the Fourier infrared spectrometer for testing, the resolution is set to 5 cm-1, and the infrared spectrum of the desired biochar sample can be obtained after scanning [9].

After mixing the dried orange peel biochar and PTh/MWCNTs modified orange peel biochar with KBr particles for grinding and tableting, the absorption characteristics of infrared radiation of different wavelengths by infrared spectrometer were used to test the modification effect of orange peel biochar, and the infrared spectral results of ordinary biochar and modified biochar are shown in Figure 6.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

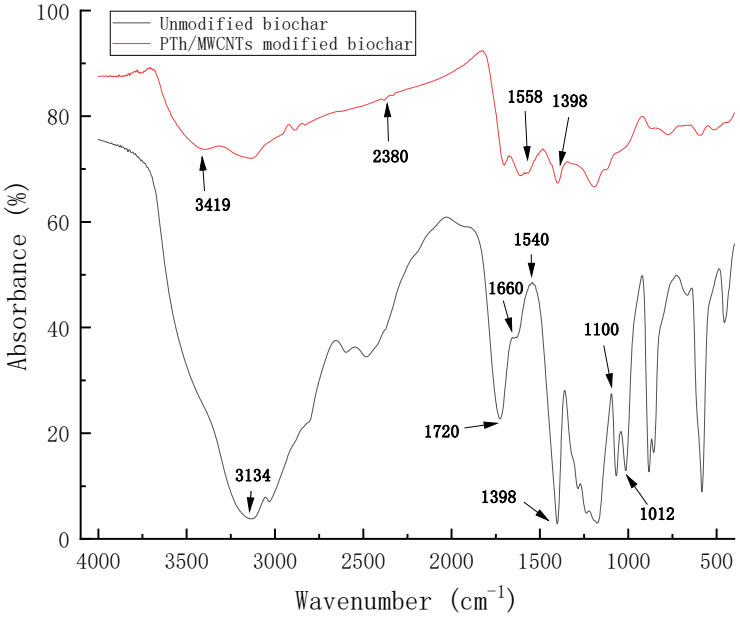


Figure 6. FTIR spectrum of orange peel biological carbon before and after modification

Figure 6 shows infrared spectroscopic (FTIR) test plot of orange peel biochar and polythiophene/multi-walled carbon nanotube modified orange peel biochar anode. According to the analysis of the above figure, in the range of wavenumber of 400~4000, there are many functional groups on the surface of the unmodified orange peel biochar electrode, a broad -OH telescopic vibration peak appears at 3419 cm^{-1}, the peak around 2380 cm^{-1} is the vibration absorption peak of C=O and C-H, the telescopic vibration peak of C=C skeleton vibration appears near 1558 cm^{-1}, and the peak displayed at 1398 cm^{-1} is generated by C-H bending vibration. After the composite modification of PTh/MWCNTs, the overall peak shape changed, and some characteristic peaks were more obvious, and the absorption peak at 1720 cm^{-1} was C=O telescopic vibration peak, which was caused by the methyl ester present in hemicellulose, and the C=O functional group decreased after composite modification, indicating that the hydrogen bond between multi-walled carbon nanotubes and polythiophene aromatic rings interacted during the modification process. The characteristic absorption peak of carbonyl group appeared near 1660 cm-1, among which the absorption peak at 1540 cm-1 indicated that it was caused by the trans-telescopic vibration of the thiophene ring, indicating that the thiophene ring did not change when the composite polymerized, and still existed. The absorption peak at 1398 cm-1 corresponds to the symmetrical telescopic vibration of the thiophene ring. The peak of 1100 cm-1 was caused by the telescopic vibration of polythiophene molecular chains, and the bending vibration peak caused by polythiophene molecular chains appeared at 1012 cm-1. Through the analysis of infrared spectroscopy, the characteristic peaks of PTh and MWCNTs appeared in the figures, indicating that PTh/MWCNTs had been successfully modified on the surface of orange peel biochar.

5.3. XRD Analysis

The Bruker D8 advance X-ray diffractometer was used to X-ray diffraction of modified orange peel biochar and unmodified orange peel biochar, and the diffraction pattern was obtained by special treatment of the experimental materials after diffraction, and the crystal structure and phase changes of orange peel biochar before and after modification were analyzed.

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

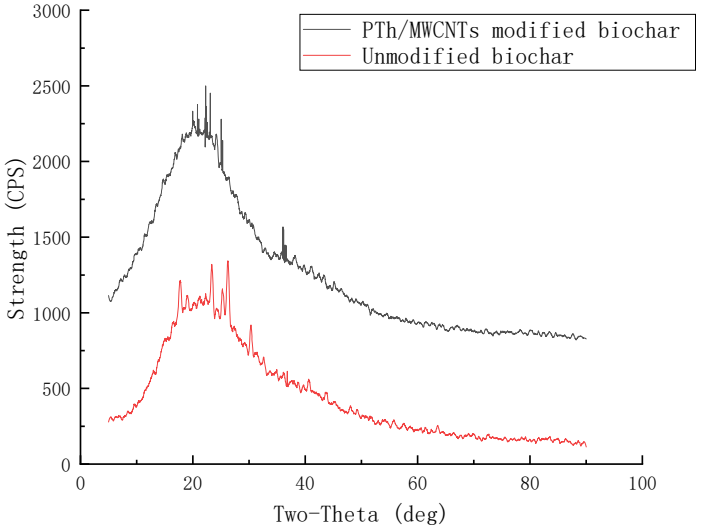


Figure 7. XRD diagram of modified orange peel biochar and unmodified orange peel biochar

From Figure 7, it can be clearly found that the unmodified orange peel biochar and the orange peel biochar modified by PTh/MWCNTs have a sharp and prominent amorphous diffraction peak on the left and right, and it is inferred that the morphological structure of the orange peel biochar itself is a chaotic graphite-like structure, and the overall strength of the orange peel biochar modified by PTh/MWCNTs is stronger than that of the unmodified orange peel biochar, mainly due to the modification of orange peel biochar by multi-walled carbon nanotubes. The surface structure changes and the degree of graphitization becomes higher. At the same time, combined with FTIR diagram analysis, the main chain conformation of polythiophene on the surface of orange peel biochar after PTh/MWCNTs composite modification has regular changes, and there is no obvious shift in the position of the diffraction peak before and after modification, indicating that the modification is only the adhesion of the surface of the biochar, which will not accompany the formation of other substances, and will not affect the crystal change of the material.

5.4. CA Analysis

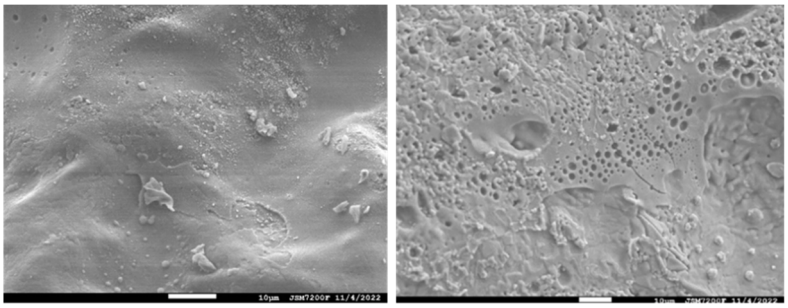


Figure 8. a. Unmodified orange peel biochar b. Modified orange peel biochar

In order to better observe the micromorphology and internal structure of orange peel biocharids, the SEM characteristics analysis of (a) before modification and (b) modification were carried out, and the comparison results are shown in Figure 8. It can be seen from the figure that the structure of orange peel biochar modified by PTh/MWCNTs is fine and porous, and cracks exist in some parts of the surface under the influence of high temperature during carbonization, which makes the surface rough and the specific surface area is greatly improved compared with before modification. Due to the decomposition of some volatile substances such

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

as fiber/hemicellulose in orange peel with the increase of temperature, the gas produced diffuses out from the inside of orange peel, and a more porous structure is formed inside the biochar in this process, so that the pore wall of orange peel after carbonization at high temperature narrows, the pore density increases, and a biochar electrode rich in porous structure is formed. The bond between PTh and MWCNTs is firmly bonded without distinguishable boundaries, so there is good synergy between the two. In addition, the intersecting fibrous PTh complex and loose porous structure present on the surface of biochar can improve the adsorption capacity, provide a good living environment for microorganisms, and accelerate the diffusion and transfer rate of electrons.

6. MICROBIAL FUEL CELL POWER PRODUCTION PERFORMANCE TEST AND CUTTING WASTE LIQUID TREATMENT EFFECT

6.1. Output Voltage Test

In this paper, according to the output voltage test method described in the literature [10], the voltage across the 1000 Ω load resistor is measured by the CT4008 data detection device. The computer automatically detects and records the MFC device data at intervals of 5 minutes [11].

Then using Equation (1), the MFC current (I) can be calculated:

$$I = \frac{U}{R} \tag{1}$$

In the above equation, U is the measured voltage of MFC and R is the load resistance.The generation process of MFC voltage is more complex than that of chemical fuel cells, and an important indicator to evaluate the performance of MFC is its ability to produce electricity. The MFC output voltage acquired by the CT4008 data monitoring system is shown in Figure 9.

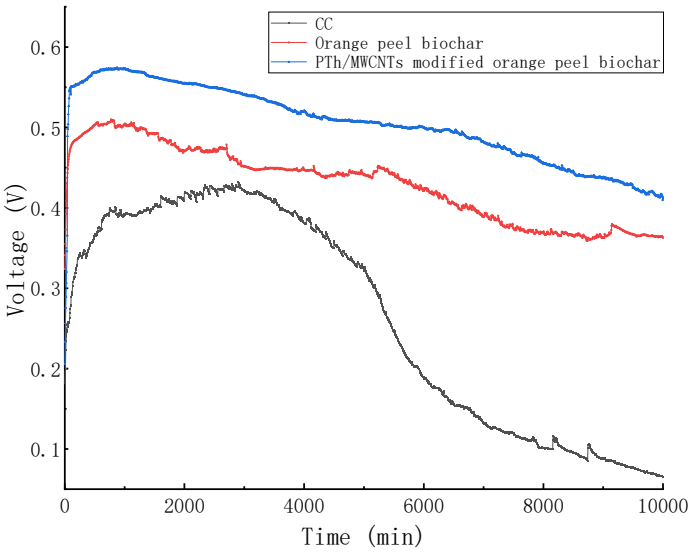


Figure 9. Output voltage graph

As can be seen from Figure 9, the output voltage of the MFC loaded with the three electrode materials rises sharply at the beginning of operation, indicating that the oxidation process and abundant inoculation sources of different species of microorganisms present in the MFC device are rising rapidly. The output voltage then stabilizes after peaking, mainly due to the series division of the external resistor. After that, the voltage begins to drop slowly, which means that

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

the microorganisms inside the MFC anode chamber have completed their life cycle tasks and begin to gradually die. The maximum output voltages of MFC devices loaded with CC, orange peel biochar and PTh/MWCNTs composite modified orange peel biochar > orange peel biochar > CC, and the maximum output voltages of MFC loaded with CC, orange peel biochar and PTh/MWCNTs composite modified orange peel biochar reached 447 mV, 515 mV, and 573 mV, respectively, and the maximum output voltage of PTh/MWCNTs composite modified orange peel biochar anode materials was higher than that of unmodified orange peel biochar electrode, respectively. CC electrode 15.21% and 11.26%. The overall performance of the MFC device equipped with PTh/MWCNTs composite modified orange peel biochar electrode was the best, which reflected that the output voltage was mainly affected by the internal resistance of the battery, the number of microbial loads and the specific surface area of the electrode. The electrode modified by PTh/MWCNTs has better biocompatibility and adsorption performance, so the output voltage is higher. PTh is embedded between MWCNTs, the specific surface area increases, the electrical signal sensitivity is strong, and the two have a better synergistic catalytic effect. At the same time, the modified electrode has the dual role of conductor and electrochemical reactant, which promotes the migration rate of electrons between bonds on the polymerization chain, and electrons can be quickly transferred between MWCNTs and nanotube walls, which improves the catalytic activity and conductivity of the composite and enhances the output electron ability.

6.2. Power Density Test

The magnitude of the power density is one of the criteria for measuring the efficiency of MFC capacity, and the power density is calculated according to the formula (2). The change of power density with current density is the power density curve [12].

$$P = \frac{U^2}{RA} \tag{2}$$

In the above equation, U is the measured voltage of MFC, V is the active area of the anode, and R is the manually programmable load resistance.

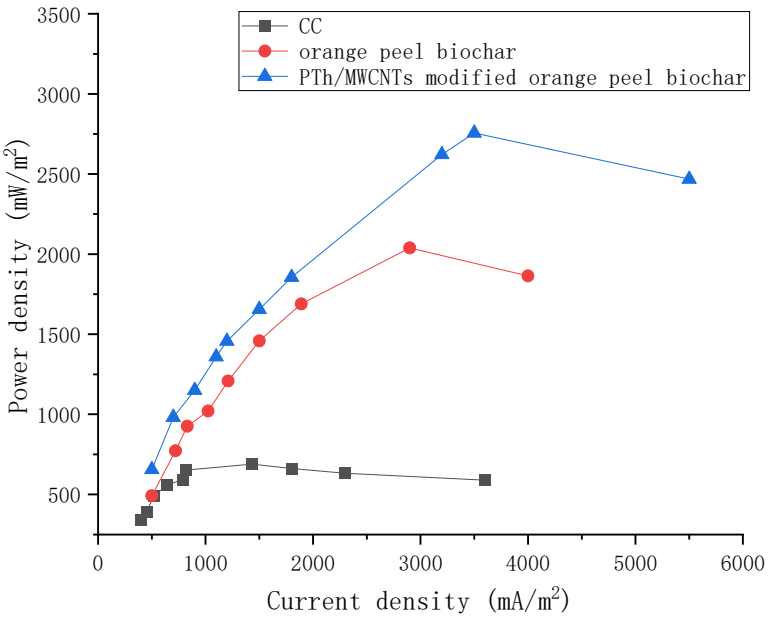


Figure 10. Output power graph

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

As can be seen from Figure 10, the maximum power density of MFC with CC anode, biochar anode and PTh/MWCNTs anode can reach 689 mW/m², 2039 mW/m², and 2757 mW/m², respectively, compared with MFC devices loaded with CC electrodes and unmodified biochar electrodes, loaded with PTh/ The maximum power density of MFC of MWCNTs-modified biochar electrode is 4.0 times that of CC anode, which is 72.12% higher than that of unmodified biochar electrode. The results showed that the new biochar anode modified by polythiophene/multi-walled carbon nanotubes was loaded into the MFC device, and the power production performance of the MFC device was greatly increased.Maximum output power compared to studies in other literature. Masapogu Yellappa[13] prepared the highly conductive polymer PANi/CNT by in situ oxidative chemical polymerization, loaded in MFC, its maximum power density was 48 mW/m², which was 1.7 times that of the control group; Farhan papaya[14] anchored TiO_2 and PANI to the graphene oxide electrode, making the maximum power density of MFC 87% higher than that of the CC electrode control group; M. Mashkour[15] modified the hybrid graphene on the electrode surface to obtain the maximum power density of MFC of GP-HG anode of 220 mW/m², which was 7.3 times that of the control group. The PTh/MWCNTs composite electrode prepared in this paper can not only show the excellent conductivity and biocompatibility of polythiophene and multi-walled carbon nanotubes, but also greatly improve the habitat conditions of microorganisms on the electrode surface, shorten the distance from microorganisms to reach the electrode surface, and increase the electron transfer rate, so that the power production effect of MFC is more prominent.

6.3. Polarization Curve Test

The polarization curve of the MFC device is tested by the constant resistance discharge method, and the external resistance is set to 10000 Ω , 9000 Ω 、 ... 、 1000 Ω according to the same gradient, and the voltage data is recorded after the MFC device is stable for 20 minutes under each resistance gradient, and then the current density is calculated according to the formula (3):

$$I = \frac{U}{RA} \tag{3}$$

In the above equation, U is the voltage of MFC, A is the active area of the anode, and R is the manually programmable load resistance. The reaction voltage of the MFC polarization curve changes with unit current density.

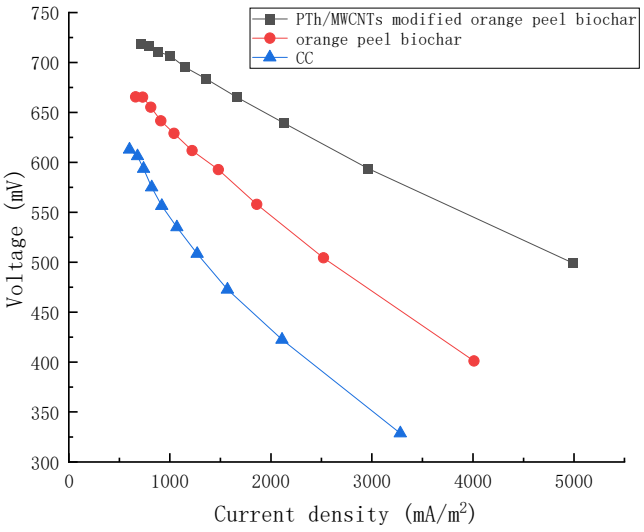


Figure 11. Polarization curve test chart

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

When the current flows through the electrode, a deviation between the electrode potential and the equilibrium potential begins, and the phenomenon of deviation is called battery polarization [16]. By changing the different resistance values of the MFC to observe the voltage and current changes, the polarization curve of the MFC device is one of the important indicators to judge the power production performance of MFC, and its change trend reflects the anti-polarization ability of the electrode. Figure 11 shows the polarization curves of an MFC loaded with three different electrode materials. As the resistance of the MFC external resistor decreases, the output voltage of MFC loaded with three different anode materials gradually decreases, and the decline range is CC anode >orange peel biochar anode > from largest to smallest PTh/MWCNTs composite modified orange peel biochar anode. In the lower activated polarization region, the MFC device loaded with CC electrode has a sharp drop, indicating that as the resistance of the external resistor increases, the electron transport efficiency between the electrodes is low, and polarization occurs. However, the MFC device equipped with unmodified biochar electrode and PTh/MWCNTs composite modified orange peel biochar electrode increased with the current output, the output voltage attenuation was small, and no polarization phenomenon occurred. In summary, the anti-polarization ability of the three different anode materials was PTh/MWCNTs composite modified orange peel biochar anode> orange peel biochar anode > CC anode, indicating that the biofilm formation rate and stability rate on the surface of the orange peel biochar electrode after PTh/MWCNTs composite modification were faster, the redox material supply rate and electron transfer rate near the electrode were significantly improved, and the biocompatibility and electrochemical performance were greatly improved, thereby improving the power production performance of MFC.

6.4. COD Removal Rate Test

According to "GB/T 32208-2015" to measure the chemical oxygen demand, the excess potassium dichromate ($K_2Cr_2O_7$) standard solution was added to the strong acidic solution, the above solution was digested by condenser tube and heating equipment, and the $(NH_4)_2Fe(SO_4)_2$ standard solution was dropped, and then the reducing analyte in the cutting waste liquid of the MFC anode chamber was oxidized, and the excess $K_2Cr_2O_7$ solution was evaluated with Cl2H8N2 as an indicator. Finally, COD is calculated by calculating the amount of $K_2Cr_2O_7$ standard solution consumed. This is the entire process of rapid COD determination by potassium dichromate method.

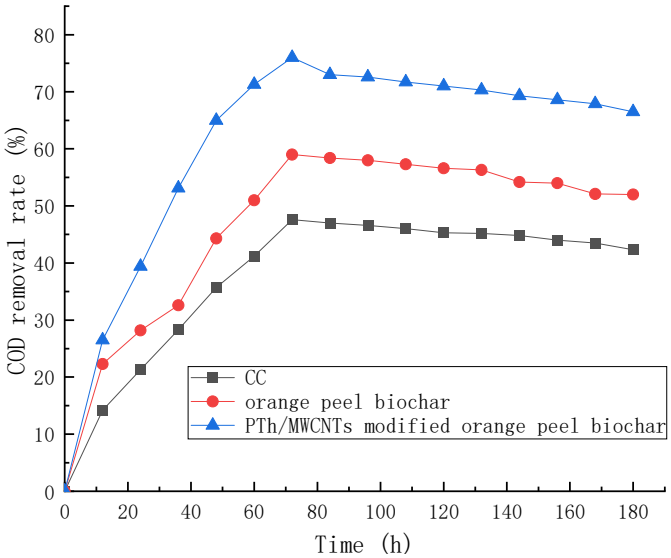


Figure 12. Removal rate of cutting waste liquid by MFC device

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

The COD removal effect of MFC of different electrode materials on cutting waste liquid is shown in Figure 12. The general trend of COD removal rate curves for the three groups of MFCs is basically the same, rising rapidly from 0% to the maximum value, followed by a small decrease, maintaining high removal efficiency. MFC devices loaded with three different electrodes move roughly the same, but the maximum COD removal rate and the final retention removal rate are very different. The COD removal rate of the MFC of the biochar electrode modified by PTh/MWCNTs to the cutting waste liquid was as high as 76%, which was 23.4% and 27% higher than that of the MFC containing biochar and CC electrode, respectively. The number and activity of microorganisms are rapidly enhanced in a short period of time, and the demand for organic matter in the anode chamber rises a lot, producing specific enzymes and surfactants and other substances, which effectively improves the removal effect of MFC device on COD in cutting waste liquid, indicating that the modified orange peel biochar electrode material has better biocompatibility, adsorption performance and conductivity.

7. CONCLUSION

(1) After the biochar electrode is carbonized at a high temperature of 400 °C, its porosity is larger and the degree of graphitization is higher. After the electrode is modified by PTh/MWCNTs, through infrared spectroscopy and XRD diffraction analysis, PTh and MWCNTs have been successfully modified on the surface of the electrode, without causing a large change in the internal crystal structure of the electrode material, and the contact angle is smaller after modification, which can be as low as and the surface roughness is improved. It is precisely because of the increase of surface roughness and the change of porosity that it provides good conditions for the attachment and growth of electrogenic bacteria on the electrode surface and the diffusion of substrate fuel.

(2) By comparing the power production and degradation performance of different electrode materials, it can be seen that the maximum voltage of MFC loaded with PTh/MWCNTs modified electrode can reach 573 mV according to the output voltage of MFC loaded with three different electrodes, which is 11.2% and 15.2% higher than that of ordinary CC electrode and orange peel biochar electrode. The maximum power density of MFC of PTh/MWCNTs modified electrodes is increased by 72.12% compared with unmodified biochar electrodes, which is 4.0 times that of CC electrodes. In addition, the polarization resistance of PTh/MWCNTs modified electrodes is higher than that of CC electrodes and ordinary orange peel biochar electrodes.

(3) According to the COD removal rate test of MFC, the COD removal rate of MFC loaded with PTh/MWCNTs modified electrode was as high as 76%, which was 23.4% and 27% higher than that of MFC loaded with orange peel biochar and CC electrode, respectively. The experimental results show that the MFC built with PTh/MWCNTs composite modified electrode has outstanding performance for the power generation and degradation of cutting waste liquid, and the utilization effect is the best.

ACKNOWLEDGMENTS

This work was funded by National Natural Science Foundation of China (51609131); Introduction and Education Plan of Young Creative Talents in Universities of Shandong Province (500076); Demonstration Base of Joint Cultivation of Graduate Students in Shandong Province. Shandong Jiaotong University “Climbing” Research Innovation Team Program (SDJTUC1802); Key research and development plan in Shandong Province (2019GHY112018); Shandong Provincial Higher Educational Science and Technology Foundation, China (KJ2018BBA015).

ISSN: 2472-3703 DOI: 10.6911/WSRJ.202305_9(5).0003

REFERENCES

[1] W. Tong: Microbial fuel cell technology for treatment of ship bilge oily sewage and its power production performance (MS. Shandong Jiaotong University, China 2021) p.25-50.

[2] X. Chen: Research on waste cutting fluid treatment process in machining industry(MS. Qingdao University of Technology, China 2019) p.20-40.

[3] C.Y. Hu: Research on power production performance and antibiotic detection of microbial fuel cells based on Pseudomonas aeruginosa (MS. Huaqiao University, China 2020) p.26-45.

[4] Y. Tang, T. Wu, X. Gou: Study on Phosphorus Removal from Water by Alkali-activated Magnesia Orange Peel Biochar, Water treatment technology, Vol. 47 (2021) No.11, p.91-95.

[5] W.Q. Wang: Preparation and electrochemical properties of polythiophene and MXene composite electrode materials (MS. Xi'an University of Architecture and Technology, China 2021) p.30-50.

[6] Y.S. Wang: Preparation and conductivity of polythiophene/carbon composites by chemical oxidation (MS. Taiyuan University of Technology, China 2017) p.32-50.

[7] Y.X. Zhang, S. Zhou, M.Z. Ma: Preparation of Fluoropolymers (PPFGs) and Properties of Their Construction of Hydrophobic Cotton Cloth, Guangzhou Chemistry, Vol. 46 (2021) No.01, p.32-38.

[8] C.N. Khuman, G.D. Bhowmick, M.M. Ghangrekar: Effect of Using a Ceramic Separator on the Performance of Hydroponic Constructed Wetland-Microbial Fuel Cell, Journal of Hazardous, Vol. 24 (2020) No.03, p.19-40.

[9] Y. Wu, J. Dong, W.D. Li: Treatment of beer production wastewater by constructed wetland microbial fuel cell, Chinese Journal of Environmental Engineering, Vol. 13 (2019) No.06, p.1292-1298.

[10] Y.Q. Tian: Treatment of copper-containing wastewater by modified anode microbial fuel cell, (MS. Qingdao University of Science and Technology, China 2019) p.15-50.

[11] H.W. Jin, D.D. Zhai, X. Wang: Effect of Graphene/Polyaniline Modified Anode on Performance of Microbial Fuel Cells, CIESC Journal, Vol. 70 (2019) No.06, p.2343-2050.

[12] H. Zhang, M.Y. Xu, J.Z. Luo: Microbial electron transport process in sedimentary microbial fuel cells, Science China: Technological Sciences, Vol. 49 (2019) No.12, p.1461-1472.

[13] Y. Masapogu, J.S. SRAVAN, S. Omprakash: Modified conductive polyaniline-carbon nanotube composite electrodes for bioelectricity generation and waste remediation, Bioresource Technology, Vol. 03 (2019) No.085, p.284.

[14] P. Farhan, P. Prasanta, K, Vikash: Sulfonated graphene oxide and titanium dioxide coated with nanostructured polyaniline nanocomposites as an efficient cathode catalyst in microbial fuel cells, Materials Science and Engineering: C, Vol. 108 (2020), p.24.

[15] M. Mashkoup, M.Rahimnejad, M. Pouralis: Catalytic performance of nano-hybrid graphene and titanium dioxide modified cathodes fabricated with facile and green technique in microbial fuel cell, Progress in Natural Science: Materials International, Vol. 27 (2017) No.06, p.647-651.

[16] X. Kang: Study on polarization correction and characteristics based on hysteresis model of lithium-ion battery (MS. Beijing Jiaotong University, China 2020) p.17-30.