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Original Research

Molasses Wastewater Treatment by Microbial Fuel Cell with MnO_2-Modified Cathode

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Abstract

An experimental system consisting of a dual chamber microbial fuel cell was constructed using simulated molasses wastewater as the inoculum and anode substrate, carbon cloth or carbon felt as the cathode base, and MnO_2 as the oxygen reduction catalyst for cathode. By testing and analyzing the output voltage, power density, and COD removal rate of the microbial fuel cell, the effects of the MnO_2-modified cathode on power generation and wastewater treatment of microbial fuel cells were studied. The steady output power density of the microbial fuel cell with carbon cloth cathode were 6.8 and 10.33 mW/m^2, respectively, before and after modification by MnO_2, that is, the power density of the microbial fuel cell with MnO_2-modified carbon cloth was increased by 51.91% more than that of unmodified carbon cloth. The stable output power density of the microbial fuel cells with carbon felt were 3.6 and 31.37 mW/m^2, respectively, before and after modification by MnO_2, that is, the power density of the microbial fuel cell with MnO_2-modified carbon felt was increased by 771.4% more than that of unmodified carbon felt. The results show that the electricity generation capacity and the wastewater treatment effect of the microbial fuel cell using molasses wastewater as the anode substrate can be improved significantly by using inexpensive MnO_2 as the cathode modifier.

Keywords: microbial fuel cell, molasses wastewater, MnO_2, cathode modification, power generation performance

Introduction

Molasses is a byproduct of the sugar production process, and it is often used as raw material for some fermentation industries such as ethanol and yeast production. Using molasses for production processes in the fermentation industry produces large amounts of molasses wastewater. Molasses wastewater belongs to high-concentration organic wastewater, which contains such organic matter as sugar, protein, amino acids, and vitamins [1]. This kind of wastewater is acidic and has high color, and is one of the most difficult and unmanageable wastewaters [2]. Directly discharging it into the water system can cause serious pollution, so an appropriate wastewater treatment system is required. The existing main treatment methods of molasses wastewater are some terminal degradation methods such as anaerobic treatment (UASB, anaerobic fluidized bed, etc.), adsorption, catalytic oxidation, flocculation precipitation, and membrane separation.

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The common characteristics of such degradation methods are high cost and toxic byproducts. In the context of facing the dual pressures of energy shortages and environmental pollution, it is necessary to explore more appropriate molasses wastewater treatment methods.

The microbial fuel cell (MFC) is a kind of biological chemical reaction device that can directly convert the chemical energy stored in organic matter into electrical energy using microbial metabolic activity. MFC produces electricity while purifying wastewater and causes no pollution to the environment during the power generation process. It is regarded as a new wastewater treatment process and a new green power generation technology that has the advantages of high efficiency, low energy consumption, and is clean [3-7].

At present, most research on MFC still stays in the laboratory. Low output power, high cost, and less satisfactory wastewater treatment effects are the primary causes that restrict its industrialization [8-9]. The main factors that affect the performance of MFC include: electricigens, structure of the MFC, substrate properties, intracellular and extracellular resistance, and electrode materials [10-14]. Among these, the activation loss of electron acceptor aside cathode is an important factor that affects the performance of MFC. Usually, carbon-based materials are adopted as the cathode of an MFC, and the dissolved oxygen (O_2) is selected as the electron acceptor. Oxygen has some advantages such as high redox potential and wide sources, but its redox activity in the carbon electrode surface is relatively low. Meanwhile, the oxygen concentration has great influence on cathodic potential. Due to its low solubility, it is necessary to keep continuous aeration so as to maintain a stable power output, which will create some additional energy consumption. On the other hand, O_2 will inevitably penetrate through the exchange membrane to the anode, which results in a decrease of the activity of microorganisms in the anode, and then affects the power generation performance of the MFC [15].

Potassium permanganate and potassium dichromate have high redox potential. When they are used as cathode electron acceptors can improve the output power of MFC significantly. However, the common defects of these substances are non-renewable and latent environmental hazards. So, oxygen is still the most commonly used cathode electron acceptor of MFC because of its environmental friendliness. In order to improve the reduction efficiency of oxygen in a cathode, a cathodic catalyst or other redox system is required to speed up the reaction rate. At present, platinum (Pt) is widely used as a cathodic catalyst. Metal platinum has the advantages of high activity, high energy efficiency and so on, and it has a great catalytic effect on the cathodic oxygen reduction of MFCs. Oh's experimental results show that the maximum output power of MFC with Pt-loaded carbon cathode is increased by about 78% compared with that of general carbon cathode [16]. But Pt is not suitable to be widely used in MFCs because of its expense. Therefore, it is necessary to find some cheaper metal oxide to replace the precious metal catalysts such as Pt. Transition metal oxides such as MnOx, CoOx, and TiOx are generally considered to be a kind of promising cathode catalyst with more potential applications because of their high catalytic activity, affordability, and wide range of sources [17-20]. In recent years, research on using MnO_x as a substitute for Pt catalysts has received increasing attention.

This paper intends to construct an MFC using molasses wastewater as the anode substrate. In order to improve the generating capacity and the purifying effect of the MFC, MnO_2 is used to modify the cathode, and we investigated the influence of MnO_2 on generating capacity and purifying effect of MFC.

Materials and Methods

Structure of the Experimental System

The experimental system is mainly composed of three parts: a dual-chamber MFC reactor, an external load, and a data acquisition system (Fig. 1).

The MFC reactor is of double-chamber construction. The sizes of the two chambers are equal at 8×8×8 cm. The anode electrode is a piece of 6×6 cm carbon cloth, and the cathode electrode is 6×6 cm MnO_2-loaded carbon felt or carbon cloth. In experiments, the electrode and the conducting wire need to be bonded with epoxy resin so as to prevent the wire from corroding. The external load is simulated by a rheostat, and its value can be adjusted according to need. The real-time output voltage of the MFC is collected and transmitted to a computer by a multi-function USB data acquisition card (MPS-010602) with 16 channels. The output voltage is collected once every 60 seconds and stored, processed, and displayed by computer. In the experiments, the load resistance of MFC was set at 500 Ω, except for the experiment of measuring polarization curve. The mixed solution of $K_3[Fe(CN)_6]$ and NaCl was used as the catholyte of MFC. All the experiments were carried out at room temperature.

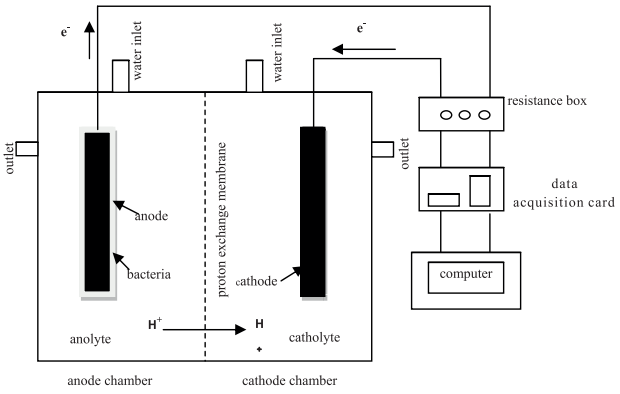

Fig. 1. Schematic view of MFC experimental system.

Experimental Materials

Preparation of Anode Substrate

The anode substrate used in the experiment was simulated molasses wastewater, which was prepared using: 3.13 g/L sodium bicarbonate ($NaHCO_3$), 0.31 g/L ammonium chloride (NH_4Cl), 6.338 g/L sodium dihydrogen phosphate ($NaH_2PO_4 \cdot H_2O$), 6.8556 g/L disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), 0.13 g/L potassium chloride (KCl), 0.2g/L Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), 0.015 g/L calcium chloride ($CaCl_2$), 0.01g/L manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$), and 3 g/L brown sugar ($C_{12}H_{22}O_{11}$).

Microbial Cultivation

The mixed microorganisms used in the anode chamber were prepared by sludge cultivation. The sludge was taken from a campus lake. In conditions of anaerobic, the prepared simulated molasses wastewater and some nutrient elements necessary for the growth of microorganisms (such as carbon, nitrogen, phosphorus, etc.) and the collected sludge were put together into a culture flask, and then were put in the biochemical incubator for acclimatization under a constant temperature of 20ºC. Microorganism acclimatization is considered to be successful when the sludge in the culture flask flocculent is suspended.

Pretreatment of the Proton Membrane

The proton exchange membrane adopted for the experiments is Nafion117, which needs to be pretreated before use by putting it into an H_2O_2 solution with 5% volume fraction to boil for one hour to remove the organic impurities, then take it out and wash it repeatedly with de-ionized water. Then you put it in 1 mol/L H_2SO_4 to boil for one hour so as to remove the metal ion impurities, subsequently taking it out and rinsing it repeatedly and boiling it again for one hour with de-ionized water to remove the residual H_2SO_4. The pretreated proton exchange membrane needs to be placed in the de-ionized water to prepare it for experimental use.

Pretreatment of Electrode Materials

Although both carbon cloth and carbon felt are made of carbon fiber wire, there are some differences between the arrangements. Carbon felt has a disorderly array and small pore spaces, while carbon cloth has an orderly array, fewer pores, and big pore spaces [21]. Therefore, the power generation performance and COD removal rate of MFC with MnO_2-modified carbon cloth and carbon felt cathode were tested and compared in this experiment.

The carbon cloth and carbon felt used as electrodes need to be pretreated before the experiment. First, put it into the analytically pure acetone to soak for two hours to remove the impurities on the surface (note that the container port must be sealed with preservative film to prevent the acetone from volatilization). Then take out the soaked carbon cloth or carbon felt and wash it repeatedly with de-ionized water until it becomes neutral, and then put it into a drying box at 65-85ºC to dry.

Preparation of MnO_2 - Modified Cathode

The MnO_2-modified cathode was prepared by loading MnO_2 in the cathode, and the MnO_2 is prepared by the oxidation reduction method, which has the advantages of easy operation and low cost. The preparation method is as follows: first, add $MnSO_4$ solution in a certain concentration to a 500 mL beaker and immerse the carbon cloth or carbon felt in it for 10 min, then the $KMnO_4$ is rapidly poured into a beaker and stirred to make them mix completely and react at room temperature for six hours; then rinse the carbon cloth or carbon felt surface with the deionized water, standby as a cathode electrode after drying.

The SEM images of the carbon felt before and after modification are shown in Fig. 2. As can be seen from the

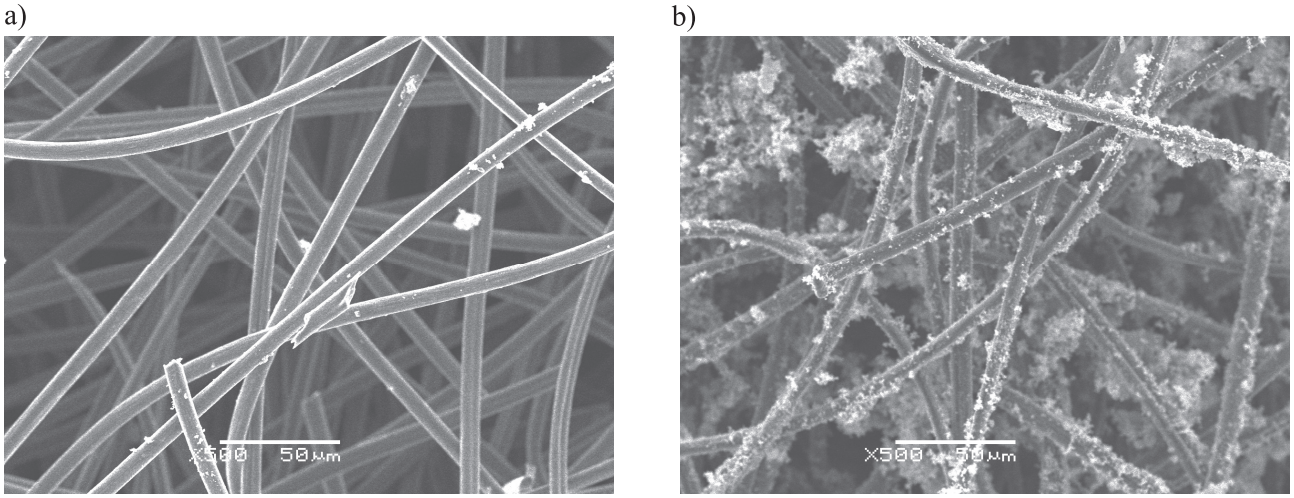

Fig. 2. SEM images of the carbon felt before a) and after b) modification.

figure, the surface morphology of the modified carbon felt is very different from that of the former. A large number of MnO_2 particles were attached to the surface of the modified carbon felt.

Analysis Items and Methods

The output voltage, current, power, and COD removal rate of the MFC under different operating conditions were analyzed.

The output voltage U of MFC is automatically collected and stored in the computer through the 16-channel data acquisition card. The output current I of the MFC can be calculated according to Ohm's law:

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

…where R is load resistance. The output current density can be calculated according to the current and the anode surface area of the MFC:

$$I_A = \frac{I}{A} = \frac{U}{RA} \tag{2}$$

By changing the external load resistance, the output voltage of MFC under different load conditions can be measured. According to equations:

$$P = UI \tag{3}$$

$$P_A = \frac{UI}{A} \tag{4}$$

…the output power P and the power density P_A of MFC can be obtained separately.

The influent and effluent COD of the anode chamber were measured by using the photoLab S6 rapid measuring instrument which made by German WTW.

Results and Discussion

The Effect of MnO_2-Modified Cathode on MFC Generating Capacity

In this experiment, three MFC experimental systems that have the same basic configuration were running at the same time so as to obtain good contrast effect. The experimental conditions of the three MFC systems are identical except for the contrast item. In the comparative experiments, all of the unspecified untreated cathodes are carbon cloth cathodes.

The voltage curves of MFC under different working conditions are shown in Fig. 3. It can be seen that the stable output voltage of MFC with an untreated carbon cloth cathode is about 3.2 mV, and the stable output voltage of MFC with MnO_2 loaded carbon cloth cathode

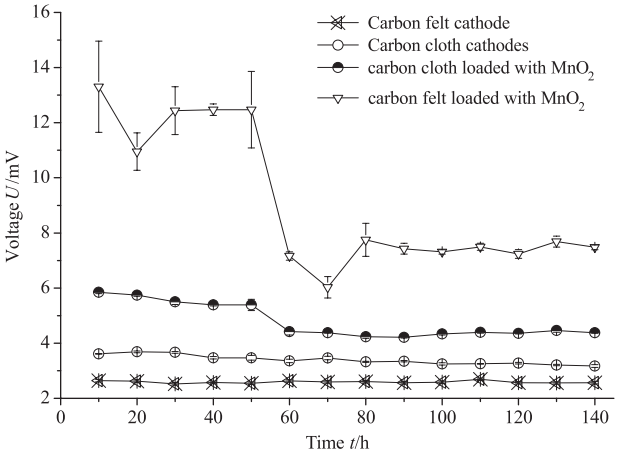

Fig. 3. Output voltage of MFC in different working conditions.

is about 4.5 mV, i.e., the output voltage of MFC with the MnO_2-modified carbon cloth cathode was increased by 40.6% over that of MFC with the untreated carbon cloth cathode. When carbon felt was used as a cathode, the stable output voltages of MFC before and after cathode modification were 2.5 mV and 7.5 mV, respectively, i.e., the output voltage of MFC with the MnO_2-modified carbon felt cathode was increased by 200% over that of MFC with an untreated carbon felt cathode.

Variation curves of the output power density of MFC under different working conditions are shown in Fig. 4. Under the conditions of using carbon cloth as a cathode, the stable output power density of the MFC before and after cathode loading MnO_2 were 6.8 and 10.33 mW/m^2, respectively, which shows that the power density of MFC with MnO_2-modified carbon cloth cathode was 51.91% higher than that of MFC with an unmodified carbon cloth cathode. When using carbon felt as a cathode, the stable output power densities of MFC before and after cathode modification were 3.6 and 31.37 mW/m^2, respectively, which shows that the power density of MFC with MnO_2-modified carbon felt cathode was 771.4% higher than that of MFC with an unmodified carbon felt cathode.

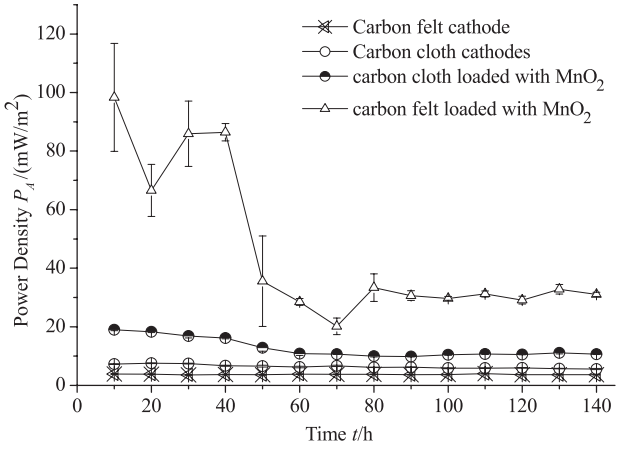

Fig. 4. Power density of MFC in different working conditions.

The comparison results above show that both the MnO_2-modified carbon cloth cathode and the MnO_2-modified carbon felt cathode can improve the power generation performance of MFC, and MnO_2-modified carbon felt can improve the power generation performance of MFC more observably. This is due to the catalytic reduction of MnO_2 accelerating the speed of the MFC cathode accepting electronics, and the porous clutter arrangement structure on the carbon felt surface allowing the catalyst to adhere more easily to the carbon felt so that its surface catalyst is much more plentiful than that of a carbon cloth, so the effect of MnO_2-modified carbon felt is much better than that of MnO_2-modified carbon cloth. The energy production capacities of MFC with unmodified carbon cloth and carbon felt cathodes are low and don't have many differences. The performance of MFC with an untreated carbon cloth cathode is slightly better than that of MFC with an untreated carbon felt cathode, which is because more sludge aggregated and adhered to the surface of the carbon felt to restrict the oxygen transfer to the carbon felt surface, the electron acceptor was reduced, and then the power production capacity of MFC decreased.

The voltage and current density of MFC with the MnO_2-modified carbon felt cathode are shown in Fig. 5.

Internal resistance is one of the main factors that affects the power generation performance of an MFC. By reducing the internal resistance of an MFC, its output power can be improved effectively. The influence of cathode modification on MFC can be understood by determining the changing situation of internal resistance. The most commonly used method for determining MFC resistance includes methods of polarization curve and power density peak [22-23]. The method of polarization curve is to plot voltage and current and then obtain the ohmic resistance, activation resistance, and mass transfer resistance by linear fitting, and the sum of these three kinds of resistance is the total apparent internal resistance of the MFC. The method of power density peak is to decide the internal resistance of MFC by finding the peak point of the power density curve. The internal resistance of an MFC equals its external load resistance when its output power reaches maximum [24-25]. According to the experimental data, the polarization curve and power density-resistance curve can be obtained under different working conditions, which are shown in Figs 6-7. The peak value of the power density can be seen clearly in Fig. 7. The internal resistance of MFC with unmodified carbon cloth cathode is 860 W, the internal resistance of MFC with MnO_2-loaded carbon cloth cathode is 765 W, and the internal resistance of MFC with MnO_2-loaded carbon felt cathode is 670 W. These results show that cathode modification by MnO_2 can reduce the internal resistance of MFC to a certain extent so as to improve the generating capacity of an MFC. By contrasting the effects of carbon felt cathode and carbon cloth cathode, it can also be found that when using MnO_2-modified carbon felt as cathode, the improvement effect on electrical property of MFC was more significant.

Effect of MnO_2-Modified Cathode on the Removal Rate of COD

For the above-mentioned operating conditions, the variation tendency of COD and its removal rate of

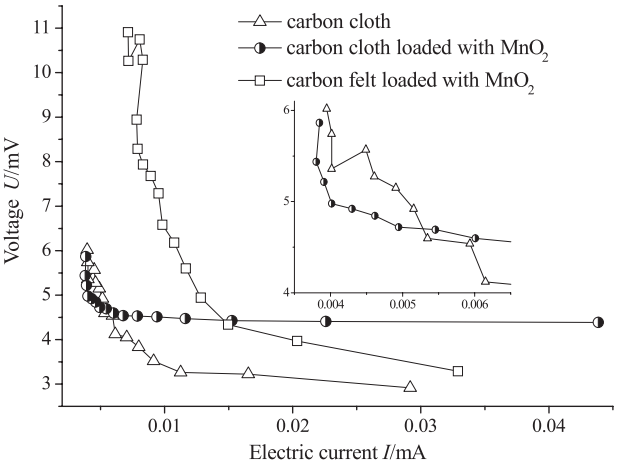

Fig. 6. Polarization curves in several different working conditions.

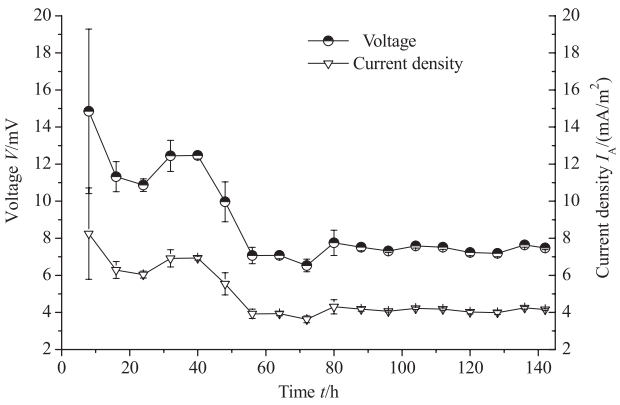

Fig. 5. Voltage and current density of MFC with MnO_2-loaded carbon felt as cathode.

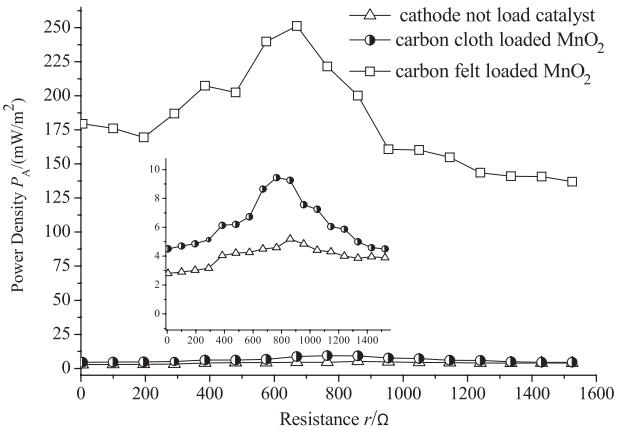

Fig. 7. Power density curves in several different working conditions.

molasses wastewater used as the anode substrate of MFC are shown in Figs 8-9.

In experiments, the initial COD concentration of molasses wastewater is 1,582 mg/L. It can be seen from Fig. 8 that along with the running of MFC, all the COD values corresponding to the three working conditions were gradually reduced, and COD decreased faster in the case of using MnO_2-modified carbon felt as a cathode. After 36 h, the COD value of the anode substrate of MFC tended toward stability. The stability values of COD for the three cases that correspond to unmodified carbon cloth cathode, MnO_2-loaded carbon cloth cathode, and MnO_2-loaded carbon felt cathode were 1,200 mg/L, 1,188 mg/L, and 1,020 mg/L, respectively.

It can be seen from Fig. 9 that the COD removal rate of anode substrate of MFC increased rapidly from start running to 36h. This is because the microbial activity is stronger and the anode substrate concentration is larger in this phase, and therefore the reaction rate of microbial degradation of organic compounds is relatively fast. Meanwhile, the MnO_2 cathode catalyst accelerates the cathodic oxygen reduction rate of MFC. Therefore, the COD removal rate of MFC with the MnO_2-loaded cathode is higher. After 36h the concentration of the anode substrate has been significantly reduced and microbial activity also decreased, the reaction rate of microbial degrading organic compounds is approaching stable, the COD removal rate has slowed down, and COD concentration is gradually becoming steady. Corresponding to the three cases of unmodified carbon cloth cathode, MnO_2-loaded carbon cloth cathode and MnO_2-loaded carbon felt cathode, the stability values of COD removal rates of MFC treating molasses wastewater were 24.15%, 24.91%, and 35.53%, respectively. It can be seen that the COD removal rate presented no obvious change when MnO_2-modified carbon cloth was used, but when MnO_2-modified carbon felt was used, the purification effect of MFC treating molasses wastewater improved greatly along with a marked improvement in generating capacity.

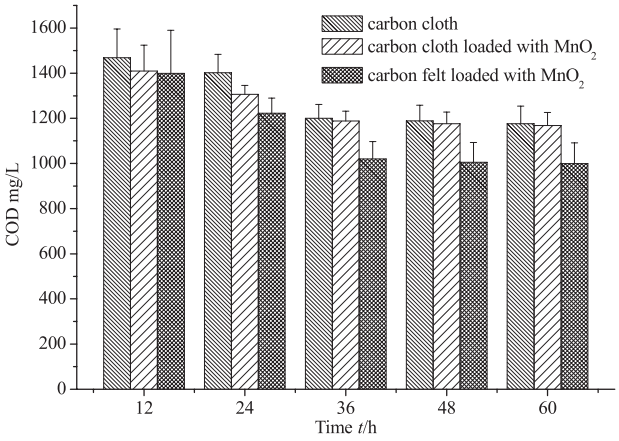

Fig. 8. Comparison of COD in different conditions.

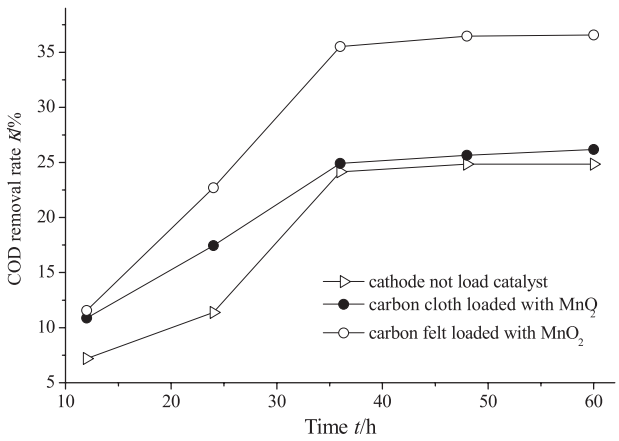

Fig. 9. Changing curves of COD removal rates.

The COD removal of this MFC can be compared with some existing main treatment methods of molasses wastewater. A study on the effect of photodegradation on COD removal in molasses wastewater was carried out and it was found that UV photolysis performed the poorest with only 2% COD removal, and the H_2O_2 /TiO_2 /UV/ zeolite hybrid system attained the highest COD removal at about 15% [26]. Investigating the oxidation with ozone of highly polluted molasses wastewater shows that chemical oxidation with ozone can provide as much as 15-25% COD reduction [27].

The Sang-Som factory at Nakhonpathom Province, Thailand, was a conventional anaerobic pond system. The COD removal efficiencies of molasses wastewater by the anaerobic pond were about 46.0% [28]. The fact is that almost all the COD removal rates of the most existing treatment methods for molasses wastewater are not too high, thus the COD removal rate of MFC is relatively not too low. To improve the COD removal rate of molasses wastewater, many researchers have considered using some combined processes. The COD removal rate of molasses wastewater by the combined process of EGSB-MFC-BAF reached 53.2% [29], and by using the EGSB-MBR combined process for molasses wastewater treatment, the COD removal rate can reach 85.5% [30].

Compared with other wastewater treatment methods, the biggest advantage of MFC is its power generation capacity along with the wastewater treatment process. Although the COD removal rate did not meet expectations, MFC is still an alternative method for molasses wastewater treatment. In practice, we can use MFC with molasses wastewater as feed for power generation while in the meantime purifying the molasses wastewater to a certain extent. More effective improvement measures for MFC are necessary in order to further improve the COD removal rate of molasses wastewater.

Conclusions

MFCs using molasses wastewater as anode substrate show good performance on electricity production, and the electricity is produced in the process of the biodegradation of organic compounds in molasses wastewater. Therefore,

MFCs using molasses wastewater as fuel can generate electricity and simultaneously purify the molasses wastewater.

Because MnO_2 has the effect of catalytic oxygen reduction, the speed of the MFC cathode accepting electronics was accelerated, the power generation performance of MFC was improved significantly, and at the same time the removal ability of COD of the molasses wastewater – which was used as the anode substrate of MFC – was improved to a certain extent. Compared with the general MFCs that use untreated carbon cloth as a cathode, the stable output voltage of the MFC using MnO_2-loaded carbon cloth and MnO_2-loaded carbon felt as cathodes was increased by 40.6% and 134.4%, respectively, and the COD removal rate was increased by approximately 3.15% and 47.12%, respectively. In summary, when the double-chamber MFC was constructed using molasses wastewater as anode substrate, the mixed solution of $K_3[Fe(CN)_6]$ and NaCl as catholyte, and MnO_2-modified carbon felt as a cathode, the power production performance and wastewater treatment effect of MFC were all significantly improved. The stable output voltage of the corresponding MFC is about 7.5 mV, the stable output power density is about 31.37 mW/m^2, and the COD removal rate is about 36%.

Acknowledgements

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