Differences in Contaminants Removal Efficiency and Electricity Production in Disposing Leachate with Chemical-Cathode and Aerobic Bio-Cathode MFC

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‖ **Abstract**

The effect of cathode type on contaminant removal efficiency and electricity production in disposing leachate was investigated in a self-assembled microbial fuel cell (MFC). When the landfill leachate was treated with the chemical-cathode MFC (CMFC) and aerobic bio-cathode MFC (ABMFC), the maximum output voltages were 699.0 mV and 459.4 mV, the maximum output powers were 197.7 mW m^{-3} and 147.6 mW m^{-3}, and the internal resistances were 900 Ω and 700 Ω, respectively. After running the MFCs for 45 days, the COD removal ratios of CMFC and ABMFC were 56.5 % and 64.3 %, the Coulombic efficiencies were 14.3 % and 17.1 %, and the ammonia nitrogen removal ratios were 53.8 % and 58.1 %, respectively.

‖ **Keywords**

Microbial fuel cell, aged landfill leachate, chemical-cathode, aerobic bio-cathode, disposal of pollutants, electricity production

1 Introduction

Microbial fuel cell (MFC) is an ideal device for directly converting the chemical energy in an organic substance into electrical energy by microorganisms. The organic substances may come from dye wastewater,[1] palm oil mill effluent,[2] or landfill leachates.[3,4] In most MFCs, the microbial communities are phylogenetically diverse, and there is the emergence of new bacterial community interactions on the basis of interspecies electron transfer.[5] MFC is usually divided into two types, non-biological cathode microbial fuel cell (NMFC) and bio-cathode microbial fuel cell (BMFC). Because of the high oxidation-reduction potential, the cathode of MFC is a major factor affecting the power output.[6] Ferricyanide is a very popular electron acceptor in MFCs for its good performance.[7] Compared to the NMFC, BMFC has many advantages, such as, low construction and operating costs, no addition of heavy metals and electron transfer media, thus avoiding secondary pollution and catalyst poisoning, and removing nitrogen from wastewater or sludge with denitrification.[8] Depending on whether oxygen is involved in the electrode reaction, BMFC can be classified into two types: ABMFC (aerobic bio-cathode microbial fuel cell) and NBMFC (anaerobic biological-cathode microbial fuel cell).

In recent years, BMFC with oxygen as electron acceptor has been developed. *Clauwaert et al.*[9] realized that the reduction in oxygen at the cathode is one of the major bottlenecks of microbial fuel cells (MFCs). *Freguia et al.*[10] found that the reduction in oxygen in the bio-cathode had improved as the anode effluent directly flowed into cathode of the double-chamber MFC. *Lee et al.*[11] evaluated the energy-conversion efficiencies of MFCs by utilizing fermentable and non-fermentable substrates. *Chung et al.*[12] held that the excess accumulation of the biofilm and chemical scale on the cathode in MFC exhibited adverse effects on the power generation due to a decrease in the active cathode surface area and an increase in diffusion resistance for oxygen. *Rago et al.*[13] confirmed that a low external resistance provides an MFC anodic biofilm with the highest content of *Geobacter* because it allows higher current intensity, which is correlated to exoelectrogenic activity.

Aged landfill leachate is a type of refractory organic wastewater. It is difficult to realize utilization of this resource because of the complex process involved and the high cost. In order to obtain electrical energy, *You et al.*[14] researched the treatment of landfill leachate with single chamber MFC and dual chamber MFC. *Puig et al.*[15] suggested that the high salinity landfill leachate was conducive to reduce the internal resistance of MFC, thus the electricity performance of MFC could be improved. MFCs can be exploited as a polishing step anaerobic pre-treatment of aged landfill leachate.[16] The cathode of MFC is a key influencing factor on cell power generation and the nitrogen removal ratio.[17] Several air bio-cathode microbial fuel cell systems (MFCs) have already been developed in recent years.[18,19] In this research, the aged landfill leachate was treated for 45 days with ABMFC (double chamber aeration bio-cathode microbial fuel cell) and CMFC (double chamber chemical-cathode microbial fuel cell) to compare the differences in the electricity production and pollutant removal.

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2 Experiments

2.1 Experimental materials and construction of MFCs

H-type MFC was constructed using an organic glass tank and two electrodes (anode and cathode), as seen in Fig. 1. The electrode materials were both carbon felt (length 4 cm, width 4.5 cm, thickness 1 cm), and the saturated calomel electrode was set in anode pool as a reference electrode. The volumes of cathode department and anode chamber were both 800 ml (size: h = 153 mm, φ = 80 mm). Electrodes were separated by the proton exchange membrane (PEM, Nafion 117, effective area: 7.07 cm^2), connected with copper wire and external resistance (1500 Ω) to form a loop. MFCs were operated at atmospheric pressure and room temperature. The dissolved oxygen in ABMFC cathode chamber was from air. Potassium ferricyanide was used as electron acceptor in CMFC.

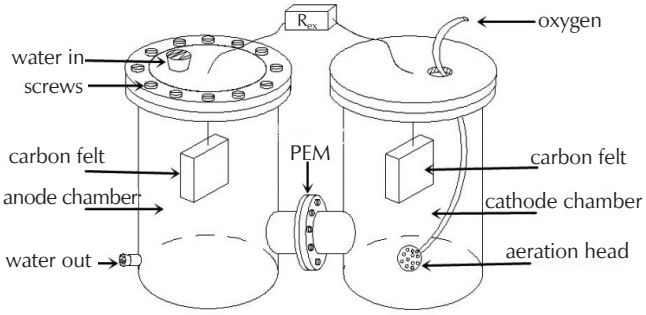

Fig. 1 – Schematic diagram of the microbial fuel cell

2.2 Inoculation and operation of MFC

The aged landfill leachate in the anode chamber was taken from the collecting well of Changshengqiao landfill in Chongqing. For the aged leachate, pH was 8.84, COD was 6842.1 mg l^{-1}, NH_3–N was 3520.9 mg l^{-1}, TP was 25.95 mg l^{-1} and conductivity was 12.0 mS cm^{-1}.

All agents in the experiments were analytically pure, and provided by Kelong Chemical Reagent Factory, Chengdu.

The original bacteria were taken from the activated sludge of secondary clarifier in a wastewater plant of Chongqing. The anode inoculation microorganisms originated from MFC anode liquid ran over one year in laboratory. Cathode microbial inoculations were from the original MFC anode bacteria liquid acclimated by aeration. In the start-up phase, MFCs operated intermittently, and the inoculation proportion was 1 : 1 both in cathode chamber and anode chamber.

In the first stage, the anode chamber was maintained under anaerobic conditions, and the domestication was done by the aged landfill leachate as substrate. The substrate and catholyte were added into chambers through the feed port. For ABMFC, cathode solution contained glucose (2.0 g l^{-1}), $Na_2HPO_4 \cdot 12H_2O$ (8.95 g l^{-1}), KH_2PO_4 (3.40 g l^{-1}), NH_4Cl (0.2 g l^{-1}), KCl (0.13 g l^{-1}), trace metal ions (12.5 mg l^{-1}), and vitamin C (5 mg l^{-1}),[11] while the cathode solution of CMFC was only $K_3Fe(CN)_6$ (25 mmol l^{-1}). In the second stage, CMFC and ABMFC were run consecutively for 45 days, regularly supplying the ferricyanide or carbon source in cathode.

2.3 Test parameters and methods

COD, NH_3–N, NO_2–N and NO_2^-–N were determined by standard method.[20] The output voltage (U) was automatically recorded and stored by Agilent 34970A. The current (I) was calculated by the formula ($I = U/R$), where R was the external resistance, 1500 Ω. The current density (j) and output power density (P) were obtained with the following formula:

$$j = I/V,\ P = U^2/RV, \tag{1}$$

where V is effective volume of the anode chamber (m^3). The internal resistance (R_{in}) was determined using polarization curve method. Coulombic efficiency (C_E) was evaluated with the change in leachate COD.

3 Results and discussion

3.1 Electricity generation performances of MFCs in disposing leachate

Hereinafter, 100 % of the aged landfill leachate is referred to as the aged landfill leachate. The aged landfill leachate was used as anolyte in CMFC and ABMFC, regularly adding potassium ferricyanide or carbon source to the cathode chamber. The relationship between the output voltages of CMFC and ABMFC and running time is shown in Fig. 2, and their polarization curves and power density plots are shown in Fig. 3 when the electricity production was in a stable period. The curves in start-up period are not shown.[15] As seen from Figs. 2 and 3, the output voltages of the two kinds of MFCs was step changed with time. The maximum output voltage (U_m), the maximum power density (P_m), and the internal resistance for CMFC and ABMFC in start-up period and run-time are listed in Table 1.

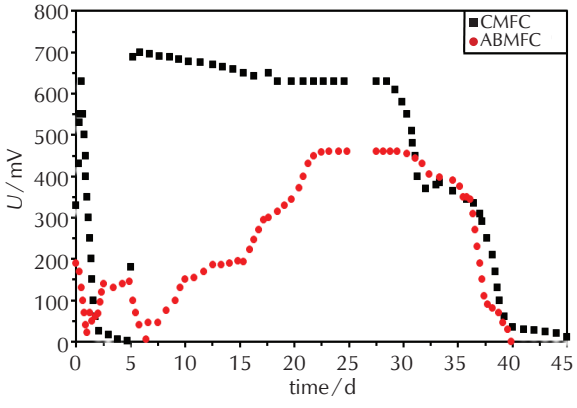

Fig. 2 – Voltage versus time plots

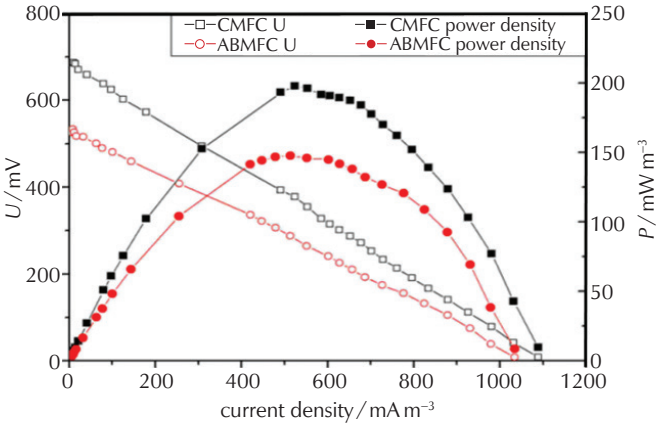

Fig. 3 – Polarization curves and power density of the two different cathodes MFCs

Table 1 – Electricity generation parameters during start-up phase and run-time

Period	Parameter	CMFC	ABMFC
start-up phase	U_m / mV	627.8	348.3
	P_m / mW m^{-3}	201.8	442.5
	R_{in} / Ω	620	600
run-time	U_m / mV	699.0	459.4
	P_m / mW m^{-3}	197.7	147.7
	R_{in} / Ω	900	700

As seen from Fig. 2, the output voltage increased to 699.0 mV rapidly, and then remained steady after adding potassium ferricyanide in CMFC. In the meantime, the largest power density of CMFC was 197.7 mW m^{-3}, and the internal resistance was 900 Ω. This meant that the anode microorganism community had been successfully enriched. After 30 days, the output voltage sharply decreased to 370.4 mV, and did not change with the addition of potassium ferricyanide after 40 days.

From Fig. 2, the output voltage increased with the time after the carbon resource was supplied to cathode chamber in ABMFC, then reached the maximum (459.4 mV) after 20 days, and remained steady for a time. At the same time, the maximum power density was 147.6 mW m^{-3}, and its internal resistance was 700 Ω. The voltage did not change with the addition of the cathode carbon source after 36 days. With MFC operation, the internal resistance of MFC had increased, while the output voltage remained steady at maximum. So, according to the formula $P = U^2/RV$, the power density decreased.

The output voltage of CMFC was higher than that of MFC reported in reference,[19] while the output voltage of ABMFC was lower. This could be explained as follows. The generation of voltage may be related to the change in the leachate composition. During the process of anaerobic degrading, the macromolecular organic compounds decomposed into a variety of volatile fatty acids and other small molecules, such as acetic acid salt, lactic acid salt, *etc*. In addition, electrogenesis microorganism can continue to use these degraded materials to produce electricity in MFC. However, the voltage had not changed with the change in cathode electron acceptor or nutrients in the later running time. The possible reason was the accumulation of toxic material after long running time of the system, which affected the activity of electrogenesis microorganism. In fact, the initial COD of leachate in this study was higher than that of reference.[19] Moreover, long time running of MFC can cause the proton exchange membrane to be stained, which leads to declined membrane exchange performance and affects the output voltage and resistance of MFCs.[12]

Compared with the performances of MFC in start-up phase, the maximum power density and voltage of CMFC and ABMFC in run-time period had obviously decreased, and the internal resistances significantly increased. Possible reasons are as follows. The aged landfill leachate is toxic and difficult to degrade. Therefore, the activity of the microorganisms in MFC was inhibited to a certain extent. Additionally, the biofilm was attached in the proton exchange membrane as MFC operated a long time, and declined the performance of membrane exchange. This resulted in the internal resistances increase of MFCs.

Compared to ABMFC, CMFC produced better electrical properties (including voltage and power density). In the anaerobic environment of anode chamber, the organic matter decomposed and released electrons and protons under the action of microorganisms. As protons migrated to the cathode through the proton exchange membrane, electrons transmitted to cathode from the external circuit. In cathode department, the electron acceptor (usually O_2) reacted with electrons to form OH^-, and protons combined with OH^- to produce water. Therefore, the performance of MFCs is currently limited by the cathode. Electron acceptor reduction rate is a key factor in electrical properties of MFCs. Potassium ferricyanide acted as electron acceptor of CMFC, while oxygen acted as electron acceptor of ABMFC cathode. Theoretically, standard potential of oxygen is higher than that of ferricyanide. However, the potential is much lower than that of the theoretical value in practical applications. Ferricyanide as cathode electron acceptor can produce higher output power and voltage.

3.2 Pollutants treatment effect with MFCs for 100 % leachate

The removal rates of COD in CMFC and ABMFC are shown in Fig. 4. As seen from Fig. 4, the COD in anode chamber decreased fast at the beginning, and then it kept steady after electricity production within 33 days. For CMFC and ABMFC, COD decreased respectively to 2752.4 mg l^{-1} and 2261.7 mg l^{-1} from the initial 6332.1 mg l^{-1}, and the removal rates of COD were 56.5 % and 64.3 %, respectively. They had not reached the emission standards requirements, so further processing was needed. This result could be explained by the fact that the higher resistance of CMFC restricted the transportation of internal ions and decreased the removal rate of COD. The change in COD in anode chamber was used to calculate the Coulombic efficiency (C_E), and C_E of CMFC and ABMFC, which were 14.3 % and 17.1 %, respectively. However, the C_E was lower, indicating

that the organic matter had not all transformed into electrical energy in anode chamber. The above results showed that MFC could not only produce electricity, but could also remove pollutants in solution. There was no significant difference in the removal rate of COD between the two MFCs. This suggests that the anode performance of MFC was not different, and the main difference in performance resulted from cathode of MFC.

Removal efficiency of NH_3–N in MFCs with 100 % of leachate is shown in Fig. 5 (An-anode, Ca-cathode). It can be seen that the concentration of NH_3–N in anode chamber solution of MFC decreased with the extension of run time, and the descent speed of NH_3–N in anode chamber of ABMFC was faster than that of CMFC. The concentration of NH_3–N in cathode solution increased, indicating an NH_3–N diffusion phenomenon from anode chamber to cathode chamber. In addition, the concentration of ammonia nitrogen in cathode chamber first rose and then dropped with extended time, and tended to be balanced in anode chamber and cathode chamber after running for 33 days. After CMFC and ABMFC ran for 45 days, the removal ratios of NH_3–N in anode chamber were 76.8 % and 78.9 %, respectively. Deducting the residual NH_3–N concentration in the cathode chamber, the removal rate of NH_3–N in landfill leachate was 53.8 % and 58.1 %, respectively. *Damiano et al.* showed that the average removal ratios of COD and ammonia in leachate with MFCs were 16 % and 20 %, respectively.[12] Therefore, the experimental data in this paper was significantly better than those in literature.

Removal efficiencies of NO_3^-–N and NO_2^-–N in 100 % leachate by CMFC and ABMFC are shown in Fig. 6. It can be seen that the NO_3^-–N in the anode chamber solution decreased with time, while NO_2^-–N hardly changed. The total amount of the two forms of nitrogen showed a decreasing trend.

In cathode chamber of CMFC and ABMFC, NO_3^-–N increased with time and then decreased, and after running for 45 days, the concentrations were 541.8 mg l^{-1} and 273.4 mg l^{-1}, respectively. The maximum concentrations of total N were 774.52 mg l^{-1} and 390.7 mg l^{-1}, accounting for 34.3 % and 16.1 % of the total ammonia nitrogen loss, respectively.

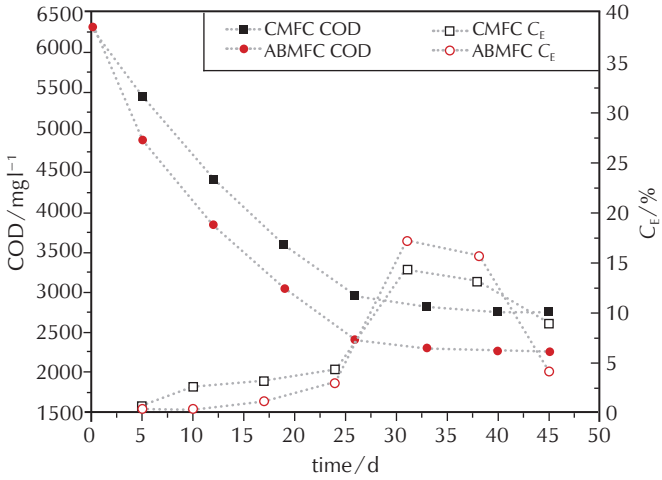

Fig. 4 – Variation of COD and Coulombic efficiency

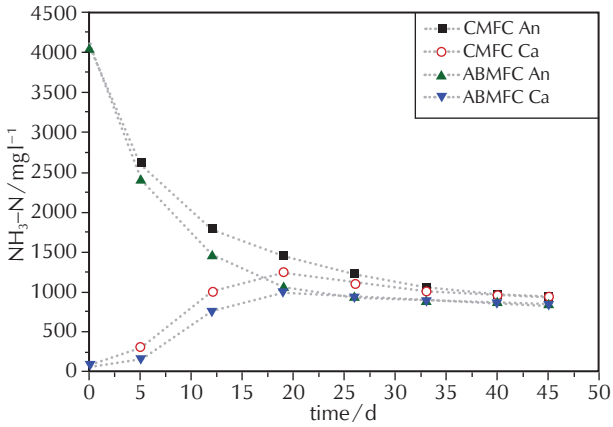

Fig. 5 – Variation of NH_3–N

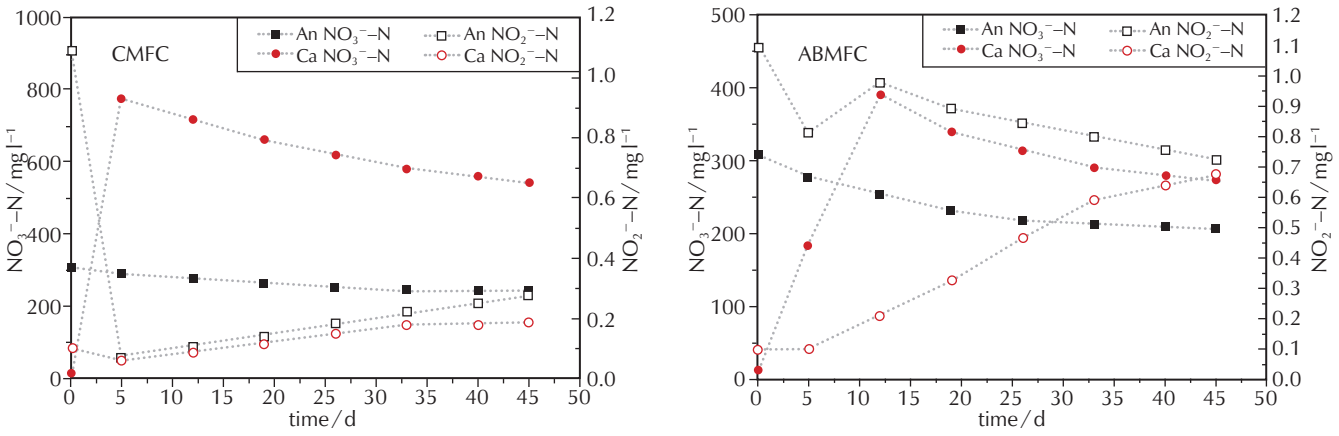

Fig. 6 – Variation of NO_3^-–N and NO_2^-–N

4 Conclusions

The double chamber aeration bio-cathode microbial fuel cell (ABMFC) and the double chamber chemical-cathode microbial fuel cell (CMFC) were built to compare the effect of cathode type on contaminant removal efficiency and electricity production in disposing leachate. As 100 % of landfill leachate was used as substrate of anode chamber for CMFC and ABMFC, the maximum output voltages were 699.0 mV and 459.4 mV, the maximum output powers were 197.7 mW m^{-3} and 147.6 mW m^{-3}, and internal resistances were 900 Ω and 700 Ω, respectively. After the MFCs ran for 45 days, COD decreased respectively to 2752.4 mg l^{-1} and 2261.7 mg l^{-1} from initial 6332.1 mg l^{-1}. Furthermore, because NH_4^+ diffused from anode to cathode, and NH_3–N net removal rates were 53.8 % and 58.1 %, respectively. MFC with the aged landfill leachate can treat hazardous wastewater during power generation and has far-reaching significance on future environmental protection.

ACKNOWLEDGEMENTS

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List of abbreviations and symbols

ABMFC – aerobic bio-cathode microbial fuel cell
BMFC – bio-cathode microbial fuel cell
CMFC – chemical-cathode microbial fuel cell
MFC – microbial fuel cell
NBMFC – anaerobic biological-cathode microbial fuel cell
NMFC – non-biological cathode microbial fuel cell
PEM – proton exchange membrane
C_E – Coulombic efficiency, %
COD – chemical oxygen demand, mg l^{-1}
h – height, mm
I – current, A
j – current density, W m^{-3}
NH_3–N – ammonia nitrogen, mg l^{-1}
NO_3^-–N – nitrite nitrogen, mg l^{-1}
NO_2^-–N – nitrate nitrogen, mg l^{-1}
P – output power, A m^{-3}
P_m – maximum output power, A m^{-3}
R – external resistance, Ω
R_{in} – internal resistance, Ω
TP – total phosphor, mg l^{-1}
U – output voltage, mV
U_m – maximum output voltage, mV
V – anode effective volume, m^3
φ – diameter, mm

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SAŽETAK

Učinkovitost uklanjanja onečišćenja i proizvodnja električne energije pri obradi procjednih voda mikrobnim gorivnim ćelijama s kemijskom katodom i aerobnom biokatodom

Jinfeng Hu, Longjun Xu, Qi Jing, Miao Xie* i *Duowen Qing*

Istraživan je utjecaj vrste katode na učinkovitost uklanjanja zagađivala i proizvodnju električne energije pri obradi procjedne vode samoorganizirajućim mikrobnim gorivnim ćelijama (MFC). Kada se procjedna voda s odlagališta obrađivala MFC-om s kemijskom katodom (CMFC) i aerobnom biokatodom (ABMFC), maksimalni izlazni naponi iznosili su 699,0 mV odnosno 459,4 mV, maksimalne izlazne snage 197,7 mW m^{-3} i 147,6 mW m^{-3}, a unutarnji otpori 900 Ω i 700 Ω. Nakon 45 dana rada gorivnih ćelija, kemijska potrošnja kisika za CMFC i ABMFC smanjena je za 56,5 % i 64,3 %, kulonska učinkovitost bila je 14,3 % i 17,1 %, a uklonjeno je 53,8 % odnosno 58,1 % amonijačnog dušika.

Ključne riječi
Mikrobna gorivna ćelija, ocjedne vode odlagališta, kemijska katoda, aerobna biokatoda, zbrinjavanje zagađivala, proizvodnja električne energije

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