Construction of an MFC Anaerobic-Aerobic Coupled Denitrification System and Its Performance Enhancement Method

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ABSTRACT

Compared with a microbial fuel cell (MFC) of single flora, the MFC of mixed flora provide much better denitrification and electricity generation performance. Therefore, in-depth analysis of the kinetic features such as the structures of various types of microflora in MFCs is of important theoretical and practical significance. There is little existing research on the electricity generation and pollutant removal process of cathode microorganisms and the functions of microfloral flora. To this end, this paper constructs an MFC anaerobic-aerobic coupled denitrification system and studies its performance enhancement method. First, the basic principle of MFC biological denitrification was expounded, the kinetics was introduced into the analysis of the reaction between the MFC microorganisms and pollutants, and the migration and transformation occurring in the reaction process and the mechanism of transformation speed changes were revealed. Then, the analysis and calculation methods for the electrochemical parameters and microbial diversity index in MFC were explained in detail, and the experimental results and analysis conclusions were given.

Keywords: MFC denitrification; anaerobic flora; aerobic flora; enhancement of electricity generation performance

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1. INTRODUCTION

A microbial fuel cell (MFC) is a electricity generation device that uses enzymes or microbial tissues as the catalyst to convert the chemical energy of fuel into electrical energy [1-7]. Thanks to its wide range of fuel sources, mild reaction conditions, and its cleanliness and environmentally friendliness, it has attracted widespread attention from scholars at home and abroad [8-15]. Studies have shown that microbial diversity in MFCs is closely related to its electricity generation efficiency. If different microbial populations that are helpful to the anaerobic treatment of sewage for electricity generation are mixed, the working potential and internal resistance of the MFC will change significantly, and the denitrification and electricity generation performance will also be greatly enhanced [16-20]. Therefore, in-depth analysis of the kinetic features such as the structures of various types of microflora in MFC is of great theoretical and practical significance.

In the continuous flow mode of wastewater treatment and electricity generation, Karra et al. [21] compared two flow modes (plug flow (PF) and complete mixing (CM)) of microbial fuel cells (MFCs) with multiple anode-cathode. The results show that PF MFC has higher electricity generation and Columbia efficiency (CE) than CM MFC, and the electricity generation varies with the flow path in PF MFC. The substrate concentration gradient along the PF MFC is the driving force for electricity generation. Comparatively, the wastewater removal efficiency of CM MFC is higher than that of PF MFC, but the power conversion efficiency and electricity generation are lower. This work demonstrates that the MFC configuration is a key factor to enhanced electricity generation and wastewater treatment. Mohan et al. [22] evaluated the performance of aerated and ferricyanide catholytes in bioelectricity generation in a dual-chamber microbial fuel cell (MFC) using a selectively enriched hydrogen-producing mixture as the anode inoculum. Two MFCs with aerated catholyte (MFCAC) and ferricyanide catholyte (MFCFC) were operated separately to clarify the differences in electricity generation potential and carbon removal efficiency under similar operating conditions. In order to better understand the effect of temperature, especially the response of biological nodes to temperature changes, Tkach et al. [23] studied the current mixed culture and pure culture MFC at two low temperatures (10°C and 5°C). The results show that the mixed culture MFCs consistently outperformed the pure culture MFCs at 10°C, but the electrogenic activity of the anodic bacteria was significantly reduced at a lower temperature of 5°C.

So far, research is mostly concentrated on the process of degradation of organic matters enriched at the MFC anode and electrode-active bacteria, while little has been done on the process of electricity generation and pollutant removal of cathode microorganisms and the functions of microbial flora. In order to further enhance the electricity generation performance of MFC, it is necessary to explore the kinetic features of the diverse microbial flora of MFC, and at the same time make up for the deficiency in the research on the kinetics of microbial fuel cells. To this end, this paper constructs an MFC anaerobic-aerobic coupled denitrification system and studies its performance enhancement method. Section 2 expounds the basic principle of MFC biological denitrification, introduces the kinetics into the analysis of the reaction between the MFC microorganisms and pollutants, and reveals the migration and transformation occurring in the reaction process and the mechanism of transformation speed changes. Section 3 explains in detail the analysis and calculation methods for the electrochemical parameters and microbial
diversity index in MFC and gives the experimental results and analysis conclusions.

2. BASIC PRINCIPLE OF MFC BIOLOGICAL DENITRIFICATION

Traditional biological denitrification technology has disadvantages in carbon-source-limited denitrification process, while MFC biological denitrification uses the microorganisms on the cathode electrode as a catalyst to directly receive the electrons transmitted from the external circuit for denitrification, which is more superior than the traditional technology. Figure 1 shows the schematic diagram of MFC denitrification.

![Diagram of MFC denitrification](image)

The anode and cathode reaction formulas of MFC biological denitrification are given below with glucose being the substrate as the electron donor and NO$_3^-$ as the electron acceptor. The anode reaction formula is:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

The cathode reaction formula is:

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad (2)$$

$$NO_2^- + e^- + 2H^+ \rightarrow NO + H_2O \quad (3)$$

$$NO + e^- + H^+ \rightarrow \frac{1}{2} NO + \frac{1}{2} H_2O \quad (4)$$

$$\frac{1}{2} N_2O + e^- + H^+ \rightarrow \frac{1}{2} N_2 + \frac{1}{2} H_2O \quad (5)$$

The traditional biological denitrification consists of two processes: nitrification and denitrification. The biological denitrification of MFC involves two forms: denitrification and simultaneous nitrification and denitrification. Considering that ammonia nitrogen is generally present in sewage, in order to reduce costs and improve the effect of MFC cathode denitrification, it is necessary to complete the nitrification of ammonia nitrogen to NO$_2$-N or NO$_3$-N before denitrification.

The following is the reaction formula of simultaneous nitrification and denitrification:

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO^+ + 2H^+ + H_2O \quad (6)$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO^- \quad (7)$$

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \quad (8)$$

3. KINETICS OF NITROGEN AND CARBON REMOVAL BY MFC ANAEROBIC + AEROBIC FLORA

The introduction of kinetics into the analysis of the reaction between MFC microorganisms and pollutants can better reveal the migration and transformation occurring in the reaction process and the mechanism of transformation speed changes. Since the concentration of NO$_3$-N is the core factor affecting the activity of denitrifying microorganisms, this study established the kinetic model of NO$_3$-N denitrification inhibition based on the results of a large number of comparative experiments, to explain the denitrification mechanism of anaerobic + aerobic bacteria in MFC under different NO$_3$-N concentrations.

3.1 Construction of the basic kinetic model

For the study of denitrification kinetics, a Monod model was established first in this paper to characterize the relationship between the microbial proliferation rate and the substrate concentration. Assuming that the maximum specific growth rate of microorganisms is represented by $v_{max}$, that the concentration of organic substrate $R$, that the saturation constant $L_r$, and that the specific growth rate of microorganisms $v$, the model is expressed as follows:

$$v = \frac{v_{max}R}{L_r + R} \quad (9)$$

This paper conducted a study of the specific degradation rate of organic substrate instead of the conventional study on microbial growth rate, in order to obtain a more visual result. Assuming that the microbial concentration is represented by $a$, that the specific degradation rate of the organic substrate $U$, and that the maximum specific degradation rate of the organic substrate $U_n$, there is:

$$v = \frac{da \cdot do}{a} = -B\frac{dr \cdot do}{a} \quad (10)$$

Let

$$-\frac{dr \cdot do}{a} = U \quad (11)$$

There are:

$$v_a = BU \quad (12)$$
The simulated sewage used for experiments in the laboratory is of ideally simple composition, so it can be considered that the degradation kinetics of MFC substrate is only related to the concentration of NO$_3$-N, which can be characterized by a power function kinetic model. Assuming that the substrate concentration at time t is denoted by $S_t$, that the initial concentration of the substrate $S_0$, and that the zero-order and first-order degradation rate constants $K_0$ and $K_1$, respectively, then based on the principle of power function kinetics, the zero-order reaction kinetic equation can be obtained as follows:

$$D_0 = D_0 - L_0 o$$

The first-order reaction kinetic equation is given as follows:

$$\ln D_o = \ln D_0 + L_1 o$$

When the first substrate does not self-inhibit, the Monod model can be used. To fit the denitrification reactions under different NO$_3$-N concentrations, the matrix inhibition kinetic model can be used. In order to explore the reason why excessively high concentration of NO$_3$-N could cause the decrease of microbial activity, the Haldane model and Han-Levenspiel model were introduced to simulate the kinetic behaviors of inhibition.

Suppose that the specific degradation rate is represented by $s$, that the maximum specific degradation rate $s_{max}$, that the half-saturation constant $L'_r$, that the mass concentration of the substrate $R$, that the Haldane inhibition constant $L_{If}$, that the complete inhibitory concentration $R_{n}$, and that the constants $n$ and $m$, respectively. The the Haldane model is expressed as follows:

$$s = \frac{s_{max} R}{L + R + \frac{R^2}{L_{If}}}$$

The Han-Levenspiel model is expressed as follows:

$$s = \frac{s_{max} R \left(1 - \frac{R}{R_{n}}\right)^n}{R + L'_r \left(1 - \frac{R}{R_{n}}\right)^m}$$

3.2 Selection of the degradation kinetic model

Compared with the Haldane model, the Han-Levenspiel model, if used for the anaerobic-aerobic flora coupled MFC, can achieve a higher correlation coefficient and lower fitting error, and better reflect the actual situation of the experiment. Therefore, the Han-Levenspiel model was selected in this paper to explore the change pattern of the denitrification rate of anaerobic-aerobic flora coupled MFC under different NO$_3$-N concentrations.

Based on the Han-Levenspiel model, the fitting equation obtained for the anaerobic flora MFC is as follows:

$$s_{AN} = \frac{9.12 (1 - \frac{r}{197.22})^{0.10}}{r + 58.71 (1 - \frac{r}{197.22})^{0.57}}$$

The fitting equation obtained for the anaerobic-aerobic flora coupled MFC is as follows:

$$s_{AN-AE} = \frac{24.51 (1 - \frac{r}{336.74})^{2.09}}{r + 17.36 (1 - \frac{r}{336.74})^{0.84}}$$

The concentration of COD in MFC can increase the removal rate of NO$_3$-N to a certain extent, but when the concentration of COD reaches a certain value, it will inhibit the increase of the removal rate. The main reason is that the excessively high COD concentration will lead to the decrease of microbial activity in MFC. Therefore, based on the choice of the kinetic model, the degradation performance of the COD concentration was analyzed.

Based on the Han-Levenspiel model, the fitting equation obtained by the anaerobic flora MFC is:

$$s_{AN} = \frac{6.13 (1 - \frac{r}{896.07})^{0.32}}{r + 814.25 (1 - \frac{r}{896.07})^{1.82}}$$

The fitting equation obtained for the anaerobic-aerobic flora coupled MFC is:

$$s_{AN-AE} = \frac{8.21 (1 - \frac{r}{921.67})^{0.28}}{r + 907.64 (1 - \frac{r}{921.67})^{1.84}}$$

4. CALCULATION OF EXPERIMENTAL PARAMETERS AND ANALYSIS OF RESULTS

4.1 Analysis and calculation of electrochemical parameters and microbial diversity index in MFC

The conventional indicators that need to be measured in this study include MFC output voltage and coulombic efficiency. At the same time, the MFC polarization curve and power density curve need to be drawn.

Record the voltage $U$ between the cathode and anode electrodes of the MFC and the external resistance value $R$, and then calculate the MFC output current value $I$ based on the following formula:

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

Change the external resistance value several times, and when the voltage becomes stable, record the corresponding MFC output voltage value and external resistance value. Assuming that the volume of the MFC anode chamber is represented by $F$, the formula for calculating the current density $DM$ is as follows:
\[ DM = \frac{U}{1000RF} \]  

(23)

The polarization curve of MFC can be drawn with DM as the x-axis and U as the y-axis. The following is the calculation formula of MFC power density GM:

\[ GM = VDM \]  

(24)

With DM as the x-axis and GM as the y-axis, the power density curve of the MFC can be drawn.

Suppose that the number of electrons transferred by metabolism per unit of chemical oxygen demand concentration is \( l \), that the electricity generation cycle of MFC \( O \), that the infinitely small time period \( do \), that the current in this time period \( I \), that the Faraday’s constant \( G \), that the difference between the concentration of chemical oxygen demand at the beginning and end of the cycle \( AGK \), and that the volume of the anode chamber \( F' \), then the Coulombic efficiency \( DP \) of the MFC can be calculated by the following formula:

\[ DP = \frac{\int Ido}{G \cdot AGK \cdot F'} \]  

(25)

**4.2 Experimental results and analysis**

In this paper, the MFC voltage trend charts were drawn, as shown in Figure 2, used to characterize the electricity generation of aerobic flora, anaerobic flora, and aerobic-anaerobic mixed flora MFC during the electricity generation process.

**Figure 2. MFC voltage change trends**

It can be seen from the figure that the electricity generation voltage of the aerobic flora MFC was the highest, and that the maximum voltage levels of the anaerobic flora and mixed flora MFC had little difference. The average maximum voltage values of aerobic flora, anaerobic flora, and mixed flora MFC were 0.19V, 0.13V, and 0.12V, respectively. Based on the variance calculation results, it can be seen that the voltage stability of aerobic and anaerobic flora MFCs was relatively close, but lower than that of the mixed flora MFC. The voltages of the three MFCs all enjoyed short plateau time and shared the same change trends - rising to the highest value and then falling. In order to improve the stability of electricity generation and achieve a longer maximum voltage duration, this paper further explored the reasons based on the MFC power density curve.
Figure 3 shows the MFC power density curves of aerobic flora, anaerobic flora, and aerobic-anaerobic mixed flora MFCs. The maximum power density and corresponding current density of aerobic flora MFC were 7.99W/m$^3$ and 52.64A/m$^3$, respectively, and the power density and corresponding maximum current density of anaerobic flora MFC were 0.36W/m$^3$ and 9.62A/m$^3$, respectively. Compared with the above two, the mixed flora MFC had a higher power density - the maximum current density and corresponding power density were 30.67A/m$^3$ and 9.07W/m$^3$ respectively. In order to improve the electricity generation performance of the MFC, an appropriate resistor can be used to help eliminate polarization and increase the output power density of the MFC.

Based on the average values of Chao1 index, Shannon index and Simpson index, the sparse analysis chart of the microbial diversity index was drawn, as shown in Figure 4. It can be seen that the microbial diversity index of the mixed flora MFC with a great variety of species was high, reaching about 8. The microbial diversity index of the MFC with relatively fewer species was low, reaching about 5.5. After the operation became stable, the microbial diversity of the mixed flora MFC (reaching about 7) was not much different from that of the anaerobic flora MFC.

Figure 5 shows the scatter plot of principal component analysis. From the principal component analysis of the microbial community, it can be seen that, after the operation became stable, the microbial species of the mixed flora MFC ($AN+AE2$) and those of the anaerobic flora MFC ($AN2$) were relatively close in terms of the distance between principal components 1, indicating that $AN+AE2$ and $AN2$ have a relatively close genetic relationship. After the operation became stable, the microbial species of the mixed flora MFC ($AN+AE1$) and the anaerobic flora MFC ($AN1$) were relatively far from each other in terms of the distance between principal components 1, indicating that $AN+AE1$ and $AN1$ have a relatively distant genetic relationship. This shows that different kinds of microorganisms were selected in the process of MFC electricity generation.
5. CONCLUSIONS

This paper constructed an MFC anaerobic-aerobic coupled denitrification system and studies its performance enhancement method. First, the basic principle of MFC biological denitrification was expounded, the kinetics was introduced into the analysis of the reaction between the MFC microorganisms and pollutants, and the migration and transformation occurring in the reaction process and the mechanism of transformation speed changes were revealed. Then, the analysis and calculation methods for the electrochemical parameters and microbial diversity index in MFC were explained in detail. Based on experiments, the MFC voltage trend charts and power density curves were drawn. It can be seen that, compared with the aerobic and anaerobic flora MFCs, the mixed flora MFC had a higher power density and higher voltage stability. The sparse analysis of the microbial diversity index was conducted, from which, it can be seen that the microbial diversity index of mixed flora MFC with abundant species was higher. The scatter plot of principal component analysis was given to verify the selection of different types of microorganisms in the process of MFC electricity generation. The species composition and relative abundance of the microbial community of the mixed flora were exhibited, which further verified that, after the operation of the mixed flora MFC became stable, the microbial community was more abundant in species and that the microbial diversity was significantly higher.


