Treatment of Simulated Wastewater by Bio-Cathode Microbial Fuel Cells at different C/N Ratio

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Abstract. The study combined the microbial fuel cells (MFC) technology with the carbon and nitrogen removal technology of sewage based on the principle of MFC, constructing and running a bio-cathode microbial fuel cells (BCMFC) which could remove the carbon and nitrogen of sewage and generate electricity at the same time. The results indicated that the BCMFC was able to deal with low C/N ratio and high ammonia concentration wastewater on the condition of continuous flow. When the BCMFC was operated at the C/N ratio of 4, 7, 10 and 13, the lower C/N ratio was, the better performance was. When the C/N ratio was 4, the BCMFC reached the maximum power density of 786mW/m3, the highest denitrification rate of 50.1 mg/(L.d) and removing of 1gN, consuming 6.99 g COD.

1. Introduction

The discharge of urban sewage is increasing, and the pollution of eutrophic elements, which are easily caused by nitrogen and phosphorus [1]. Although there are many biological nitrogen and phosphorus removal processes at present, many defects still remain, such as the contradiction of carbon source, the competition of bacteria group and the contradiction of mud age, which often restrict the effect of nitrogen and phosphorus removal process. By using graphite as the electrode material, Gregory and his team [2] confirmed that the Geobacter, contained in which microbial fuel cells (MFCs) can obtain electrons directly from the graphite electrode without hydrogen production and use the electron for the reduction of NO3-N and NO2-N. Clauwaert [3] and Virdis [4] reported MFC had the ability of simultaneous removal of carbon and nitrogen. Virdis's research results even proved that BCMFC (Bio-Cathode Microbial Fuel Cell) could effectively reduce the carbon source needed for nitrogen removal. Based on the preliminary experimental research, BCMFC removed carbon and nitrogen simultaneously to produce electricity [5]. This provides a new way of thinking for the removal of nitrogen from sewage. The wastewater treatment technology of BCMFC is not only the target for the discharge of sewage, but also the development and utilization of the sewage biomass energy, which makes the significance of this study more prominent [6,7].

2. Methods and Materials

2.1. Experimental device

The experimental device of this test is mainly composed of three systems (Figure 1): BCMFC system, nitrification system and data acquisition and monitoring system. The BCMFC system used the mixed bacteria in the anode to remove the current from the COD in the simulated wastewater. Nitrate
nitrogen was removed by denitrifying bacteria in the cathode of the nitrifying reactor. The nitrification system converted ammonia nitrogen from BCMFC anode effluent to nitrate nitrogen and supplied it to the cathode of BCMFC. The data acquisition and monitoring system monitored the voltage data of BCMFC in real time.

Fig.1 A schematic diagram of BCMFC device

2.2. Simulated wastewater
The operating temperature of BCMFC was controlled at 32 °C at constant temperature incubator, the pH value was adjusted to about 7.4, and the external resistance of BCMFC was 5 ohm. The nitrification reactor controlled DO concentration by 4mg/L and HRT was 48 h. The formula of simulated wastewater was: NaAC (0.9 g/L), NaHCO₃ (0.42 g/L), KCl (0.13 g/L), NaH₂PO₄·2H₂O (5.49 g/L), Na₂HPO₄ (2.75 g/L), MgSO₄·7H₂O (0.2 g/L). The carbon and nitrogen ratio of the traditional sewage treatment process was usually around 7 [4]. Therefore, the ratio of carbon and nitrogen to the water was set at four different C/N ratio levels: 4 (low), 7 (normal), 10 (high) and 13 (higher).

2.3. Measurement of water quality and power production
In this experiment, four parallel groups of BCMFC operation methods were used to measure the COD, nitrate nitrogen, ammonia nitrogen, nitrite nitrogen and electricity production of before and after treatment of the BCMFC.

3. Results

3.1. Carbon and nitrogen removal of BCMFC at different C/N ratios
In the case of different influent C/N ratios, the water quality parameters and carbon and nitrogen removal of each reactor were shown in Tables 1 and 2.

It was showed in Table 1 that, the removal rate of COD after BCMFC anode treatment at different carbon and nitrogen ratio was above 97.5%, which ensured that the carbon source used for denitrification could not be lost into the nitrification reactor. When the C / N ratio was 4, 7, 10, and 13, the nitrogen removal rate accounted for 14.6%, 12.8%, 22.7% and 24.5% of the total nitrogen removal rate respectively. In this process, the removal of ammonia was mainly composed of two parts: some were converted into nitrogen by the action of the anodic microorganism, and a small part was directly into the cathode through the membrane. When ammonia nitrogen was nitrifying reactor, it was basically converted to nitrate nitrogen, and in continuous operation, the content of nitrite nitrogen detected in water samples was very small, and no accumulation was found. This indicated that the operating conditions of the nitrification reactor were well controlled and suitable for nitrifying bacteria to complete the normal nitrification. In addition to the carbon and nitrogen ratio of 4, there was still
more nitrogen in the effluent of the BCMFC cathode, and the removal rate of total nitrogen was up to 90% under the other 3 C/N ratios (Table 2). It can be seen from the experimental results that the system built on the basis of BCMFC had the ability to remove carbon and denitrification under the condition of continuous flow, and achieve normal denitrification under low C/N ratio.

### Table 1 Water quality parameters of each reactor at different C/N ratio

| C/N ratios | WQP (mg/mL) | BCMFC Anode | Nitrification System | BCMFC Cathode |
|------------|-------------|-------------|----------------------|---------------|
|            | Inlet       | Outlet      | Inlet                | Outlet        |
| 4          | COD         | 700         | 16.6                 | 0             | 0             |
|            | NH4-N       | 175         | 160.4                | 11.4          | 4.6           |
|            | NO3-N       | 0           | 0                    | 114.7         | 68.2          |
|            | NO2-N       | 0           | 0                    | 2.4           | 2.1           |
| 7          | COD         | 700         | 13.8                 | 0             | 0             |
|            | NH4-N       | 100         | 78.4                 | 8.4           | 4.5           |
|            | NO3-N       | 0           | 0                    | 63.7          | 2.5           |
|            | NO2-N       | 0           | 0                    | 1.9           | 2.2           |
| 10         | COD         | 700         | 17.4                 | 0             | 0             |
|            | NH4-N       | 70          | 55.2                 | 4.9           | 2.7           |
|            | NO3-N       | 0           | 0                    | 48.7          | 1.7           |
|            | NO2-N       | 0           | 0                    | 1.5           | 0.5           |
| 13         | COD         | 700         | 11.7                 | 0             | 0             |
|            | NH4-N       | 54          | 41.5                 | 3.8           | 1.4           |
|            | NO3-N       | 0           | 0                    | 36.3          | 1.1           |
|            | NO2-N       | 0           | 0                    | 0.7           | 0.5           |

WQP water quality parameters

### Table 2 Carbon and nitrogen removal rates and actual C/N ratios

| C/N ratios | Carbon removal rate (%) | Nitrogen Removal of BCMFC Anode (mg/L) | Total Nitrogen Removal (mg/L/%) | ΔCOD/ΔNO3-N of BCMFC | Total ΔCOD/ΔNO3-N |
|------------|-------------------------|----------------------------------------|---------------------------------|----------------------|-------------------|
| 4          | 100%                    | 14.6                                   | 100.1/57.2                      | 9.15                 | 6.99              |
| 7          | 100%                    | 11.6                                   | 90.8/90.8                       | 11.44               | 7.71              |
| 10         | 100%                    | 14.8                                   | 65.1/93.0                       | 14.89               | 10.75             |
| 13         | 100%                    | 12.5                                   | 51.0/94.1                       | 19.89               | 13.73             |

3.2. The electric property of BCMFC under the condition of different C/N ratio

When the C / N ratio of water was 4, 7, 10 and 13, the open circuit voltage of BCMFC were 0.657V, 0.661V, 0.653V and 0.674V, respectively (Figure 2). When the C / N ratio was 4, the power generation performance of BCMFC was the best and the maximum output power density was 786mW/m³. With the increase of C/N ratio, the power generation performance decreased. When the C / N ratio was 13, the maximum output power density was 614 mW/m³ (Figure 3). By fitting the linear part of the polarization curve, the internal resistance of BCMFC under different C/N conditions were 53, 64, 73, and 78, respectively. The results of Liu and other’s [8] studies showed that when the ion concentration
was increased in the single chamber MFC, the conductivity of the solution could be increased, the internal resistance of the battery was reduced and the output power can be increased. The concentration of NH₄Cl in the water was different, making the ion concentration slightly different, which was one aspect of the difference of internal resistance. Another more important aspect was that the microbial structure and the electrochemical activity of bacteria were different under the conditions of different carbon and nitrogen ratio, which would directly influence the internal resistance of BCMFC, and then make it produce electricity. When the BCMFC external circuit was loaded with 5 Ohm load, the sampling frequency of the data acquisition card is set to 5 min. After the system is stable, the voltage data of different carbon and nitrogen ratio were measured in the 24 h (Figure 4). Voltage data were stable and fluctuating in operation.

![Fig.2 Polarization curves at different C/N ratios](image1)

![Fig.3 Power density at different C/N ratios](image2)
4. Conclusion
The BCMFC could remove the carbon and nitrogen of sewage and generate electricity at the same time. When the C/N ratio was 4, the BCMFC reached the maximum power density of 786mW/m3, the highest denitrification rate of 50.1 mg/(L.d) and removing of 1gN, consuming 6.99 g COD.

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