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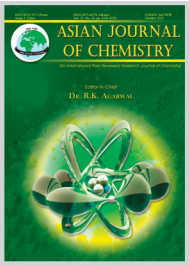

Effect of Nitrate on the Performance of a Single-Chamber Microbial Fuel Cell Equipped With a Titanium Based Lead-dioxide Cathode

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The biodegradation of nitrate in the wastewater was studied when using a single-chamber microbial fuel cell (SMFC) equipped with a titanium based lead-dioxide cathode. The results showed that the cell could readily degrade the nitrate, but high concentration nitrate would affect the electricity production of the cell. After raising the COD concentration in the single-chamber microbial fuel cell, the cell got good unity in dentrification and electricity production. Two different nitrate-treating methods(static and continuously feed system) were investigated respectively on the single-chamber microbial fuel cell's performance. The results demonstrated that the continuously feed system was better in both the electricity production and dentrification than the static system, which indicated the continuously feed system would more satisfy the need of practial application in denitrification treatment.

Key Words: Microbial fuel cell, Nitrate, Biodegradation, Electricity production, PbO_2 cathode.

INTRODUCTION

Recently nitrate's pollution has been very serious world-widely. In regard to water environment, the high nitrate concentration will lead eutrophication, arouse an algae explosion and make water body anoxia. The person who drinks the water with high nitrate concentration will be endangered greatly. Nitrate toxicity's function mechanism may be physiological complications due to hypoxic conditions that occur when the body converts nitrate to nitrite, which oxidizes ferrous iron in hemoglobin and forms methemoglobin, which doesn't transfer oxygenas eficiently[1].

Nitrate-rich wastewater is mainly generated by two processes: drainage of industrial waste water and the town sewage, which is so-called point source pollution; drainage of chemical fertilizer, agrochemicals and livestock excrement *etc.*, which is so-called local area source pollution. How to remove the nitrate pollution in the groundwater within a big area is a cosmopolitan difficulty. The chief shortcoming of current normal physical and chemical repair methods is their high energy consuming and poor efficiency.

Microbial fuel cell has been subjected to people's extensive concern because it can degrade organic substance in wastewater readily and generate the electric power at the same time. It probably ovecomes the weakness of high energy consuming technics in the application of current wastewater processing field. In recent years reports to the microbial fuel cell research can be seen in several aspects as follows: the nourishment carbon source which can be used in microbial fuel cells, including easily degraded organic substances[2-6]and refractory compounds[7,8]; electrode material and its improvement, including the catalyst material of cathode[9-12], microbial fuel cell's structure: construction and improvement, including microbial fuel cell with or without proton exchange membrane (PEM), dual-chamber microbial fuel cell and single-chamber microbial fuel cell[13-16], *etc.*

Recently people try to use microbial fuel cells in treating high concentration of nitrate wastewater and some research reports can be seen. Virdis *et al.*[17-19] carried out a research of removing the carbon and nitrogen at the same time in wastewater with microbial fuel cells.The resluts expressed the process was efficiently not only because of electricity generation during the denitrification process, but also lowering the aeration cost of the aerophile microbe consuming the organic carbon. They also studied the influence of cathode performance on the denitrification process. Morris *et al.*[11] used a microbial

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fuel cell with a steel cathode to enhance *in situ* of groundwater contaminated by nitrate and strengthen the denitrification process using the iron electrode to deliver electronics. Sukkasem *et al.*[20] studied the influence of nitrate on the air-cathode microbial fuel cell.

As it was seen from the above, some significant researches had been done in the removal of nitrate in wastewater with microbial fuel cells, but there were still many things to do in this field. In this study, we used a special single-chamber microbial fuel cell equipped with a titanium based lead-dioxide cathode to (a) improve the catalytic performance and to (b) determine the relation between the electricity generation and the biodegradation efficiency of this type of microbial fuel cell.

EXPERIMENTAL

Construction of single-chamber microbial fuel cell: The single-chamber microbial fuel cell was made of plexiglass and constructed by two parts. The upper part was a cathode chamber and the lower part was an anode chamber. The lower part was a cylindrical container with internal diameter 48 mm, height 25 cm and thus its volume was 603 mL. Two holes used as water outlet were punched from the side of the container for the purpose of measuring the effluent. The anode, made of pieces of carbon cloth with the surface area 64 cm^2, was placed in this container. The upper part was a open rectangular container with a volume of 947 mL, in which an aerating apparatus and a titanium based β-lead-dioxide cathode were placed. According to the literature[21], β-PbO_2 as a catalyst was better than Pt. Here we used a self-made titanium based β-PbO_2 cathode to ensure the high catalysis. The two containers were interlinked directly without diaphragm.The solution was phosphoric acid buffer mixed with nitrate. The two electrodes were linked to out resistors repectively through a copper wire and a data logger (ADC16; Pico Technologies limited, UK) was used to acqurie the single-chamber microbial fuel cell's voltage.

Microbial inoculum and medium: Anode and cathode compartments were inoculated with a microbial consortium. Anaerobic sludge was collected from Wangxiaoying Wastewater Treatment plant. Glucose was used as an energy source in a nutrient solution (pH = 7) containing (per liter of deionized water): KCl (0.13 g/L), NaH_2PO_4 (4.22 g/L), Na_2HPO_4 (2.75 g/L) and metal (12.5 mL) and vitamin (5 mL) solutions. And the biotic reactor had been fed with nutrient medium and operated for several days to allow the development of microbial community. All microbial fuel cells were operated at a fixed external resistance of 1000 Ω initially. COD concentration in the serial microbial fuel cells was 500 mg/L if not particularly indicated.

Chemical analysis and calculations: A subsample of each water sample was filtered (0.4 μm) and analyzed for nitrate-nitrogen (NO_3^-N) and nitrite-nitrogen (NO_2^-N), which was determined by using Nessler-agent and ultraviolet spectrophotometry. Voltage was continuously measured by a multimeter with a data acquisition system and converted to power according to P = iV, where P = power, i = current and V = voltage. Power was normalized by the total surface area of the cathode. COD concentration were measured according to standard methods. Total electron flow was calculated by summing the product of the time interval and the current passed through the circuit. Coulombic efficiency (CE) was calculated as $E_c = C_p \times 100\ \%/C_t$ based on COD reduction in each cell according to Liu and Logan[22].

RESULTS AND DISCUSSION

Nitrate degradation in open circuit system and closed circuit system single-chamber microbial fuel cell: Two single-chamber microbial fuel cells were constructed in order to study the effect of nitrate (100 mg/L) degradation in the wastewater. Each of them run for 120 h under the condition of the open circuit or closed circuit system, respectively. The data of nitrate in two devices was monitored every 24 h. After one day's operation, nitrate concentration in the closed cirtuit system was 44 mg/L and the value in the open circuit system was 90 mg/L (Fig. 1).

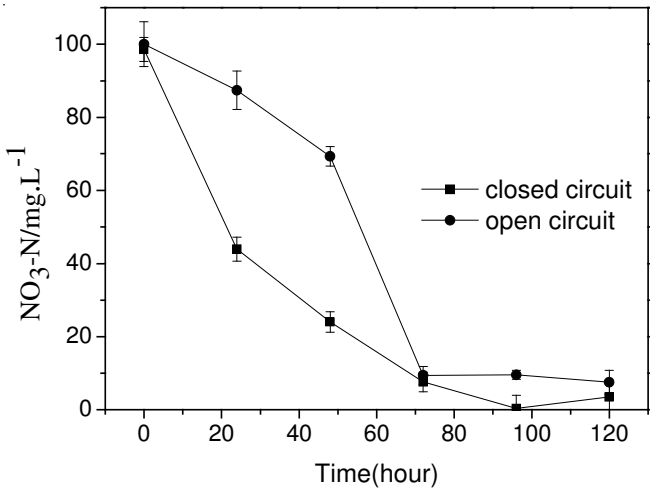

Fig. 1. Nitrate degradation in open circuit and closed circuit system of single-chamber microbial fuel cell

Two days later, nitrate concentration in the open circuit and closed circuit system was 24 and 70 mg/L, respectively; Nitrate concentration in the open circuit and closed circuit system was both about 10 mg/L after three days' operation, which had reached the standard of the United States Environmental Protection Agency (USEPA). The nitrate in the closed system was degraded completely after four days. The experiment results showed that the single-chamber microbial fuel cell can effectively degrade the high concentration of the nitrate in the wastewater whether in open circuit or closed circuit system. It also showed that electrochemical system played a large role within 72 h in the closed circuit system of microbial fuel cell.The degradation efficiency of the nitrate concentration of 100 mg/L reached 90% in three days,and the degradation velocity was about 38 mg/L/day in first 2 days.Nitrate in the open system was degraded to 10 mg/L 3 days later too, but its degradation velocity was only about 16 mg/L/day in first 2 days. It was obvious to see that the closed-circuit system microbial fuel cell had higher denitrification efficiency than that of the open-circuit system. This was due to the electrochemistry system in the closed cirduit single-chamber microbial fuel cell.

Effect of nitrate concentration on the electricity production and dentrification of single-chamber microbial fuel cell: The following test studied the situation of a closed circuit single-chamber microbial fuel cell system treating the wastewater with different nitrate concentration. Three single-chamber microbial fuel cells were constructed,in which the nitrate concentration in the wastewater was 0, 50 and 100 mg/L respectively.The electricity production curve and polarization curves were shown in Figs. 2 and 3.

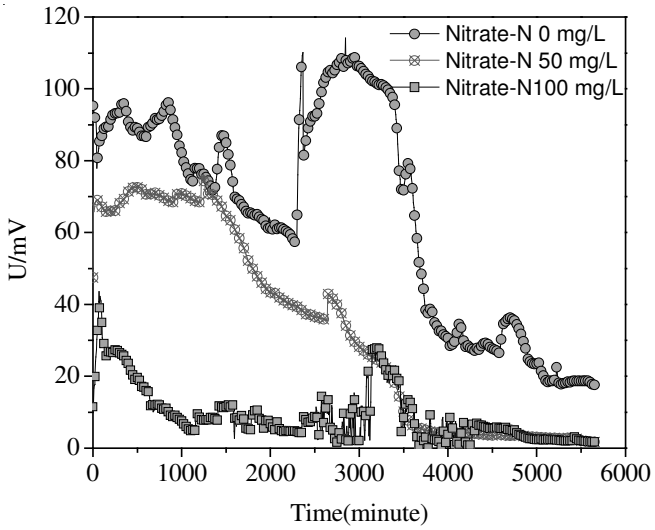

Fig. 2. Effect of nitrate concentration on the electricity production of single-chamber microbial fuel cell

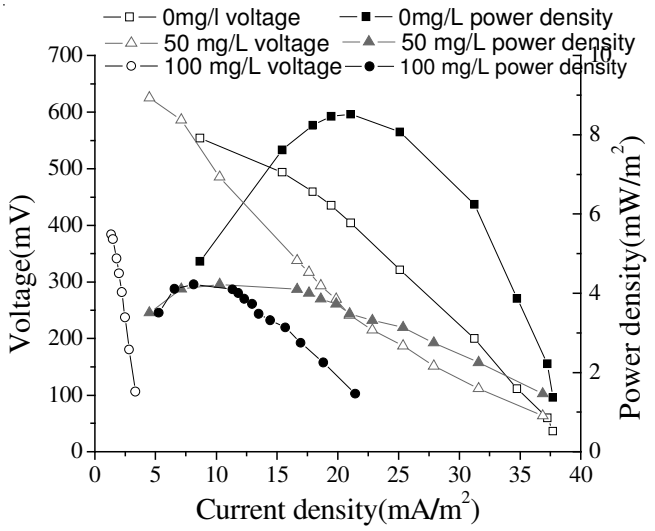

Fig. 3. Polarization curves generated by single-chamber microbial fuel cells treating different concentration nitrate

As shown in the graphs, the maximum output voltage of the single-chamber microbial fuel cell was 109 mv (0 mg/L), 73 mv (50 mg/L) and 28 mv (100 mg/L), respectively; the high power density of the single-chamber microbial fuel cell was 8.5 mW m^{-2} (0 mg/L), 4.2 W m^{-2} (50 mg/L), .2 mW m^{-2} (100 mg/L), respectively; the coulomb efficiency was 7.3 % (0 mg/L), 4.3 % (50 mg/L) and 1.1 % (100 mg/L), respectively. The results showed that the voltage with 0 mg/L nitrate was the highest, the voltage with 50 mg/L nitrate was higher, which meant that the single-chamber microbial fuel cell with certain nitrate concentration could operate in good condition. It was also found that the voltage in the single-chamber microbial fuel cell with 100 mg/L nitrate circumstance dropped quickly. Comparing the current density data of the three single-chamber microbial fuel cell, we found that the power density in the system of single-chamber microbial fuel cell without nitrate was greater than that containing nitrate. From the above,we could deduce that the higher nitrate circumstances had a great effect on the electricity production of single-chamber microbial fuel cell. The reseaon may be the different C/N ratio in these single-chamber microbial fuel cells.

Effect of COD concentration on the electricity production of single-chamber microbial fuel cell in processing wastewater with high nitrate concentration: The test above showed that when nitrate concentration was 100 mg/L and COD was 500 mg/L, each of the output voltage, the power density and the coulomb efficiency was very low. In order to study whether microbial fuel cell could be used to degrade high concentration of nitrate in wastewater, the amount of COD in solution was adjusted. When it was increased to 1600 mg/L, nitrate concentration remained 100 mg/L, the electricity generation curve and the polarization curve were shown in Figs. 4 and 5.

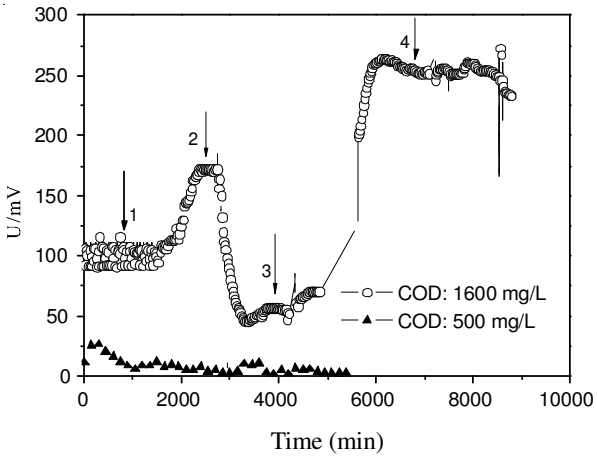

Fig. 4. Voltage-time curve of single-chamber microbial fuel cell with different COD concentration

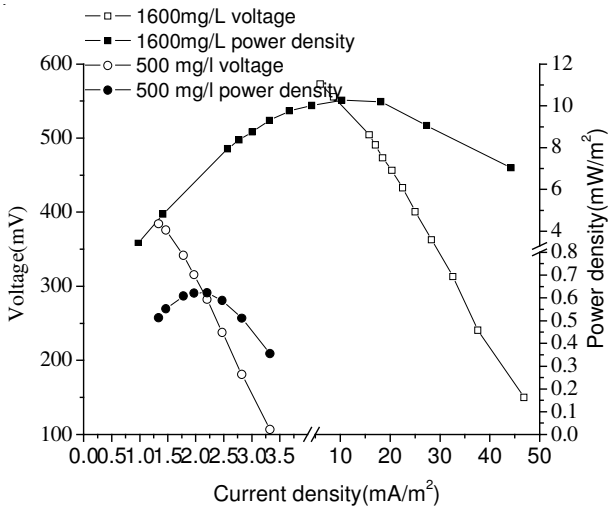

Fig. 5. Polarization curves of single-chamber microbial fuel cell with different COD concentration

The results showed that the cell was in good condition, the external output voltage was significantly increased and the coulomb efficiency of the battery reached 7.1 % (the value was 1.1 % when COD concentration was 500 mg/L). From the electricity generation curve of battery with COD of 1600 mg/L, four platforms segment could be observed. The first platform was from the reaction begining to about 1730 min, while the degradation of nitrate, the microbial fuel cell output voltage was smooth with the value of 115 mv; The second platform was from 2298 min to about 2749 min, microbial fuel cell's producing electrical properties had been improved, the output voltage reached 173 mv. The third platform was from 3363 min and continued until about 4786 min, the output voltage was 56 mv. At this stage, the lower external output voltage of the system was because of the continuous degradation of the nitrate in the system. The fourth platform started from about 6136 min when nitrate in the system had been completely degraded. At this stage the single-chamber microbial fuel cell was in better running condition after going through denitrification and the output voltage was about 265 mv or so. The results domenstrated that the single-chamber microbial fuel cell device we used in the experiment could be used well in the nitrate degradation treatment of wastewater if the C/N rate was improved a bit.

Effect of a static system and a continuously fed system on single-chamber microbial fuel cell' s dentrification and electricity production performance: Considering that it was needed to operate continuously when treating wastewater, two single-chamber microbial fuel cells were constructed to investigate the performance of degrading nitrate. Buffer solution containing nitrate was put into microbial fuel cell one time, which was called the static microbial fuel cell; buffer solution containing nitrate was pumped to microbial fuel cell continuously at a certain rate through the bottom of the reactor by a peristaltic pump,which was called the continuously fed microbial fuel cell.

Effect of a static microbial fuel cell and a continuously fed microbial fuel cell on single-chamber microbial fuel cell' s dentrification performance: Two single-chamber microbial fuel cells were constructed (COD 500 mg/L, nitrate 90 mg/L) and operated in the manner as described above. The curves of nitrate and nitrite degradation were shown in Figs. 6 and 7.

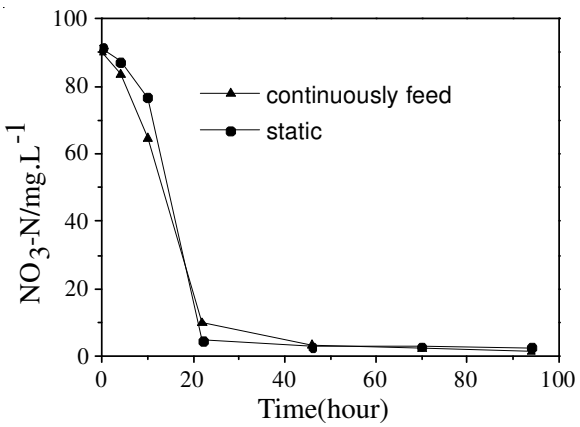

Fig. 6. Nitrate degradation curves of a static single-chamber microbial fuel cell and a continuously feed single-chamber microbial fuel cell

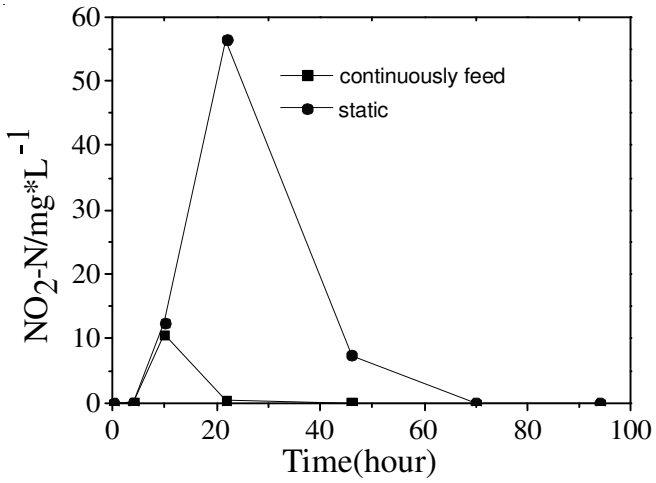

Fig. 7. Nitrite degradation curves of a static single-chamber microbial fuel cell and a continuously fed single-chamber microbial fuel cell

Fig. 6 showed that degradation of nitrate was not affected by the operation methods of microbial fuel cell. Nitrate decreased from 90 mg/L to 10 mg/L in 20 h and decreased completely in 100 h, which showed that microbial fuel cell could degrade nitrate quickly. Fig. 7 showed that there was large difference in the degradation of nitrite between the two single-chamber microbial fuel cells. The amount of accumulation of nitrite in static microbial fuel cell reached 60 mg/L in 24 h and nitrite was degraded completely in 70 h. However, the amount of accumulation of nitrite in the continously fed single-chamber microbial fuel cell only reached 10 mg/L in 10 h and nitrite was degraded completely in 20 h. The results showed that the continously fed microbial fuel cell could rapidly degrade nitrate and nitrite, which was more suitable for nitrate wastewater treatment practicaly.

Effect of a static system and a continuously feed system on single-chamber microbial fuel cell's electricity production performance: The output voltage performance of single-chamber microbial fuel cell under static and continously feed condition was greatly affected by the operation methods of single-chamber microbial fuel cell. Figs. 8 and 9 were curves of voltage and power density of the two cells. Fig. 8 showed

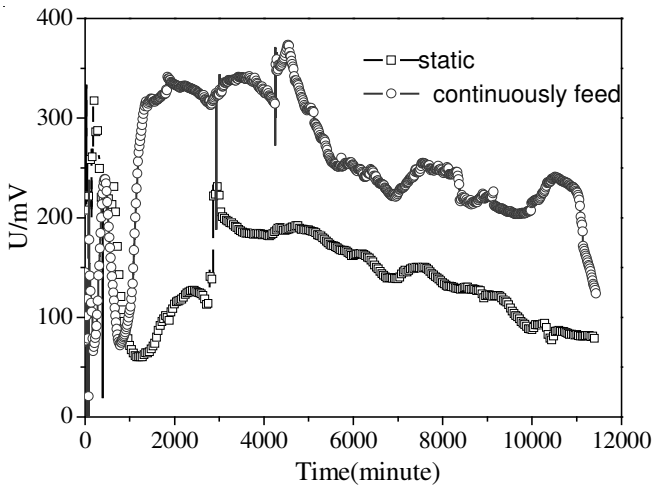

Fig. 8. Voltage-time curves of a static single-chamber microbial fuel cell and a continuously feed single-chamber microbial fuel cell

that the continuously feed cell obtained maximum voltage 375 mV, but value in the static microbial fuel cell was only 232 mV. There was great different in coulombic efficiency between the continuously feed cell (34.5 %) and the static microbial fuel cell (15.5 %) (Fig. 9).

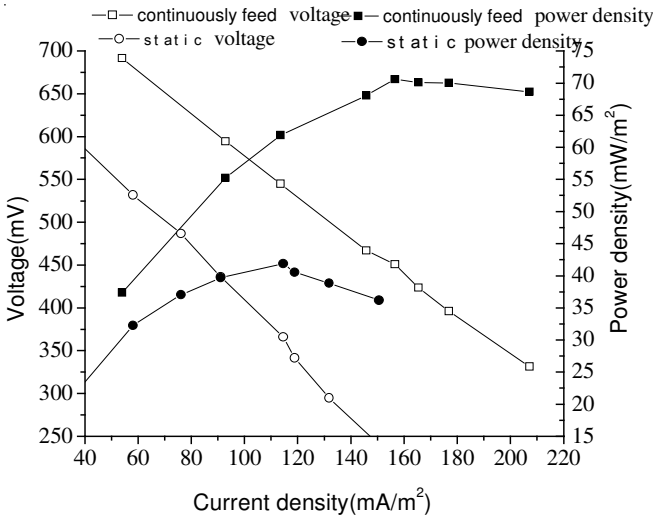

Fig. 9. Polarization curves of a static single-chamber microbial fuel cell and a continuously feed single-chamber microbial fuel cell

It was unrealistic to operate in static manner when treating wastewater practicaly because the amount of carbon source may not be calculated accurately. The results showed that the continuously feed single-chamber microbial fuel cell with higher denitrify efficiency and higher output voltage performance was more operable for practical applications. It provided theoretical basis for treating nitrate wastewater by microbial fuel cell.

Conclusion

Results from this study indicated that single-chamber microbial fuel cell can degrade nitrate of wastewater both in open circuit and closed circuit and closed circuit system had much rapidly dentrification rate if supplied by enough carbon resource. High nitrate concentration in the wastewater affected the electricity generation performance of single-chamber microbial fuel cell with the COD concentration of 500 mg/L, the power output decreaed below 10 mV. Increasing the COD concentration can ovecome the shortcoming. Results also showed that the cell got good unity between dentrification and electricity production when COD concentration was increased to 1600 mg/L in the single-chamber microbial fuel cell. Both a static system and a continuously feed system can degrade nitrate in the wastewater readily, but the continuously feed system removed the nitrite more rapidly than the static system. The continuously feed system also had better electricity generation performance, which was more suitable for practical nitrate wastewater treatment.

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