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Effects of ammonium ions from the anolyte within bio-cathode microbial fuel cells on nitrate reduction and current density

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ABSTRACT

This study was to determine the effects of the ammonium ion in the anolyte of the two-chamber bio-cathode MFC, which uses nitrate ions as the final electron acceptor, on the nitrate reduction and the current density. The ammonium nitrogen mass transfer coefficient was 3×10^{-6} cm/s and the diffusivity was 6×10^{-8} cm^2/s through Nafion 117 under abiotic conditions, with the circuit disconnected. When the TCBC-MFC was operated at 96.6 ± 11.2 mg/L of $SCOD_{cr}$ in the anode chamber and 37.9 ± 2.8 mg/L of nitrate nitrogen in the cathode chamber at an external resistance 100 Ω, the analytical denitrification rate was being 7.89 ± 0.78 g/m^3 d in the presence of ammonium ions and 3.07 ± 0.26 g/m^3 d in the absence of ammonium ions. The current density was 176.1 ± 31.7 mA/m^2 when NH_4^+-N was present in the anolyte and 28.2 ± 19.4 mA/m^2 without NH_4^+-N. Thus, it was determined that the ammonium ions in the anolyte were promoted electron movement, which increased the denitrification rate to twice that in the ammonium-free system.

1. Introduction

Nitrogen removal methods are typically classified as either abiotic or biological. Some abiotic methods that are commonly used to remove nitrates from water are reverse osmosis, ion-exchange, electroadsorption, and nanofiltration (Schoeman and Steyn, 2003; Han and Chang, 2013). However, these methods suffer from various drawbacks such as the production of brine or other by-products (Ghafari et al., 2008). Biological methods can be employed to reduce nitrates to nitrogen gas by using heterotrophic and autotrophic denitrifiers. Heterotrophic denitrification is a removal method that combines biological nitrification and denitrification, with organic carbon as an electron donor, while autotrophic denitrification utilizes hydrogen and sulfur as electron donors (Chang et al., 1999; Zhao et al., 2011). Moreover, autotrophic denitrification using bio-electrochemical systems has recently been studied (Park et al., 2005; Jeremiasse et al., 2010).

Microbial fuel cells (MFCs) have recently been employed as a novel technology for wastewater treatment since they are capable of removing organic matter and generating electrical power (Logan et al., 2006). Furthermore, many researchers have developed MFCs for nitrogen removal and recovery (Gregory et al., 2004; Oh and Logan, 2005; Heijne et al., 2010; Fang et al., 2011).

Clauwaert et al. (2007) initially examined the simultaneous removal of an organic substrate, power production, and denitrification by using an MFC without relying on the formation of H_2 or an external power source, under the assumption of the conversion of NH_4^+-N into NO_3^--N. Modified processes for the total removal of organic substrates and nitrogen in wastewater based on bio-cathode MFCs have been previously reported. Virdis et al. (2008) demonstrated the operation of a bio-cathode MFC using a separate nitrification tank, while Zhang and He (2012) attempted to integrate the nitrification and denitrification processes within a single MFC by using two aerobic and anoxic cathodes.

During wastewater treatment with MFCs, NH_4^+-N within the wastewater diffuses through the membrane and reaches the cathode chamber (Logan, 1999), subsequently maintaining the charge balance (Rozendal et al., 2006). When the wastewater was treated with the two-chamber MFC, the ammonium ions were detected in higher concentrations within the cathode effluent as a result of the movement of these ions (Virdis et al., 2008). Previous studies involving the loss of ammonium ions in single- and two-chamber MFCs reported that the ammonium transport rate increased as the generation of electricity increased, and that the NH_4^+-N was not necessary for the production of electricity (Kim et al., 2008).

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The aim of this investigation was to determine the effects of the ammonium ion in the anolyte of the two-chamber bio-cathode MFC (TCBC-MFC), which uses nitrate ions as the final electron acceptor, on the nitrate reduction and the current density.

2. Materials and methods

2.1. TCBC-MFC setup and operation

In this study, a two-chamber bio-cathode MFC (TCBC-MFC) was constructed using a bench-scale reactor to remove the organic matter and nitrate ions in the wastewater. The organic matter was removed in the bio-anode chamber, and the nitrate ions were removed as N_2 gas in the bio-cathode chamber.

The TCBC-MFC was constructed from acryl, with a working volume of 360 mL ($6 \times 6 \times 10$ cm^3) for the anode and cathode chambers. The anode and cathode electrodes were made of graphite felt with an area of 36 cm^2 (6×6 cm^2) each. The electrodes and each of the reactors were divided by Nafion 117 (DuPont, USA) membranes (separator). The electrodes were pretreated by following the procedures described by Chae et al. (2008). Graphite felts were immersed in 100% ethanol for 30 min. The electrodes were successively washed with 1 M HCl and 1 M NaOH for 60 min. Nafion 117 was boiled in H_2O_2 (30% v/v), soaked sequentially with deionized water, 0.5 M H_2SO_4, and deionized water, each for 60 min. The electrodes and separator were stored in distilled water, as described by Liu and Logan (2004).

To attach microorganisms on the surface of each electrode in the TCBC-MFC, the return sludge to achieve inoculum was obtained from the Dea-jeon city municipal wastewater treatment plant in Korea. After mixing the synthetic wastewater and microorganisms, inoculums were injected into each reactor. The chambers were stirred to attach the inoculums to the electrode surface. The substrates were replaced periodically. The suspended sludge was removed from the TCBC-MFC after two weeks. The external resistance (R_{ext}) was 1000 Ω during the microbial enrichment step and decreased 100–5 Ω.

The synthetic wastewater was prepared from M9 medium and a trace element solution, as described by Clauwaert et al. (2007), and Rabaey and Verstraete (2005). The M9 medium comprised 4.4 g/L KH_2PO_4, 3.4 g/L K_2HPO_4, 2.0 g/L $NaHCO_3$, 0.5 g/L NaCl, 0.2 g/L $MgSO_4$, and 0.0146 g/L $CaCl_2$. The trace element solution comprised 1 g $FeSO_4 \cdot 7H_2O$, 0.07 g $ZnCl_2$, 0.1 g $MnCl_2 \cdot 4H_2O$, 0.006 g H_3BO_3, and 0.002 g $CaCl_2 \cdot 6H_2O$ per 1 L deionized water, which was added to 1 mL of the M9 medium.

$SCOD_{cr}$ was 96.6 ± 11.2 mg/L using glucose in the anode-fed solution, and the nitrate nitrogen concentration was 37.9 ± 2.8 mg/L as the final electron acceptor using KNO_3 in the cathode-fed solution. The pH of the influent was 7.31 ± 0.1 and 7.28 ± 0.13 in the anolyte and catholyte, respectively, during the operation; conductivity was not measured. To evaluate the effects of ammonium ions in the anolyte, ammonium was only fed into mode 1 at a concentration of 39.0 ± 2.2 mg/L NH_4^+-N. The two TCBC-MFCs were operated as the batch type, and all the fed solutions were changed by monitoring the cell voltages. Lab-scale reactors were installed in the incubator, and the operating temperature of the incubator was 20 °C.

The anode and the cathode electrodes were connected by a wire and a fixed external resistance. The voltage (V) from the TCBC-MFC was measured every 10 min by a multimeter (model 2700, Keithley, USA). The current (I) was calculated using the equation $I = V/R$, using the measured average voltage (V) for each batch and a fixed external resistance (R). Coulombic efficiency (C_E) was calculated as previously described by Oh et al. (2004). The current density (mA/m^2) was calculated using I/A, where A is the electrode surface area.

Influent wastewater was collected at the first batch time, and effluent was collected at the final batch time in the anode and cathode chambers, respectively. The chemical analysis of samples was carried out after filtering using a 0.45 μm syringe membrane filter. The concentrations of $SCOD_{cr}$, NH_4^+-N, NO_2^--N, and NO_3^--N in the influent and effluent were analyzed using the Humas kit (Humas Ltd., Korea), and the pH was measured using HM-31P (TOADK, Japan).

2.2. Batch test for analysis of ammonium mass transfer

To evaluate the behavior of the ammonium ions, the TCBC-MFC reactor was operated under abiotic conditions without microorganisms on the anode and cathode electrode surfaces, with the circuit disconnected. Nafion 117 was used as the separator. The standard thickness of the used Nafion 117 was 0.019 cm (Kim et al., 2007).

The anode-fed solution was prepared by mixing 34.6 mg/L NH_4^+-N with 100 mM phosphate buffer, and the cathode was filled with only 100 mM phosphate buffer. The ammonium mass transfer was evaluated by monitoring the NH_4^+-N concentration and pH in the anode and cathode chambers for 89 h.

2.3. Calculations

The chemical flux through the membrane was calculated in terms of the mass transfer coefficient, K_{Cm}. For chemicals that cannot be maintained at a constant concentration in one of the chambers, the calculation was slightly different. The mass transfer coefficient is shown in Eq. (1) (Kim et al., 2007):

$$K_{Cm} = -\frac{V}{2A_m t}\ln\left[C^*\right] \quad (1)$$

$$C^* = \frac{\left(C_{An,0} - 2C_{Cat,(t)}\right)}{C_{An,0}} \quad (2)$$

where V is the volume of the liquid in the anode chamber, A_m is the membrane cross-sectional area, $C_{An,0}$ is the initial ammonium concentration in the anode chamber, and $C_{Cat,(t)}$ is the ammonium concentration in the cathode chamber at time t.

Slope can be obtained from the relationship of $\ln C^*$ and t, K_{Cm} is determined using Eq. (3).

$$\ln C^* = -\frac{-2A_m K_{Cm}}{V} t \quad (3)$$

The chemical diffusivity inside the membrane, D_{Cm}, can be calculated from the membrane thickness (δm), as shown in Eq. (4):

$$D_{Cm} = K_{Cm}\,\delta m \quad (4)$$

According to Clauwaert et al. (2007), the theoretical denitrification rate (T-DNR) could be expressed when complete denitrification occurred, using the following equation:

$$\mathrm{T-DNR}\left(\mathrm{kg\,N/m^3/d}\right) = \frac{IM}{Fn}\frac{86400(\mathrm{s/d})}{1000(\mathrm{g/kg})} = 2.507 \times 10^{-3} \times I \quad (5)$$

where I is the volumetric current density (A/m^3), M is the molar mass of nitrogen (14 gN/mol), F is the Faraday constant (96,485 C/mol), and n is the number of moles of electrons exchanged for every mole of nitrate that was reduced (5 for complete denitrification).