

Effect of Ammonium and Nitrate on Current Generation Using Dual-Cathode Microbial Fuel Cells

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These studies were conducted to determine the effects of various concentrations of ammonium and nitrate on current generation using dual-cathode microbial fuel cells (MFCs). Current generation was not affected by ammonium up to 51.8±0.0 mg/l, whereas 103.5±0.0 mg/l ammonium chloride reduced the current slightly. On the other hand, when 60.0±0.0 and 123.3±0.1 mg/l nitrate were supplied, the current was decreased from 10.23±0.07 mA to 3.20±0.24 and 0.20±0.01 mA, respectively. Nitrate did not seem to serve as a fuel for current generation in these studies. At this time, COD and nitrate removal were increased except at 123±0.1 mg NO₃⁻/l. These results show that proper management of ammonium and nitrate is very important for increasing the current in a microbial fuel cell.

Keywords: Dual-cathode microbial fuel cell, electron acceptor, electricity, ammonium, nitrate

Microbial fuel cells (MFCs) are an innovative wastewater treatment technology for removing reduced compounds from wastewater with electricity generation [3, 5, 6, 7, 12]. In the anode compartment of MFCs, electrons produced from reduced electron donors by microorganisms including electrochemically active bacteria are transferred through an external circuit to the cathode compartment where they are consumed, reducing electron acceptors, typically oxygen with protons. In this process, wastewater is treated and electricity is generated. Therefore, MFCs can be used as an alternative energy device as well as a wastewater disposal process. Recently, current and power densities of MFCs were improved considerably through various studies involving scale-up and optimization in order to commercialize this

technology. However, not many studies have focused on the treatment of wastewater containing carbonaceous and nitrogenous compounds such as animal waste from livestock farming. Carbonaceous and nitrogenous compounds can be effectively removed in conventional wastewater treatment plants. Nitrogenous compounds can be removed through sequential aerobic-anoxic processes. However, these processes require elaborate controls and high-energy consumption. Nitrate reduction in the cathode compartment has been known to occur, but few studies have been conducted on the behavior of ammonium and nitrate in the MFC anode compartment. The objective of this research was to evaluate the effective treatment of and current generation by ammonium- and nitrate-containing wastewater using dual-cathode microbial fuel cells. MFCs with dual cathodes operated over 3 years after being enriched with artificial wastewater (AWW) using acetate were used in this study. Graphite felt with a size of 25×25×20 mm (GF series; Electrosynthesis, Amherst, NY, USA) was used for both electrodes (Fig. 1).

The graphite felt was coated with platinum (0.5 mg Pt/C/m² surface area) to use as the cathode, according to a previously described method [5]. The proton-exchange membrane was cleaned by immersing in boiling 3% hydrogen peroxide in water for 1 h, and then in boiling sulfuric acid for another hour, to ensure protonation of the sulfonate groups. The membrane was then rinsed in boiling deionized water for 1 h to remove any remaining acid [11]. Platinum wire (0.5 mm thickness) was used to connect the electrodes and the electronic ports. The anode and cathode were connected to a voltmeter (Keithley Instruments Inc., Cleveland, OH, USA) via a resistance (R_{load}) of 10 W throughout the study to monitor the current under closed circuit conditions. The current (I) was calculated according to Ohm's law, $I = V/R_{load}$, where V is the potential drop across R_{load} . AWW was fed through the injection port of

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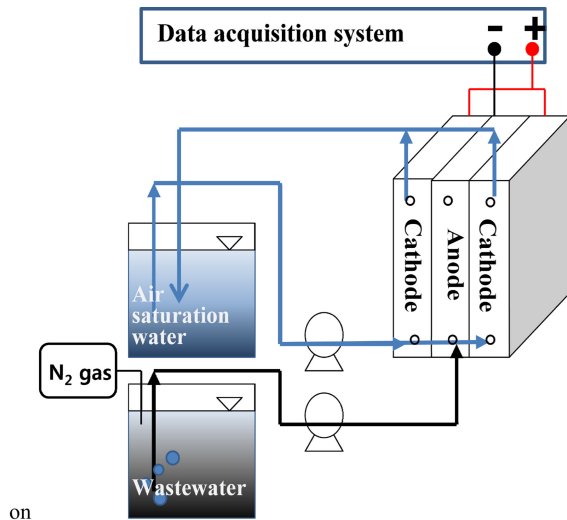


Fig. 1. Schematic illustration of the microbial fuel cell process.

the anode compartment at a rate of around 0.24 ml/min using a peristaltic pump (505S; Watson-Marlow, Falmouth, Cornwall, UK) equipped with Marprene II tubing (Watson-Marlow). A peristaltic pump (505S; Watson-Marlow) was used to recycle air-saturated tap water from a reservoir to the cathode compartment as the oxidant at a flow-rate of 15 ml/min. The MFCs were installed in a temperature-controlled chamber at 30°C. The potential was measured using a voltmeter and recorded every 5 min to a personal computer through a data acquisition system (Won-A Tech Co., Seoul, Korea). AWW containing 250 mg/l COD, phosphate buffer, salt solution and trace minerals was prepared as previously described [5]. The AWW was added with potassium nitrate or ammonium chloride at a concentration of 0–120 mg/l. The COD_{Cr} was determined by standard methods using chromate as the oxidant [1]. Nitrogen species [NH₃⁺, NO₃⁻, and total nitrogen (TN)] were measured using an HACH kit as follows: Nessler reagent set (NH₃⁺); Test 'N Tube, HR, NitroVer X Test 'N Tube reagent set (NO₃⁻); Test 'N Tube, HR Total nitrogen acid solution reagent set (TN). The coulomb efficiency was calculated as follows: (observed current/theoretical current) × 100(%), where the theoretical current was calculated based on the COD consumption rate using the equation 1 mg COD/sec = 12 C/sec = 12 A. All experiments were conducted in triplicate and mean values are presented. In order to evaluate the effect of ammonium and nitrate on current generation, AWW containing 0–120 mg/l NH₃Cl (1.0±0.0, 27.0±0.1, 51.8±0.0, and 103.5±0.0 mg/l) and KNO₃ (1.0±0.0, 31.4±0.4, 60.0±0.0, and 123.3±0.1 mg/l) was fed to the anode when MFCs generated a stable current. When NH₄Cl was fed to the anode compartment, there was no change in the current value compared with that of the control until an ammonium (NH₃⁺) concentration of

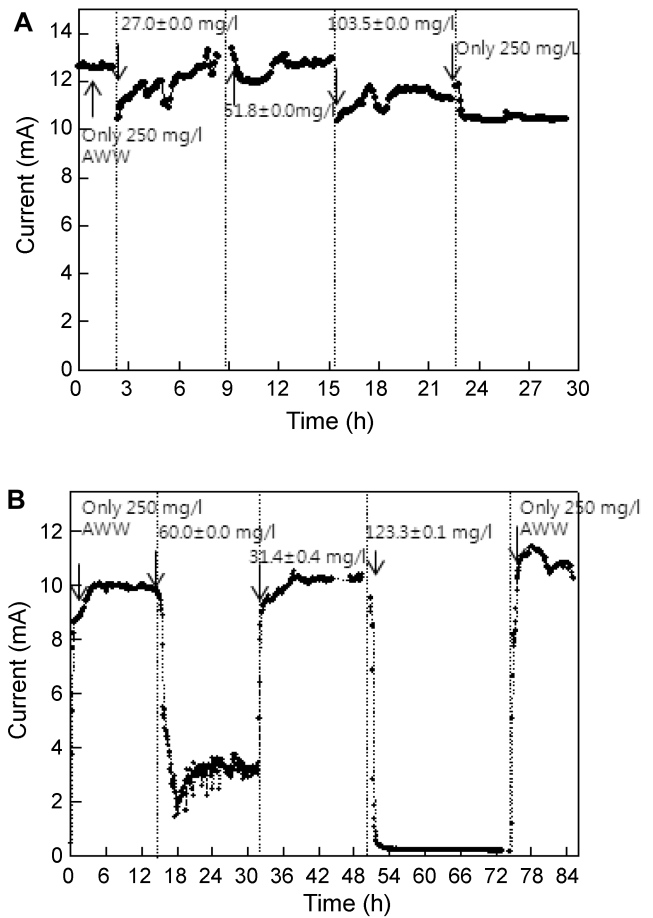


Fig. 2. Effect of ammonium and nitrate concentration on current generation using a dual-cathode MFC.

Fig. 2(B) was cited from abstract no. 110771 of 2011 ASABE.

51.8±0.0 mg/l. However, with 103.5±0.0 mg/l NH₄Cl, the current was slightly decreased to 11.40±0.14 mA from 12.57±0.11 mA (Fig. 2A).

When the control AWW was fed after 103.5±0.0 mg/l ammonium chloride, the current was slightly decreased from the initial value. This result showed that a low ammonium concentration did not influence current generation, but MFC performance was affected by a high ammonium concentration. He *et al.* [4] reported that the peak current increased with an increasing amount of ammonium up to 62.3 mM ammonium chloride, suggesting that ammonium was involved in electricity generation either directly as the anodic fuel or indirectly as a substrate for nitrifiers to produce organic compounds for heterotrophs acclimated to ammonium. However, Nam *et al.* [9] reported that MFC current generation was significantly inhibited by an initial total ammonia nitrogen concentration of over 500 mg-N/l, similar to our results. These findings seem to indicate that an ammonia-oxidizing bacterial consortium in an MFC must be well built and domesticated to ammonia nitrogen conditions. The result mentioned by Kim *et al.* [10], in

Table 1. Nitrate and COD removal and current generation in dual-cathode microbial fuel cells (MFCs).

Conditions		NO ₃ ⁻ (mg/l) (Removal %)	NO ₂ ⁻ (mg/l)	NH ₄ ⁺ (mg/l)	TN (mg/l)	COD removal (%)	Current (mA)
AWW + w/o NO ₃ ⁻	Influent	1.00±0.00	0.01±0.00	1.04±0.01	2.05±0.00	42	9.08±0.11
	Effluent	0.65±0.07 (35%)	0.01±0.01	0.08±0.01	0.74±0.00		
AWW + 31.4±0.4 mg NO ₃ ⁻ /l	Influent	31.35±0.40	11.06±0.00	0.59±0.00	43.00±0.00	77	8.68±0.22
	Effluent	2.10±0.00 (93%)	0.01±0.00	0.03±0.01	2.14±0.00		
AWW + 60.0±0.0 mg NO ₃ ⁻ /l	Influent	60.00±0.00	23.92±0.00	0.58±0.01	84.50±3.54	94	2.51±0.17
	Effluent	1.95±0.07 (97%)	0.01±0.00	0.08±0.01	2.04±0.00		
AWW + 123.3±0.1 mg NO ₃ ⁻ /l	Influent	123.25±0.07	28.65±0.00	0.60±0.02	152.42±0.00	96	0.16±0.02
	Effluent	44.75±0.07 (64%)	0.02±0.01	0.18±0.010	44.95±0.00		

which adapted electrical performance can affect power density, may be a basis for this hypothesis. Fig. 2B shows the current generated by MFCs fed with AWW containing KNO₃ at a concentration of 0–120 mg/l. The nitrate concentration in the anode effluent was reduced by up to 97% when 60.0 ± 0.0 mg/l nitrate was fed. Moreover, when AWW containing 60.0±0.0 and 123.3±0.0 mg/l nitrate was supplied, COD removal was 80% and 96%, respectively, which was much higher than that from the control AWW (41%). However, although COD removal and nitrate reduction were increased, the current changed from 9.08±0.11 mA to 8.68±0.22, 2.51±0.17 and 0.16±0.02 mA when AWW containing 1.0±0.0, 31.4±0.4, 60.0±0.0, and 123.3±0.1 mg NO₃⁻/l was supplied, respectively. Unlike ammonium, nitrate at concentrations of 60.0±0.0 and 123.3±0.1 mg/l inhibited current generation severely. This result is similar to that of Chang *et al.* [2], in which current generation was decreased depending on the nitrate concentration owing to its effects as an alternative electron acceptor. The electrons from metabolic pathways (NO₃⁻ → NO₂⁻ → NH₄⁺ → NO → N₂O → N₂) are consumed, reducing nitrate and nitrite to ammonium and, finally, these nitrogen species are reduced to gaseous nitrogen (N₂) [8]. The reduction of nitrate was not coupled with the increase in ammonium concentration (Table 1).

Gil *et al.* [3] showed that the current was generated in proportion to the amount of organic matter decomposition by microorganisms. However, in this case, the current was not proportional to COD removal, suggesting that nitrate is preferentially used as an electron acceptor over the anode. Sukkasem *et al.* [13] also reported that nitrate affected current generation at low resistance (150 Ω), unlike at high external resistance (270–1,000 Ω). From the above results, it can be concluded that nitrate can negatively influence current generation.

Therefore, these results show that the presence of electron acceptors such as nitrate, ferric iron, oxygen, *etc.* in the anode may increase biodegradation of organic matter, but electricity generation is negatively influenced. When ammonium- and nitrate-including wastewater such as swine wastewater is used, control of these ions is a very important factor in increasing current generation. Electrolysis could be used to control ammonium and nitrate ions.

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