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Two-chamber microbial fuel cell to simultaneously remove ethanolamine and nitrate

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ABSTRACT

Microbial fuel cells (MFCs) are a promising technology to treat wastewater while recovering bioenergy and have been studied to remove carbon and nitrogen. Electrons generated at the anode from the oxidation of organic electron donors are used to reduce nitrate at the cathode, and these processes produce power. In this study, a two-chamber MFC that coupled an anode chamber and biocathode chamber was investigated to remove ethanolamine and nitrate. We developed an MFC in which micro-organisms at the cathode performed complete denitrification using electrons supplied by ethanolamine oxidation at the anode. The biocathode MFC produced a maximum power density of 8.41 W/m^3 with a corresponding current and cell voltage of 2.9 mA and 170 mV, respectively. This research demonstrates that an MFC with both a biological anode and cathode simultaneously removed ethanolamine, produced power, and denitrified. Results from this study indicate that ethanolamine might be a suitable resource for generating electricity with MFC technology.

Keywords: Microbial fuel cell; Two-chamber; Ethanolamine; Biodegradation; Biocathode

1. Introduction

Nuclear power plants (NPP) generate nearly 20% of the total electricity in the world. In NPPs, water in secondary and cooling systems controls heat created from fission of uranium fuel, to produce steam, which is used to generate electricity. Corrosion and scale inside pipes in the secondary and cooling systems can increase maintenance time and cost and decrease power generation [1]. In secondary systems, ammonia was used as an alkaline reagent, due to its widespread availability. However, ammonia largely has been replaced by ethanolamine (ETA), which is less volatile and improves corrosion protection in the liquid phase. ETA remains in high concentration in discharged water system. It is difficult to degrade naturally, besides, the byproduct can cause water pollution, increasing the chemical oxygen demand (COD) in water [2]. Although it has been treated by ion-exchange resin, bipolar electrolysis, and oxidation, these methods generally require large amounts of energy and chemicals with long degradation reactions [3].

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Consequently, there has been a strong demand for an alternative process.

Microbial fuel cells (MFCs) are a promising technology while recovering bioenergy and have been studied to treat wastewater. MFCs are typically designed as two-chamber systems in which micro-organism oxidize various organic or inorganic compounds in the anode and produce protons and electrons. The electrons flow from the anode through an electrical circuit toward a high redox electron acceptor, such as oxygen, in the cathode. The cation makes up the charge balance by diffusing from the anode to the cathode through a charge-selective separator [4]. In addition, micro-organisms can consume electrons at the cathode by reducing electrochemically positive electron acceptors such as nitrate, perchlorate, or metals [5–7]. In fact, MFCs cannot only convert organic matter to electricity, but also use substances such as nitrate and sulfate as biocathodic electron acceptors [8], which shows the promise of using MFCs to simultaneously remove organic carbon and nitrate from wastewater.

In this study, a two-chamber MFC that coupled an anode chamber and biocathode chamber was investigated to remove ETA and nitrate simultaneously. Major breakdown products of ETA biodegradation are acetaldehyde and ammonium [9]. Acetaldehyde is hydrolyzed to ethanol and acetate, and then these two products are finally degraded to CO_2 and water by micro-organisms (Eq. (1)) [10]. At cathode, nitrate is used as an electron acceptor and transformed into nitrogen gas under anoxic conditions in the denitrification (Eq. (2)). Such an anaerobic respiration process was demonstrated for the first time with *Geobacter* species: a pure culture of *Geobacter metallireducens* was found to be able to reduce nitrate to nitrite with an electrode in MFC [11]. Clauwaert et al. demonstrated the simultaneous anodic carbon oxidation and cathodic nitrate reduction from two separate liquid streams [12]. The electrons generated at the anode from the oxidation of the organic electron donors are used to drive the nitrate reduction at the cathode, their process produced power. In the present study, we aim to further investigate this concept and to establish whether it is possible to achieve simultaneous ETA and nitrate removal. Afterward the effects of external resistance, nitrate concentration, phosphate solution density, and carbon source on MFC performance were investigated.

$$\text{Anodic reaction:}\ C_2H_7NO + 3H_2O \rightarrow 2CO_2 + 10H^+ + 10e^- + NH_3 \tag{1}$$

$$\text{Cathodic reaction:}\ 2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \tag{2}$$

2. Materials and methods

2.1. MFC configurations

Two-chamber MFCs were constructed by assembling two equal rectangular plexiglas chamber with internal size of 5 × 5 × 3 cm. A cation exchange membrane (Ultrex CMI-7000, Membranes International) was placed between the anode and cathode chambers (Fig. 1). Sealing was ensured by a rubber gasket inserted between the chambers. Prior to use, the cation exchange membrane was treated with NaCl solution (5%) at 40˚C for 24 h, and then rinsed with deionized water. The total empty volume of each chamber was 75 mL. Granular graphite with a diameter ranging from 2 to 4 mm was used as the electrode in both the anode and cathode chambers, reducing the working volume to 50 mL. Granular graphite was sieved to remove large (>4 mm) and small (<2 mm) particles and was filled into the chambers as an electrode. Two graphite rods were inserted into each chamber, and they were connected with an electric wire through an external resistance. Before installation, the graphite rods were pre-treated by being immersed overnight in pure acetone and heated to 450˚C for 30 min, as described [13]. Also the granular graphite was submerged overnight in 1 M HCl, washed with deionized water, then submerged overnight in 3-M NaOH and finally washed several times in deionized water [4].

2.2. MFC operation

The anode and cathode chambers of the MFC were seeded with anaerobic and anoxic sludge, respectively, which were collected from an anaerobic/anoxic/oxic (A2/O) wastewater treatment facility (Jungrang Sewage Treatment Plant, South Korea). Before the sludge was used, it was washed with phosphate buffer solution three times to increase conductivity and stabilize the pH. To improve micro-organism growth, the medium was injected into the reactor with the sludge. The medium contained (per liter) KCl, 0.13 g; Na_2HPO_4, 8.19 g; $NaH_2PO_4{\cdot}2H_2O$, 6.6 g; Wolfe's mineral solution (12.5 mL); and Wolfe's vitamin solution (12.5 mL). The anode chamber was inoculated with a 50:50 mixture of anaerobic sludge and medium. Also the cathode chamber was inoculated with anoxic sludge and medium. The medium was continuously purged with 99.9% N_2 gas before being fed into the reactor.

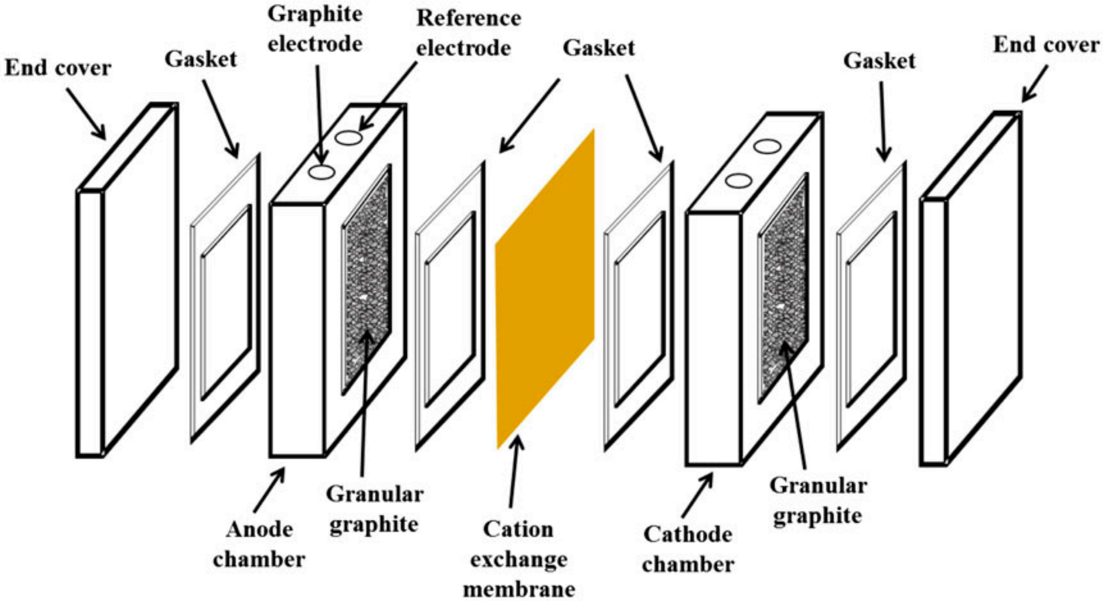

Fig. 1. A schematic of the two-chamber MFC used in this study.

The experiments were performed in fed-batch mode. The objective was to adapt microbial communities to each electrode by feeding medium into the chamber. The anodic solution contained ethanolamine (500 mg/L) as the sole electron donor and the cathodic solution consisted of sodium hydrogen carbonate with potassium nitrate as the final electron acceptor. The feed was replaced every 3 d. Both chambers were recirculated at a rate of approximately 2 mL/min to avoid concentration gradients or clogging of the granular matrix. The MFC operation was carried out in a temperature-controlled room at 25 ± 2°C.

2.3. Analysis and calculations

The anode and cathode chambers were connected through an external resistor (100 Ω) to close the circuit. The half-cell potentials were measured by placing an Ag/AgCl reference electrode (MF-2079, BAS) in each chamber. The cell voltages were measured every 10 min with a voltage recorder (VR-71, T&D Corporation). External resistance was set up by a resistance decade box (380400, Extech Instruments). Samples were immediately filtered through a 0.2 μm syringe filter before analysis. COD was measured by standard method 5220 (Hach COD system, Hach Company). Nitrate, nitrite, and ammonium were also measured with a HACH (DR-2800) spectrophotometer.

Current, I (in milliamperes; mA), was calculated according to $I = V/R_{\mathrm{ex}}$, where V (in millivolts, mV) is the voltage and R_{ex} (in ohms, Ω) is the external resistance. Power, P (in milliwatts, mW), was calculated according to $P = IV$. Current and power density were normalized to the chamber volume. The coulombic efficiency, CE (%), for ethanolamine biodegradation was calculated based on the current generated under steady condition by Eq. (3).

$$\mathrm{CE} = \frac{MI}{Fbq\Delta \mathrm{COD}} \times 100 \tag{3}$$

where M is the molecular weight of oxygen, F is Faraday's constant (96,485 C/mol of e^-), b is the number of electrons exchanged per mole of oxygen, q is the volumetric influent flow rate and ΔCOD is the difference between the influent, and effluent CODs [4]. The coulombic efficiency for nitrate reduction was calculated as the ratio of the current flowing across the MFCs and the theoretical current estimated from oxidized nitrogen compounds removed at the cathode (Eq. (4)).

$$\mathrm{CE}\ (\varepsilon \mathrm{NO_x}) = \frac{I}{n\Delta C_{\mathrm{NO_x}} Q_{\mathrm{in}} F} \times 100 \tag{4}$$

where I is the current (A); n is the number of electrons that can be accepted by 1 mol of oxidized nitrate compound in the cathodic compartment assuming N_2 is the final product, hence 5 for nitrate (e^- mol); $\Delta C_{\mathrm{NO_x}}$ is the difference between the nitrate concentration in the cathodic influent and effluent (mol N/L); Q_{in} is in the influent flow rate (L/s) and F is Faraday's constant [7].

3. Results and discussion

3.1. Electricity generation

After one month, the MFC generated electricity. Upon replacing the medium solution, both chambers produced electric currents (Fig. 2). The gap between the anode and cathode potentials increased with time, and consequently the cell current reached 1.1 mA with a voltage around 114 mV and external resistance of 100 Ω. This result showed that the electrochemically active bacteria in each chamber were well developed. The maximum power density was evaluated by examining a polarization curve, which characterizes voltage as a function of current. Polarization was obtained by varying the external resistance from 10 to 1,000 Ω after a one-month startup, as shown in Fig. 3. The maximum power density was 8.41 W/m^3, while the corresponding current and cell voltage were 2.9 mA and 170 mV, respectively. As the current increased, the voltage decreased linearly (power curve). In this region, the slope of the linear regression indicated that the internal resistance of the MFC was 81 Ω.

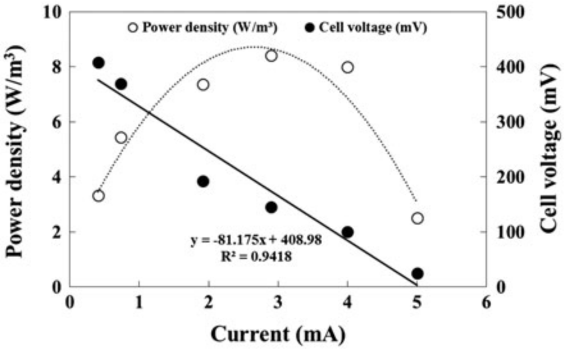

Fig. 3. Polarization and power curve as a function of the current using various external resistors.

3.2. MFC performance under different external resistances

Tables 1 and 2 summarize the average concentrations of COD, ammonium, nitrate, and nitrite in each chamber during the batch-fed operation with different resistances applied. Ethanolamine consumption increased with increasing current flows across the compartments causing the COD concentration to drop from 718 mg/L in the anode influent to 129 mg/L in the anode effluent at 5 Ω and from 716 to 143 mg/L at 1,000 Ω. As the COD concentration in the cathode effluent was always below the detection limits, the total COD removal efficiency was close to 82% at any applied resistance. In the cathode chamber, nitrate was reduced by the electrons provided by ethanolamine oxidation at the anode. At 1,000 Ω the nitrate usage was low due to a limited electron supply by the cathode. Thus, the nitrate concentration only decreased from 21 to 7.3 mg/L. Traces of nitrite were also detected when the reactor was operated at higher external resistances. At 50 Ω (highest current), the nitrate concentration dropped from 21 to 4.7 mg/L, thus giving reasonable nitrate use.

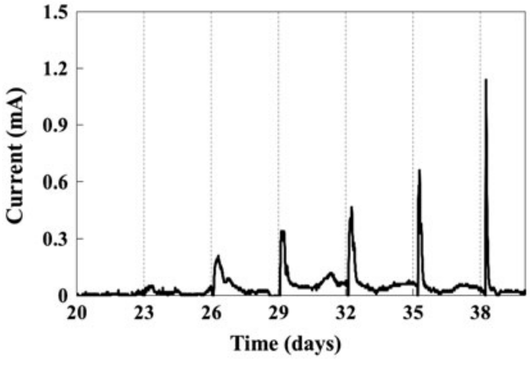

Fig. 2. Current generation in the startup period.

Table 3 summarizes the parameters used to describe the electrical performance of the MFC. The current produced by the MFC depended on the resistance applied, with higher currents corresponding to lower external resistances [5]. The current production ranged from 0.408 to 5 mA, while the maximum power varied between 0.125 and 0.421 mW. The maximum power was obtained in this reactor when a 50 Ω resistor was applied. Although higher currents led to more efficient electron use, as suggested by the coulombic efficiency, this dependence had a larger effect on nitrate reduction at the cathode than on ethanolamine oxidation at the anode. While the coulombic efficiency at the anode ranged between 8.18 and 28.56%, substantially higher values were observed at the cathode, where up to 52.48% of the electrons delivered by the electrode were used to reduce incoming nitrate. The results demonstrated that higher external resistances inhibited denitrification due to lower electrical currents produced.

3.3. Effects of nitrate concentration on MFC performance

The effects of different nitrate concentrations and voltage output were investigated at a fixed external resistance of 50 Ω. The MFC system was operated in batch mode with four influent concentrations (20, 40, 60, and 80 mg/L) in the cathode chamber and a fixed ethanolamine concentration of 500 mg/L in the anode

Table 1
Anode chamber—Analyses results of samples taken during the operation of MFC at different external resistances

Applied resistance (Ω)		COD (mg/L)	COD removal (%)	NH_4^+ (mg/L)	pH
5	Influent	718	82.03	6.1	6.98
	Effluent	129		83.7	6.87
25	Influent	729	82.03	5.7	6.97
	Effluent	131		76.2	6.87
50	Influent	729	82.17	5.7	6.97
	Effluent	130		79.5	6.83
100	Influent	716	83.1	5.8	6.98
	Effluent	121		84.9	6.84
500	Influent	716	81.28	5.8	6.97
	Effluent	134		75.3	6.88
1,000	Influent	716	80.03	5.8	6.97
	Effluent	143		77.6	6.87

Table 2
Cathode chamber—Analyses results of samples taken during the operation of MFC at different external resistances

Applied resistance (Ω)		NH_4^+ (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	pH
5	Influent	N.D.	N.D.	20	6.88
	Effluent	7	0.006	4.7	7.04
25	Influent	N.D.	N.D.	21	6.88
	Effluent	8.4	0.005	4.7	7.00
50	Influent	N.D.	N.D.	21	6.88
	Effluent	6.6	0.005	4.7	7.01
100	Influent	N.D.	N.D.	21	6.88
	Effluent	7.4	0.006	5.4	7.01
500	Influent	N.D.	N.D.	21	6.88
	Effluent	13.7	0.098	6.9	7.01
1,000	Influent	N.D.	N.D.	21	6.88
	Effluent	15.7	0.154	7.3	7.04

Note: N.D.: not detected.

Table 3
Summary of the parameters used to describe the electrical performances of MFC

Applied resistance (Ω)	Maximum current production (mA)	Maximum power production (mW)	Maximum voltage production (mV)	Coulombic efficiency on ETA oxidation (%)	Coulombic efficiency on Nitrate reduction (%)
5	5	0.125	25	23.33	44.90
25	4	0.4	100	20.63	37.85
50	2.9	0.421	145	28.56	52.48
100	1.92	0.369	192	23.65	45.11
500	0.738	0.272	369	10.46	21.60
1,000	0.408	0.166	408	8.18	17.11

chamber. An illustration of the typical cell current profiles produced is shown in Fig. 4. The results showed that a cell current was generated by increasing nitrate concentration. Increasing the nitrate concentration from 20 to 60 mg/L improved the average current production by almost twofold (from 0.77 to 1.36 mA). Previous work suggested that the current production depended on nitrate concentration [14].

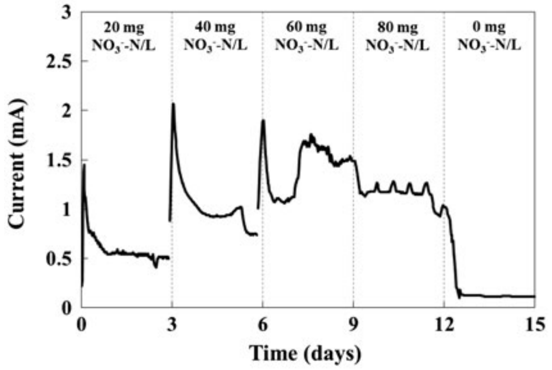

Fig. 4. Effects of nitrate concentration on current performance.

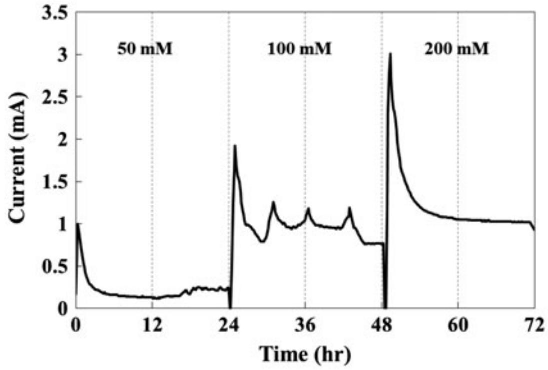

Fig. 5. Effect of phosphate buffer solution on current generation.

The experimental results obtained here confirmed this conclusion and also demonstrated that the denitrification rate was supported by current production which depended on nitrate. However, the system was also operated without nitrate as an electron acceptor in the cathode chamber, and a low electrical current was observed.

3.4. MFC performance under phosphate buffer solution

The effects of electrolyte conductivity on MFC performance were investigated with three influent concentrations in each chamber: 50, 100, and 200 mM phosphate buffer solution (PBS). Fig. 5 shows the current generation with each phosphate solution. The current with 50 mM PBS initially reached 1 mA, then stabilized at 0.25 mA over 18 h. The current with 200 mM PBS rapidly increased, then stabilized at 1.11 mA. The maximum current with 200 mM PBS was substantially higher than 3.01 mA. The increase in almost 300% in current density with 200 mM phosphate was due to increased conductivity in each chamber (Table 4). This result indicated that high conductivity (ionic strength) of the medium in MFC is crucial for high power generation.

In addition, when the PBS density was increased, additional ETA and nitrate were removed (Table 4). In this test, the high conductivity at the anode did not noticeably improve the anodic performance resulting in a COD removal difference of about 4%. In comparison, the cathode performance resulted in nitrate removal difference of about 21% by changing the PBS density. This result suggests that some limitations on microbial

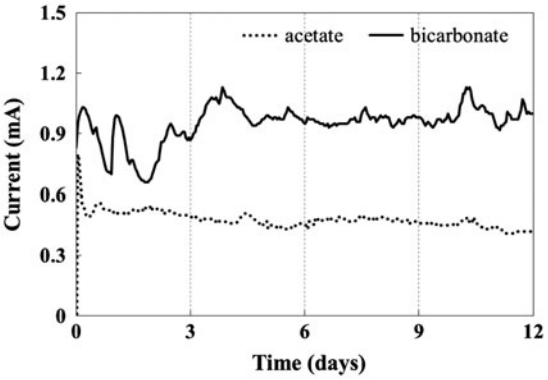

Fig. 6. Current generation in MFC with organic and inorganic carbon sources; cathode medium containing acetate (organic) and sodium bicarbonate (inorganic).

Table 4
Effluent characteristics, cell voltage, current, and power density with different electrolyte conductivity

Phosphate buffer solution (mM)	Conductivity (mS/cm)		COD removal (anode)		Nitrate removal (cathode)		Maximum voltage (mV)	Current density (A/m^3)	Power density (W/m^3)
	Anode	Cathode	(mg/L)	(%)	(mg/L)	(%)			
50	6.34	7.14	588	80.99	12.9	58.64	100	4.29	0.09
100	10.68	11.79	595	83.1	15.6	74.29	192	19.67	1.96
200	18.07	19.25	610	84.02	17.6	80	301	24.04	2.89

Table 5
Summary of nitrate removal, current production, and nitrate reduction with organic and inorganic carbon sources

Carbon source (for denitrification)	Nitrate removal		Average current production (mA)	Coulombic efficiency on nitrate reduction (%)
	(mg/L)	(%)		
Acetate	43	75	0.48	28
Bicarbonate	44	76	0.95	58

metabolism at low PBS concentration led to different effluent qualities. At high conductivity, electrons originating from organic matter in the anode were transferred to oxidized nitrate to build up a proton motive force usable for autotrophic generation. However, at low conductivities, the resistances increased, limiting electron and proton transport. In conclusion, ionic strength influenced denitrification, ethanolamine oxidation, and current production in the MFC.

3.5. Comparison of organic and inorganic carbon sources

To investigate the effects of the carbon source on MFC performance, the cathode chamber was fed with two types of carbon source, organic, and inorganic. The organic medium contained sodium acetate and nitrate as the carbon and nitrogen sources. The inorganic medium contained sodium carbonate and nitrate. The cathode chamber was fed with two different carbon sources, acetate, and bicarbonate, with a fixed nitrate concentration of 60 mg/L. The ratio of COD to nitrate was controlled at about 5.0. The cell current profiles are shown in Fig. 6. With the organic medium with acetate, a 0.48 mA current was generated. In contrast, the inorganic medium with sodium bicarbonate generated a 0.95 mA current during the 12 d. The efficiency of nitrate removal with acetate and bicarbonate approached 75 and 76%, respectively (Table 5). Meanwhile, nitrate reduction using acetate and bicarbonate reached 28 and 58%, respectively. These findings suggest that inorganic carbon sources had a stronger influence on current generation than did organic carbon. In addition, a higher current was more favorable for autotrophic denitrification than for heterotrophic denitrification.

4. Conclusions

This study demonstrated the feasibility of using two chambers to simultaneously remove ethanolamine and nitrate while generating electricity. Under different external resistances, the maximum power density was 8.41 W/m^3 with ETA wastewater as a substrate. In the anode chamber, the total COD removal efficiency was close to 80% at any applied resistance. The MFC also simultaneously removed nitrate in the cathode chamber. Factors such as external resistance, nitrate concentration, phosphate solution density, and cathodic carbon source affected MFC performance. The optimal MFC performance was obtained with a 50 Ω resistor. High PBS density (conductivity) of the MFC medium is crucial for high power generation. In addition, by increasing the PBS density, COD and nitrate were more completely removed. Sodium carbonate was more favorable for generating a high current than was sodium acetate. In conclusion, this research showed that an MFC with both a biological anode and cathode simultaneously removed ethanolamine, produced power, and denitrified substrates. Results from this study indicate that ethanolamine might be a suitable resource for generating electricity with MFC technology.

Acknowledgments

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