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Treatment of ethanolamine using an Fe(III)-based, two-chamber microbial fuel cell with continuous Fe(II) oxidation at the air cathode

Seok-Ju Seo, Ja-Won Shin, Hubdar Ali Maitlo and Joo-Yang Park*

Abstract

BACKGROUND: The objective of this study was to investigate the feasibility of developing an integrated bio-electrochemical system for the removal of ethanolamine from wastewater by combining an Fe(III)-based microbial fuel cell (MFC) with a continuous Fe(II) oxidation system for simultaneous oxidation and reduction of iron in the same compartment. The ethanolamine in the Fe(III)-based MFC can be effectively converted to electrical energy by using the catalytic activity of microorganisms. In this respect, the authors investigated whether the introduction of a system for Fe(III) regeneration could enhance the sustainability of both power generation and the removal of ethanolamine in this integrated system.

RESULTS: The experimental results obtained with a traditional Fe(III)-based MFC, operated with a ferric sulfate solution of 25 or 50 mmol L⁻¹ Fe(III) mixed with ethylenediaminetetraacetic acid (EDTA) solution of 10 mmol L⁻¹, showed that increasing the Fe(III) concentration leads to improved performance of the MFC; the maximum power density, open circle voltage (OCV), and Coulombic efficiency (CE) were all improved. However, the effluents from the cathode chamber contained a low concentration of Fe(III) due to deficient regeneration of Fe(III). In the integrated bio-electrochemical system developed in this work (enhanced Fe(III)-based MFC), the generated Fe(II) was oxidized at the air cathode via favorable oxygen diffusion and a Fe(II)-based fuel cell (FC).

CONCLUSION: Electricity was sustainably generated from the enhanced MFC with 25 mmol L⁻¹ Fe(III); the highest performance, in terms of maximum power density, OCV and CE, was achieved using 50 mmol L⁻¹ Fe(III), thus indicating the increased efficiency of this integrated system.

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Keywords: environmental biotechnology; environmental chemistry; energy; microbial fuel cell

INTRODUCTION

Currently, nearly 20–30% of the total electricity used in the USA and EU is generated by nuclear power plants (NPPs).^{1,2} Because of the extensive use of ethanolamine as a pH adjuster in the pipes of secondary and cooling systems of NPPs (i.e. the pH is maintained at values ranging between 9.5 and 9.8) to prevent corrosion and scaling problems,^{3,4} the wastewater generated contains a high concentration of this compound. Therefore, this wastewater requires treatment to remove the ethanolamine in such a manner that meets the quality imposed by standards. As a result, many technologies have been developed and explored for the remediation of this wastewater effluent. Some of these methods are based on electrochemical treatment processes⁵ (e.g. electrodialysis reversal followed by electrochemical wastewater treatment) or physicochemical processes⁶ (e.g. ion exchange). However, there are still many bottlenecks restricting the field application of these methods, including the high operating cost of electrolysis and the difficulty of implementing treatments based on ion exchange resins. Fortunately, these challenges can be partially solved by applying technologies based on microbial fuel cells (MFCs).

Over the past few decades, the significant development of MFC technologies has led to their recognition as versatile and promising techniques that can be used to produce electricity from a diverse range of organic contaminants contained in wastewater.^{7,8} These technologies are suitable for the simultaneous production of energy and the degradation of contaminants contained in wastewater. In addition, in a previous study, we demonstrated how ethanolamine can be used as a valuable energy source in air cathode single-chamber MFC experiments.⁹ This MFC consisted of five essential components: an anode chamber, electrochemically active bacteria, the ethanolamine as an organic substrate inside the anode chamber, a membrane, and an air cathode electrode. The metabolic activity of microorganisms in the anode can directly convert ethanolamine to electrons,

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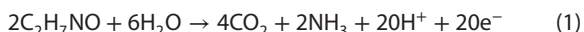
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hydrogen ions, carbon dioxide, and ammonia. We achieved removal of up to 91% of the chemical oxygen demand (COD) and 36.6% of ammonia using an air cathode MFC with 8.2 mmol L⁻¹ ethanolamine. Air cathode single-chamber MFC systems in particular represent an innovative electrochemical biotechnology that can generate electricity from diverse organic substances using a simple mechanism.¹⁰ Moreover, this system demands no additional energy because it uses oxygen in the air as an electron acceptor. However, although the use of oxygen from air as an electron acceptor has been proven to be more sustainable for power generation,^{7,11} the performance recorded in our previous study generated only 0.24 W m⁻² at a current density of 0.98 A m⁻². The use of oxygen as an electron acceptor could be limited because the consumption rate is higher than the solubilization rate in two-compartment MFCs that use an aeration chamber.^{12,13} Alternatively, bio-cathodes often run at a low rate, due to poor reaction kinetics, and require a sufficient period of time for stabilization of the microbial growth.¹⁴ Therefore, the selection of the electron acceptor appears to be a factor influencing the performance of MFCs.

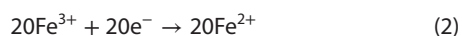
According to several previous studies,^{15,16} unlike other alternative cathode reaction systems, using Fe(III) instead of oxygen as the electron acceptor can increase the cathode performance in MFCs. However, owing to the difficulty of Fe(III) regeneration, many previous studies have focused on the development of a method to oxidize the resultant Fe(II) into Fe(III) by coupling MFCs with either an external fuel cell (FC)^{17,18} or with a biological oxidation system.¹⁹ However, even though the regeneration of Fe(III) has been successfully achieved, the periodic pumping process to circulate the solution into the external reactor requires additional energy consumption.

The objective of this work is to develop the two-chamber MFC characterized by the continuous regeneration of Fe(III) by Fe(II) oxidation using favorable oxygen diffusion via an additional air cathode to obtain sustainably regenerated catholyte (Fig. 1). Simultaneously, by adding an additional external circuit of anode and air cathode, generated Fe(II) is oxidized to Fe(III) by the Fe(II)-based FC. In this manner, the feasibility of using an additional anode and air cathode in the cathode chamber of the MFC is investigated to continuously oxidize the Fe(II), thereby continuously regenerating the Fe(III)-ethylenediaminetetraacetic acid (EDTA) couple, which is used as the catholyte. Specifically, our premise is that the reactions presented below can describe the chemical and biological processes taking place in such a system. These reactions are as follows:

Biological reaction of ethanolamine oxidation (anode):



Electrochemical reaction of Fe(III) reduction (cathode):



Electrochemical reaction of Fe(III) regeneration by diffusion oxygen (air cathode):



The application of an Fe(III)-based, two-chamber MFC with continuous oxidation at the air cathode was evaluated based on both its sustainability for electricity generation and its ability to treat ethanolamine.

MATERIALS AND METHODS

Construction of the experimental reaction cells

Two types of reactors (an Fe(III) and an enhanced Fe(III)-based MFC with continuous Fe(II) oxidation) were used in this study. These reactors were made from cubic Plexiglas, as shown in Fig. 1(a) and (b). Each reactor consisted of an anode chamber and a cathode chamber, separated by a cation exchange membrane (CEM, model CMI-7000S, Membranes International Inc, USA). Prior to use, the CEM was immersed in a 5% NaCl solution at 40°C for 24 h, followed by thorough rinsing with deionized water. Each chamber had a volume of 160 mL (5 cm × 5 cm × 6.4 cm), an installed electrode, and an Ag/AgCl reference electrode (model MF-2052, Bioanalytical Systems, Inc, USA), which recorded the individual electrode potentials. Specifically, all electrodes (except the ones used as air cathodes) were made from carbon cloth without water-proofing (model 1071 HCB, AvCarb®, USA) and were 5.0 cm × 5.0 cm. The CEM was installed between the electrodes in order to separate the anode and cathode electrodes. The major differences between these reactors are the additional anode and air cathode electrodes that were inserted at the end of the cathode chamber in the enhanced Fe(III)-based MFC, which were installed for the regeneration of Fe(III). The air cathode electrode (5.0 cm × 5.0 cm) was manufactured by overlaying a carbon base layer and four polytetrafluoroethylene (PTFE) diffusion layers on the air-facing side of the carbon cloth (30% water-proofed type). A Pt catalyst layer (10% Pt on Vulcan XC 72, Premetek) with Nafion binder was also coated on the solution-facing side.²⁰ In addition, a mesh polypropylene (PP) (pore size 710 × 710 μm, open area 41%, Spectrum Medical Industries Inc.) separator was installed between the additional anode and the air cathode to increase the diffusion rate of oxygen and to separate the anode and air cathode electrodes. As Zhang *et al.*²¹ found, this PP mesh can be used in an MFC to transfer this technology into the field because the cost for PP mesh (\$13–\$26 per m⁻²) is much less than a CEM (\$83 per m⁻²). Furthermore, although oxygen mass transport and diffusion coefficient were unnoticeable, the high diffusivity of the oxygen as well as other molecules could be possibly due to the large open area (41%) of the PP mesh.

The cell voltage across the external resistance was automatically recorded at 5-min intervals utilizing a data logger (model VR-71, T&D Co., USA) connected to a computer. All experiments were operated at a fixed external circuit resistance of 1000 Ω.

The anode chamber of the MFC was fed with artificial wastewater consisting of 10 mmol L⁻¹ ethanolamine (H₂NCH₂CH₂OH, > 99.0%, JUNSEI) as the organic substrate, 0.13 g L⁻¹ of potassium chloride (KCl, > 99.0%, SHOWA), 6.6 g L⁻¹ of sodium dihydrogen phosphate dihydrate (NaH₂PO₄·2H₂O, > 99.0%, JUNSEI), 8.19 g L⁻¹ of sodium phosphate (Na₂HPO₄, > 99.0%, Yakuri Pure Chemicals), 12.5 mL L⁻¹ of a mineral solution, and 12.5 mL L⁻¹ of a vitamin solution.²² Before introducing these solutions into the anode chamber, nitrogen gas was sparged for 30 min to remove any oxygen. To reduce the unexpected differences in terms of efficiency and to accelerate the start-up period, the anode chamber was inoculated with electrochemically active bacteria. These microorganisms were stabilized with ethanolamine for more than 1 year.⁹ The cathode chamber of the MFC contains Fe(III) in the form of sulfate n-hydrate (Fe₂(SO₄)₃·nH₂O, > 60.0%, SHOWA) and EDTA (>99.4%, Sigma-Aldrich Inc.). The reactor was operated in batch mode at 28 ± 0.3°C and stirred at 200 rpm using a digital hotplate stirrer (model MSH-30D, WiseStir®, USA).

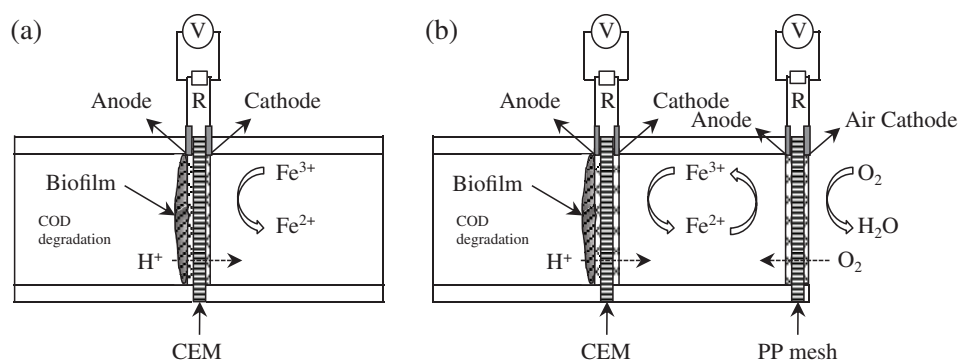


Figure 1. Schematic diagram of the MFC experimental reactors: (a) Fe(III)-based MFC; and (b) enhanced Fe(III)-based MFC with continuous Fe(II) oxidation; CEM – cation exchange membrane, PP mesh – polypropylene mesh.

Operating conditions

The solutions in both the anode and cathode chambers were renewed with new ones when the main cell voltage output across the external resistance of each experiment fell below 150 mV. Experiments M1 and M2 (control experiments) were carried out to evaluate the efficiency of the conventional Fe(III)-based MFC as a function of Fe(III) concentration. This was done by using different catholyte solutions, namely ferric sulfate solutions of 25 or 50 mmol L⁻¹ Fe(III) mixed with 10 mmol L⁻¹ EDTA. Experiments M3 and M4 investigated the effect of Fe(III) regeneration on voltage stability using an enhanced Fe(III)-based MFC with continuous Fe(II) oxidation. All experiments were conducted in two duplicated cycles for each experimental condition in order to investigate reproducibility of removal of COD and Fe(III), by-product formation, and performance of MFC. Thereafter, when experiment M4 (cycle 2) was completed, only the anode solution was replaced in order to investigate the possibility of reusing Fe(III) in experiment M5.

Measurement and analyses

To evaluate MFC performance, the maximum power density and the voltage as a function of current density were obtained from the power density curves, which were determined using variable external resistances (10–10 000 Ω). In addition, the Coulombic efficiency (CE) (%) is usually determined by integrating the current over time (t_b) as $CE = M \int_0^{t_b} I dt / F b v_{An} \Delta COD$, where M is the molecular weight of acetate (59 g mole⁻¹), F is Faraday's constant, b is the number of electrons produced per mole of acetate (8 mol-e⁻ mol⁻¹), v_{An} is the liquid volume of the anode chamber, and ΔCOD is the change in the COD of the substrate. However, because all our experiments used 10 mmol L⁻¹ of ethanolamine as a substrate, CE was calculated based on the difference in substrate concentration (ΔCOD), as suggested by Logan¹⁰ for complex organic matter, as $CE = 8 \int_0^{t_b} I dt / F v_{An} \Delta COD$, where 8 is constant on the basis of the molecular weight of oxygen and the number of moles of electrons exchanged per mole of oxygen.

The pH of the anode and cathode effluents was measured at the end of each experiment using a pH meter (Orion™, 720A+, USA) equipped with a glass electrode (Orion™, 8156BNUWP, USA). The concentrations of ethanolamine in terms of the COD (in the anode chamber) and the by-products in terms of ammonia, nitrate and nitrite (in the anode and cathode chambers) were measured twice a day while studying the MFC processes. Before measuring

these concentrations, the anode samples were filtered through a 0.45-μm pore diameter PP syringe filter (Whatman®, USA) to remove the microorganisms. The COD, NH₄⁺-N and NH₃⁺-N, NO₃⁻, and NO₂⁻ were determined by the closed flux colorimetric, salicylate, chromotropic acid and diazotization methods, respectively. All determinations were performed three times using a HACH spectrophotometer (HACH Co., Loveland, CO, USA).

The total iron and Fe(II) concentrations in the cathode chamber were determined by the 1,10-phenanthroline colorimetric method.²³ Before measuring these concentrations, 1 mL of solution from the cathode chamber was acidified with 4 mL of a 6.0 mol L⁻¹ hydrogen chloride (HCl) solution via continuous stirring at 25°C for 15 min. To determine the total iron concentration, the first step consisted of mixing 1 mL of this mixture with 9 mL of 0.29 mol L⁻¹ hydroxylamine hydrochloride (NH₂OH·HCl) solution via continuous stirring at 25°C for 30 min. Then, a 1 mL aliquot was added into a mixture consisting of 5 mL of 1.2 mol L⁻¹ sodium acetate and 5 mL 1,10-phenanthroline solution followed by stirring and analysis after 10 min. The Fe(II) concentration was determined by acidification of 1 mL of sample with a mixture consisting of 5 mL of 1.3 mol L⁻¹ ammonium acetate, 2 mL of 2.0 mol L⁻¹ ammonium fluoride, and 5 mL 1,10-phenanthroline solution, followed by stirring and analysis after 10 min. Analyses were performed with a UV spectrophotometer (model UV mini 1240, Shimadzu, Japan) at a wavelength of 508 nm. The concentration of Fe(III) was computed from the difference between the total iron concentration and the Fe(II) concentrations, as determined by the aforementioned methods.

RESULTS AND DISCUSSION

Electricity generation and Fe(III) removal of Fe(III)-based MFC performance

As was previously specified in the literature,²⁴ using the redox couple Fe(III)/Fe(II) in a MFC has advantages in terms of enhancing the voltage output via a high standard potential (i.e. +0.77 V as against a normal hydrogen electrode (NHE) for the same concentrations of Fe(III) and Fe(II) at low pH) and fast reaction kinetics. In order to investigate the effect of different concentrations of Fe(III) on the cell voltage of conventional Fe(III)-based MFCs, comparative experiments (M1 and M2) were conducted. Figure 2(a) shows the influence of Fe(III) concentration on the whole voltage output in two repetitive cycles as a function of each experimental condition. As can be seen in Fig. 2(a), the voltage outputs of M1 and M2 rapidly reached their maximum within 5 h. Specifically, in M1, which was carried out using 25 mmol L⁻¹ Fe(III) mixed with

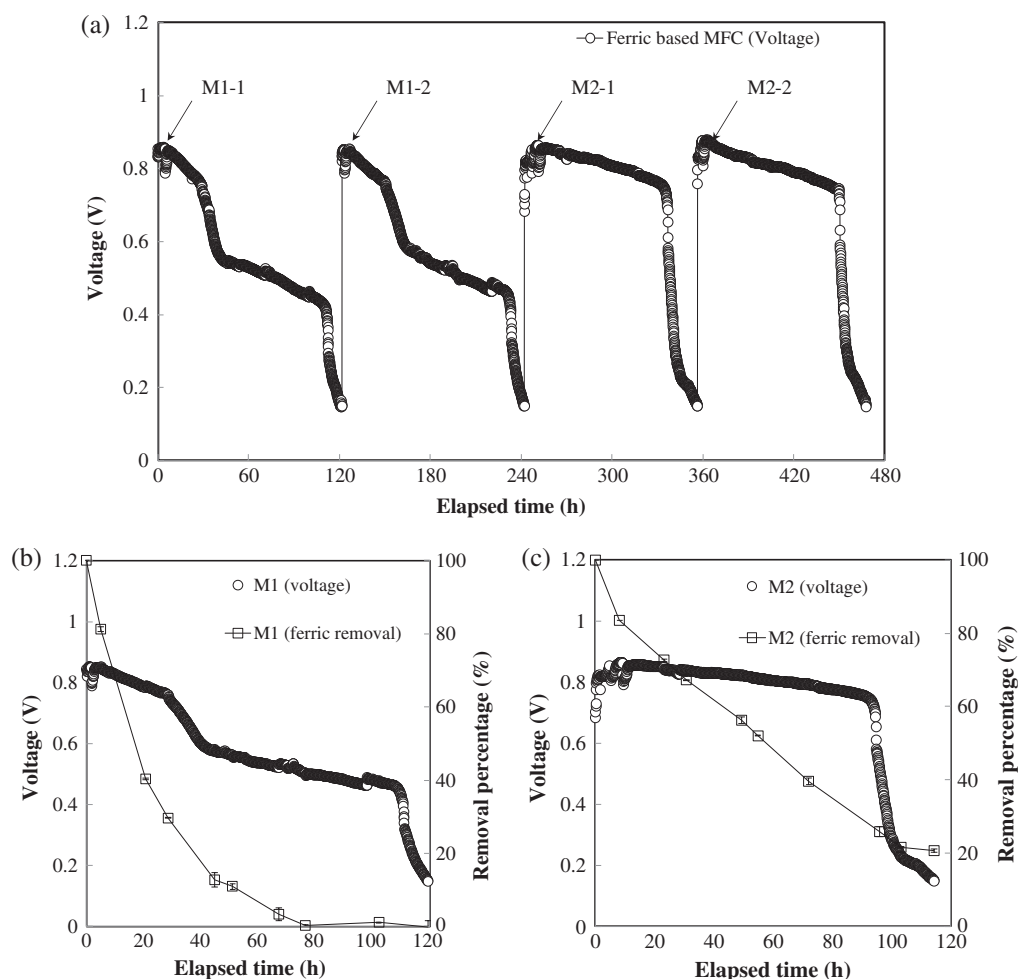


Figure 2. Cell voltage over the entire experimental operation period. (a) Expanded view of cell voltage and Fe(III) removal in accordance with different concentrations of catholytes in Fe(III)-based MFC: (b) 25 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA and (c) 50 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA.

10 mmol L⁻¹ EDTA, the maximum voltage outputs were 858 mV (cycle 1) and 853 mV (cycle 2). In M2, which was carried out using 50 mmol L⁻¹ Fe(III) mixed with 10 mmol L⁻¹ EDTA, the maximum voltage outputs were 853 mV (cycle 1) and 879 mV (cycle 2). As these results show, the maximum voltage outputs did not significantly differ in M1 and M2. However, the initial slope (from 0 to 28.5 h) of the voltage outputs of M1 was steep compared with that of M2 due to the differences in Fe(III) concentration. The concentration of Fe(III) of M1 at 28.5 h (approximately 7.25 mmol L⁻¹) was lower than that of Fe(III) at the end of experiment M2 (approximately 10.5 mmol L⁻¹). As a result, the initial slope of M1 was significantly increased due to low concentration of Fe(III).

Figure 2(b) and (c) show expanded views of the variation in cell voltage and Fe(III) removal as a function of elapsed time in M1 and M2. The voltage in M1 started at 844 mV and then moderately decreased to 605 mV after 40 h; approximately 80% of the Fe(III) was consumed (Fig. 2(b)). In addition, the reduction in Fe(III) was nearly completed within 80 h. Therefore, the rapid drop in the cell voltage from 844 to 605 mV in M1 was most likely caused by the scarcity of Fe(III) as an electron acceptor. Conversely, the presence of a high concentration of Fe(III) seems to be essential for maintaining the high voltage in this system. In this respect, as can be seen in Fig. 2(c), cell voltage values above 700 mV in M2

were maintained for 94.5 h. Moreover, the reduction rate of Fe(III) might be influenced by the voltage values. This can be observed comparing Fig. 2(b) and (c). In experiment M1, the removal rate of Fe(III) between 40 and 80 h is lower than that between 0 and 40 h. This is most probably due to the decrease in cell voltage from approximately 700 mV to approximately 400 mV. In the same way, the removal of Fe(III) in M2 decreased constantly but slowly, most probably due to the stable cell voltage generated (approximately 750 mV). These results suggest that the concentration of Fe(III), used as an electron acceptor, affects the performance of MFCs with respect to voltage. As the experimental results show, using 50 mmol L⁻¹ Fe(III) sulfate mixed with 10 mmol L⁻¹ EDTA increases the cell voltage stability. However, the Fe(III) used as a cathodic terminal electron acceptor should be replenished in order to increase the performance of the reactor in terms of ethanolamine removal and generated electricity.

Electrode potential and COD removal of Fe(III)-based MFC performance

The effects of Fe(III) removal and substrate degradation (expressed as COD loss) on electrode performance were investigated by measuring the potential of both the anode and cathode during the experimental programs. These results are presented in Fig. 3(a) and (b). As can be seen, similar results regarding the

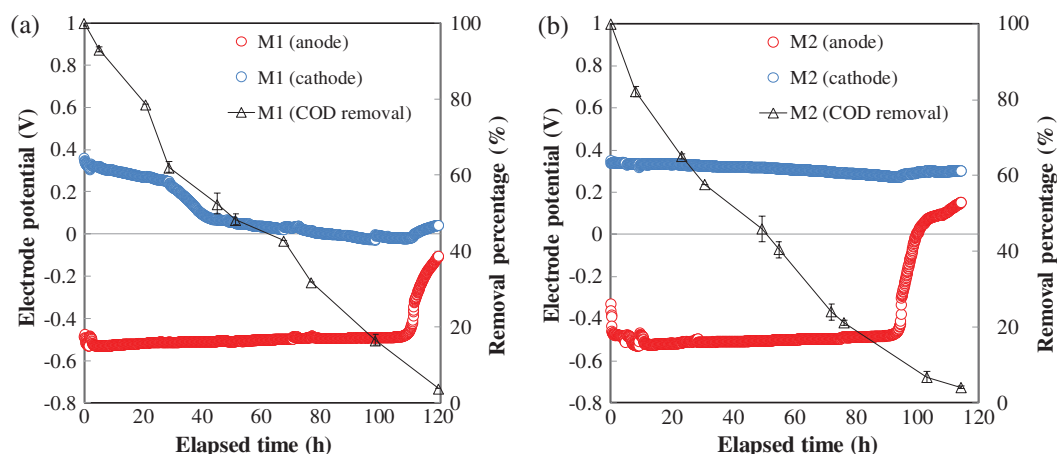


Figure 3. Anode and cathode potentials and COD removal in accordance with different concentrations of catholytes in the Fe(III)-based MFC: (a) 25 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA and (b) 50 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA.

anode potential were recorded for experiments conducted in Fe(III)-based MFCs with 10 mmol L⁻¹ ethanolamine. When the ethanolamine was fed as a new substrate into the anode chamber, the ethanolamine-enriched MFC rapidly generated electrical energy as the ethanolamine degraded (Fig. 3(a) and (b)). The anode potential was maintained at a constant value for approximately similar periods of time (110 h in M1 and 95 h in M2). As a result, the COD removal percentages were 96% in M1 and 95% in M2. These similar results highlight ethanolamine's major role as a valuable fuel in the MFC process. Conversely, the cathode potential values varied as a function of Fe(III) concentration. Thus, with 25 mmol L⁻¹ Fe(III), the cathode potential significantly decreased from 248 to 80 mV between 28.5 and 41.5 h. The observed cathode potential of Fe(III) reduction is positively proportional to the natural logarithm of the ratio Fe(III)/Fe(II).

$$E_{\text{cathode}}(\text{Fe}^{2+}, \text{Fe}^{3+}) = E_{\text{cathode}}^0 - \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (4)$$

In the above Nernst equation, where E_{cathode}^0 is 0.77 V vs. NHE, the cathode potential is dominated by Fe(III)/Fe(II) ratios. As a result, with 25 mmol L⁻¹ Fe(III) in the conventional Fe(III)-based MFC, the voltage output significantly decreased due to decreased cathode potential. However, with 50 mmol L⁻¹ Fe(III), a stable cathode potential was found (Fig. 3(b)), suggesting the generation of a stable voltage output.

Electricity generation and Fe(III) removal of an enhanced Fe(III)-based MFC with continuous Fe(II) oxidation

As was described above, the performance of traditional Fe(III)-based MFCs can be enhanced by the regeneration of Fe(III), which leads to stable voltage generation. Therefore, the main objective of this study was to sustainably operate an enhanced Fe(III)-based MFC reactor without the need for additional energy consumption. As Cheng *et al.*²⁵ found, the oxidation of Fe(II) is negatively affected by a decrease in the cathode chamber pH. Accordingly, this can lead to a decrease in the degree of Fe(III) regeneration in this chamber. In addition, increasing the pH of the catholyte causes the soluble Fe(III) to precipitate. This also has a negative effect on MFC performance. To solve these problems, adding a combination of Fe(II) and EDTA leads to an increase in oxidation and reduction in a low pH medium.²⁶ Furthermore, we

used a Fe-EDTA couple as an electron acceptor due to the slow rate of re-oxidation of potassium hexacyanoferrate which is commonly used in conventional MFC cathodes. Unlike other iron complexes, the reactivity of regenerated Fe(III)-EDTA by oxygen has already been highlighted according to a previous research.²⁶ Furthermore, in previous research using a combined MFC and FC system,¹⁷ the reduction period of 10 mmol L⁻¹ Fe(III) by MFC was more than 140 h; however, Fe(II) oxidation by FC with dissolved air was completed within 8 h. Although the stability of oxygen reduction via Pt catalyst was unnoticeable to maintain longer operation than current experiments, higher activity towards oxygen reduction than Pt catalyst (i.e. using iron phthalocyanine supported on Ketjen black carbon²⁷) was needed to improve Fe(III) regeneration efficiency in this system.

Figure 4 shows the voltage output for the two different conditions set in the experiments that analyzed the enhanced Fe(III)-based MFCs. Comparing the value of the voltage output in experiment M3 with that obtained in M1 (both experiments used 25 mmol L⁻¹ Fe(III)), it can be seen that there is a significant difference between them with significantly higher values for M3. This could be due to the high diffusion rate of oxygen that is involved in the continuous Fe(II) oxidation process at the additional anode and air cathode. This indicates that the regeneration of Fe(II) has a significant effect on the voltage output. Therefore, the voltage output in M3, which has the same concentrations of anolyte and catholyte as M1, was maintained above 700 mV for 100 h. The performance of M3 was similar to M2, most likely due to the effective regeneration of Fe(III). In addition, the decrease in the rate of Fe(III) removal between 0 and 100 h of operation was more gradual than was observed in M1. Although the Fe(III) removal rate in M3 was higher than was observed in M1, most likely due to the highly stable voltage; the higher Fe(III) concentration detected in M3 suggests the effective regeneration of Fe(III). As can be understood from Fig. 4(b), the effect of continuous Fe(II) oxidation at the air cathode could be associated with the increased concentration of Fe(III) after 115 h. At this time, the reduction of Fe(III) decreased and the regeneration of Fe(III) increased due to the decreased voltage output (from 700 to 250 mV). Furthermore, in experiment M4, which was conducted with 50 mmol L⁻¹ Fe(III) in the enhanced Fe(III)-based MFC, the highest maximum voltage outputs were recorded at about 950 mV (cycle 1) and 906 mV (cycle 2). These results might suggest the substantial role that an increase in the diffusion rate of oxygen

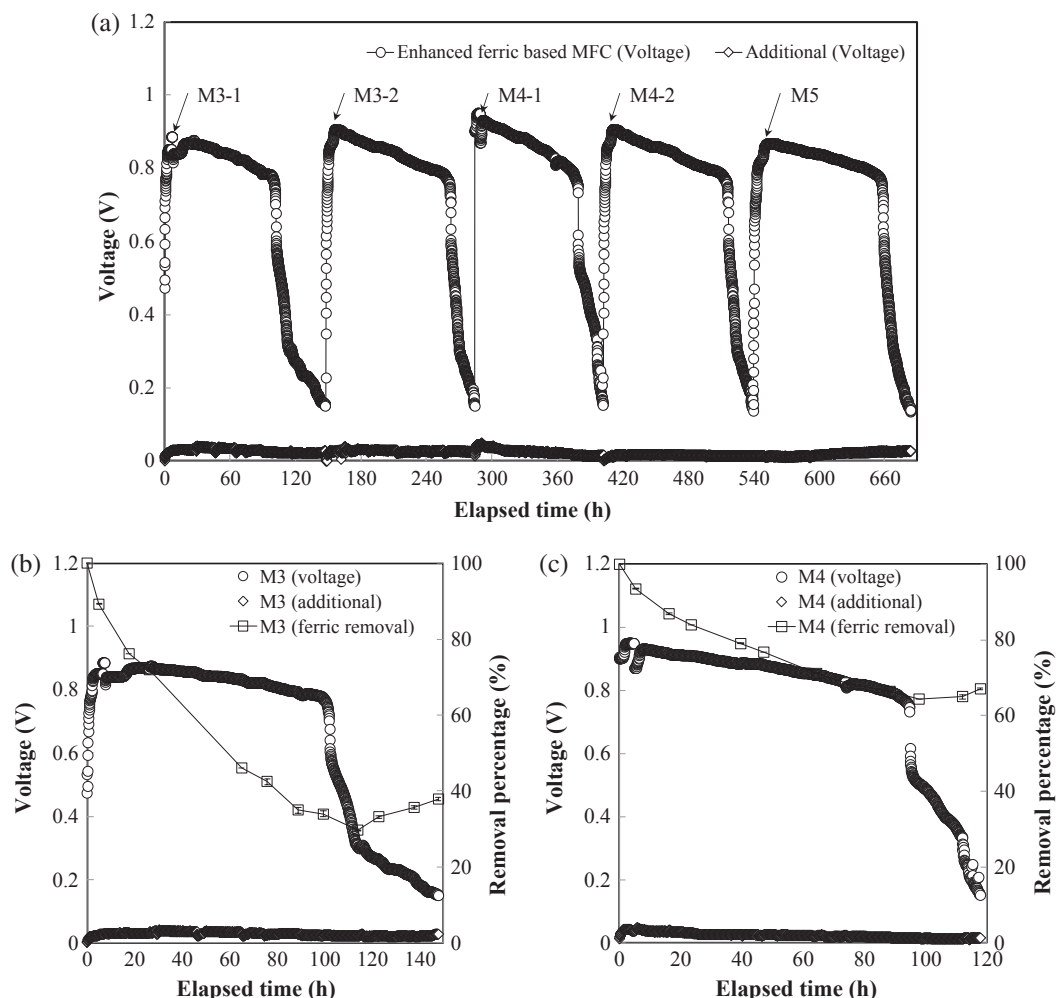


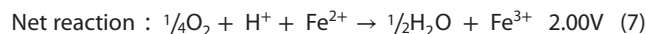
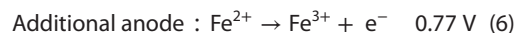
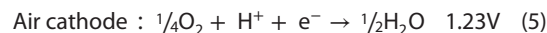
Figure 4. Cell voltage over the entire experimental operation period. (a) Expanded view of cell voltage and Fe(III) removal in accordance with different concentrations of catholytes in enhanced Fe(III)-based MFC with continuous Fe(II) oxidation: (b) 25 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA and (c) 50 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA.

could play, which enhances the voltage output. As these results suggest, the diffusion layer caused a noticeable decrease in the removal rate of Fe(III) in this type of system; the generated Fe(II) is incrementally oxidized by the dissolved oxygen that is present in the air cathode chamber (Fig. 4(b) and (c)). As a result, the enhanced Fe(III)-based MFC with the continuous Fe(II) oxidation system exhibits high performance and sustainability in its electricity generation due to the improved cathodic performance. As is shown in Fig. 4(a), when this experiment is conducted without refreshing the Fe(III), but with continuous oxidation of the resultant Fe(II), the generated main and additional voltages of this system were enhanced to 867 mV and 27 mV, respectively. Moreover, these voltage values were maintained for 120 h until the biological treatment for the removal of ethanolamine was completed. Although the pH value of the catholyte that was used in experiment M4 increases when it is reused in M5 (from 2.5 to 4.2), it seems that EDTA plays a key role in preventing Fe(III) precipitation under increased pH conditions. Thus, there is no loss in either the total Fe(III) concentration or the voltage output.

The additional voltage output was generated to enhance the re-oxidation of Fe(II) using additional anode and air cathode. The Fe(II) generated is oxidized at the additional anode and oxygen is

reduced at the air cathode using the Fe(II)-based FC. The reactions are as shown below.

$$E^0$$



Unlike maximum voltages based on thermodynamic relationships between additional anode and air cathode, the Fe(III)-based MFC with the continuous Fe(II) oxidation system did not generate a significant additional voltage output (around 20 mV at external resistance of 1000 Ω for both M3 and M4). This could be attributed to the characteristics of the PP mesh used as a separator. In a separate experiment that used an enhanced Fe(III)-based MFC with continuous Fe(II) oxidation, where a membrane was used as a separator between the anode electrode and the air cathode electrode (data not shown), a higher additional voltage

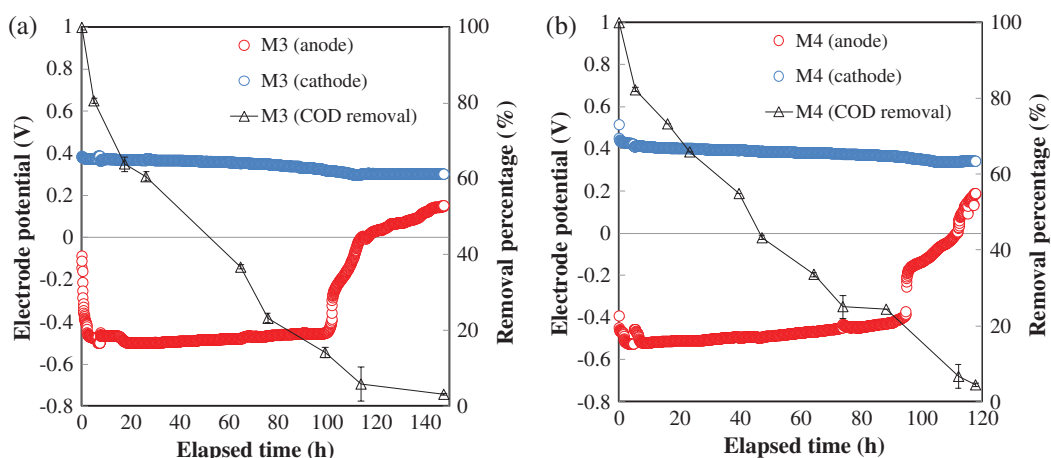


Figure 5. Anode and cathode potentials and COD removal in accordance with different concentrations of catholytes in enhanced Fe(III)-based MFC with continuous Fe(II) oxidation: (a) 25 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA and (b) 50 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA.

Table 1. Maximum power density, current density corresponding to a maximum power density, open circuit voltage (OCV), Coulombic efficiency (CE), initial and final pH values of anolyte and catholyte for different operating conditions

	M1	M2	M3	M4
Maximum power density (W m ⁻²)	0.78	0.9	0.8	1.4
Current density corresponding to a maximum power density (A m ⁻²)	1.25	1.34	1.26	1.68
OCV (mV)	917	937	899	987
CE (%)	18.63	21.78	22.86	23.03
Initial pH	Anolyte	7.05	7.19	7.04
	Catholyte	1.22	1.61	1.42
Final pH	Anolyte	6.34	6.16	5.63
	Catholyte	1.47	1.71	2.5

was generated (around 120 mV at external resistance of 1000 Ω for 100 h) compared with the experiments that utilized the PP mesh. However, according to reaction 7, the oxidation of 1 mole of Fe(II) requires 0.25 moles of dissolved oxygen, which is provided through the diffusion layer of the air cathode. As a result, using the membrane may lead to a decrease in the oxidation rate of the Fe(II) generated due to the much lower rate of oxygen diffusion relative to the PP mesh. The voltage output, cathode potential, Fe(III) removal, and maximum power density were determined to be similar to M1 (which utilized a traditional Fe(III)-based MFC). Thus, the separator CEM was supplanted with PP mesh in order to enhance the diffusion rate of oxygen for the effective regeneration of Fe(III). Even though the additional voltage output significantly decreased, we still obtained satisfactory results regarding the regeneration of Fe(III) in M3 and M4.

Electrode potential and COD removal of an enhanced Fe(III)-based MFC with continuous Fe(II) oxidation

The performance recorded in experiments M3 and M4 was also confirmed by the cathode potential values, which were measured in order to investigate the effect of the additional anode and air cathode (Fig. 5(a) and (b)). According to the comparison made between the experiments using the two types of MFC systems (Fe(III)-based MFC and enhanced Fe(III)-based MFC), the results appear to be similar for all stable anode potentials and COD removal rates. In this respect, the COD removal percentages of M3 and M4 were 96.9% and 95.5%, respectively. As was specified in a

previous study,²⁸ a system utilizing potassium Fe(III) cyanide and dissolved oxygen (provided by sparging with air) as two electron acceptors did not achieve any improvements in power generation. However, the cathode potential in experiment M3, which has the same concentration of Fe(III) as experiment M1, was stable until the completion of ethanolamine biodegradation; this was caused by the regeneration of Fe(III) by the oxygen that diffused into the chamber.

By-product formation

Apart from simultaneous achievement of ethanolamine treatment and Fe(III) regeneration with no additional energy consumption through the use of enhanced Fe(III)-based MFCs, there is also the need to dispose of the ammonium, which is an intermediate contaminant derived from the ethanolamine. Figure 6 shows the distribution of the ammonia, nitrate and nitrite concentrations in the anode and cathode chambers during experiments M1–M4. The concentrations of nitrate and nitrite remained almost unchanged in both Fe(III)-based MFC and enhanced Fe(III)-based MFC experiments. However, the concentration of the ammonium ions increases rapidly at the beginning of the process due to the decomposition of ethanolamine by the microorganisms. This was especially true in the experiments where the ethanolamine was enriched at the anode. Ammonium ions are transported through the membrane in the two-chamber MFCs via charge balancing between the anode and the cathode.²⁹ The diffusion of ammonium ions from the anode chamber to the cathode chamber

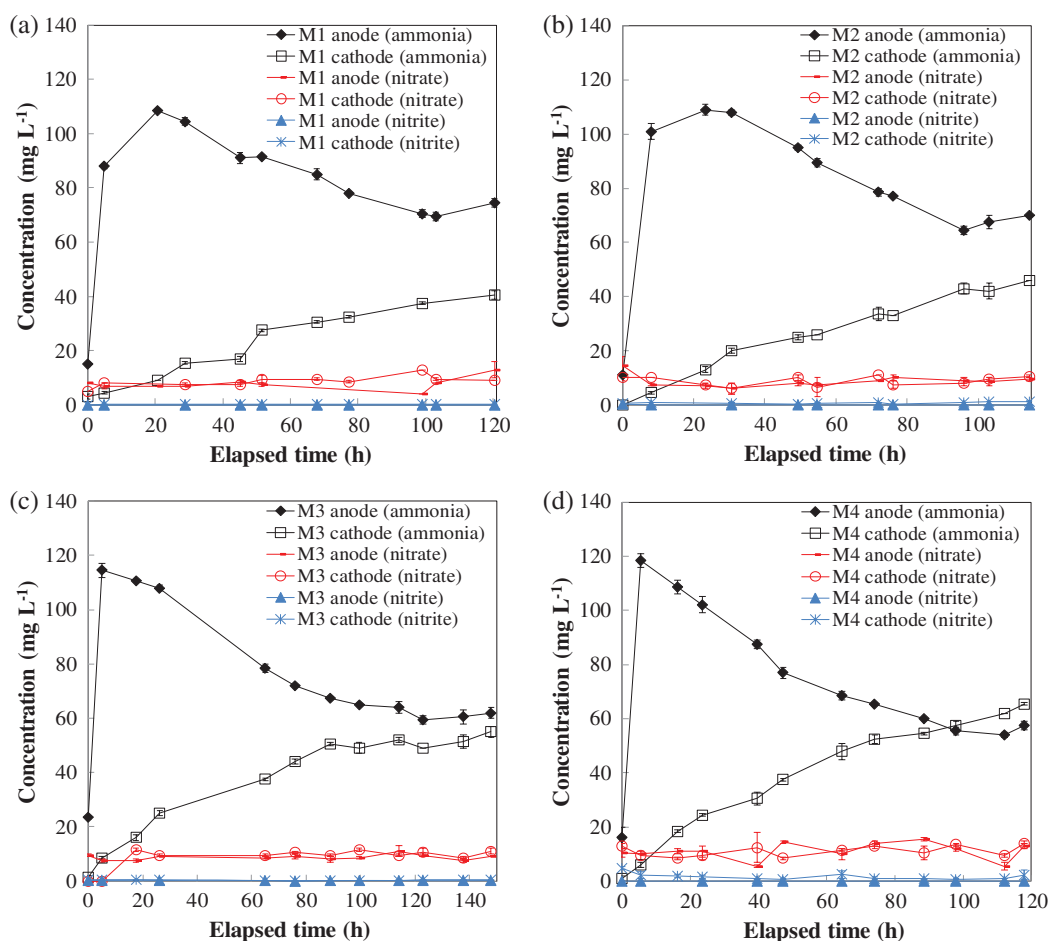


Figure 6. By-product formation in accordance with different concentrations of catholytes in the Fe(III)-based (a) and (b) and enhanced Fe(III)-based MFC experiments (c) and (d): (a), (c) 25 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA and (b), (d) 50 mmol L⁻¹ of Fe(III) with 10 mmol L⁻¹ EDTA.

occurs continuously until the concentrations in the two chambers are equilibrated. Consequently, the experimental results show that the ammonium concentration was significantly higher in the cathode chamber during all experiments. Moreover, our experimental results suggest that ammonia transportation from the anode chamber to cathode chamber was faster in the enhanced Fe(III)-based MFCs with continuous Fe(II) oxidation at the air cathode than it was in conventional Fe(III)-based MFCs. Due to the regeneration reaction of Fe(III), the pH values in the cathode increased from 1.42 to 2.5 in M3 and 1.33 to 2.11 in M4. Conversely, due to the absence of oxygen diffusion, the pH values did not significantly differ in M1 (from 1.22 to 1.47) or M2 (from 1.61 to 1.71). These results appear to be in good agreement with the results obtained by Kim *et al.*³⁰ They found that the presence of oxygen in the cathode chamber is responsible for a charge imbalance, which is caused by the loss of protons in the cathode chamber. Although this leads to an increase in the rate of ammonium ion diffusion from the anode chamber to the cathode chamber, which consequently causes an accumulation of ammonium ions in the cathode chamber, the performance of the MFC (in terms of power generation, voltage output and electrode potential) was not influenced by the presence of this by-product. In addition, the results obtained regarding the ammonia infiltration rate indicate that there are no problems with membrane fouling, which could be caused by the presence of microorganisms and iron during the experiments. However, further research is still required in order to

enhance the removal of ammonium from the treated effluents so that these waste products meet the required quality standards.

Power density, open circuit voltage (OCV) and CE

The performance obtained in experiments M1–M4, as evidenced by power density curves, is shown in Fig. 7. As can be seen from this figure, the power density curves indicate different power outputs depending on the cathode conditions. The values of maximum power density ranged from 0.78 to 1.4 W m⁻². Comparing the experimental results obtained in M1/M2 and M3/M4, it seems that the cathode performance was enhanced by increasing the concentration of Fe(III). Specifically, when the concentration of Fe(III) was increased from 25 to 50 mmol L⁻¹, the maximum power density for conventional Fe(III)-based MFCs increased from 0.78 to 0.9 W m⁻². In addition, the experiments with the enhanced Fe(III)-based MFCs show that the maximum power density obtained in M4 (1.4 W m⁻²) is higher than that obtained in M3 (0.8 W m⁻²). Thus, increased Fe(III) concentration correlates directly with enhanced cathode performance.

CE is directly proportional to the performance of MFCs in terms of their maximum power density. The calculated CE for M1 is 18.63% (corresponding to a maximum power density of 0.78 W m⁻²) and increases between M1 and M4 by 4.4% (the CE is 23.03% for M4, corresponding to a maximum power density of 1.4 W m⁻²). The OCV appears to have the same trend, with the exception of M3. It is also evident that increasing the Fe(III) concentration from

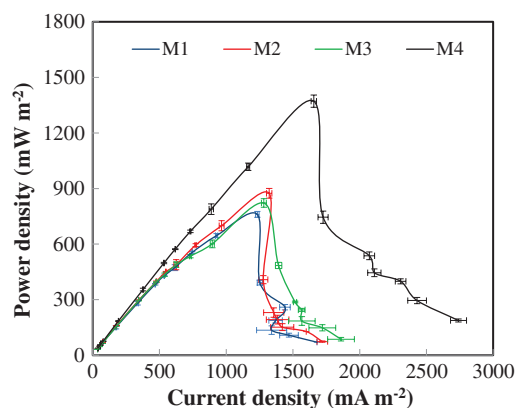


Figure 7. Power density curves as a function of current density for different operating conditions.

25 mmol L⁻¹ to 50 mmol L⁻¹ has a positive effect on both the CE and OCV; this observation can be correlated with the increasing maximum power density with higher Fe(III) concentration. Although these results share a common problem where low CE values are obtained when complex substrates are used in MFCs, the CE values obtained in this work are slightly enhanced compared with our previous experiments, which utilized single-chamber MFCs (approximately 18.2%). It is evident that the best performance in terms of OCV and CE was obtained in experiment M4, which used an air cathode for Fe(III) regeneration in the cathode chamber. These values indicate that a higher percentage of the organic matter could be effectively used to generate an electric current.

CONCLUSIONS

The use of 25 mmol L⁻¹ Fe(III) in a conventional Fe(III)-based MFC process, without any enhancement, led to an unsustainable voltage output. Although using 50 mmol L⁻¹ Fe(III) led to a sustainable voltage output, it was necessary to replenish the exhausted Fe(III) solution. A new, enhanced Fe(III)-based MFC with continuous Fe(II) oxidation in the cathode chamber was successfully developed. Using this system, a sustainable electric current can be generated, even at low concentrations of Fe(III) (i.e. 25 mmol L⁻¹ Fe(III)). This increased performance in terms of the electricity generated was associated with the regeneration process that is performed by using an additional anode and air cathode. We demonstrated that the favorable oxygen diffusion and Fe(II)-based FC in the cathode chamber leads to enhanced performance of the MFC in terms of the sustainability of the cathode potential and the possibility of reusing the iron solution. Moreover, we also confirmed that the highest maximum power density, OCV and CE were obtained in an enhanced Fe(III)-based MFC using a 50 mmol L⁻¹ Fe(III) concentration without the need for any additional energy consumption. However, because of the expensive components for enhanced MFC construction, such as the additional PP mesh and electrodes, further studies should be focused on how the potential problems under conditions using less expensive alternatives affect this utilized system.

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