Original Article

Application of a Dialysis-Based pH Control System to a Microbial Fuel Cell Using Ferric-EDTA Electron Acceptor

Naoyuki Kishimoto ^a, Hideto Yoshida ^b, Yoshitaka Murakami ^c

^a Department of Environmental Solution Technology, Ryukoku University, Otsu, Japan

^b Graduate School of Science and Technology, Ryukoku University, Otsu, Japan

^c Water Environment Division, Maezawa Kasei Industries, Kumagaya, Japan

ABSTRACT

A double-chamber microbial fuel cell (MFC) using ferric-EDTA chelates (Fe (III)-EDTA) as electron acceptors was developed and a dialysis-based system was introduced into the catholyte pH control in this research. In the developed MFC system, Fe (III)-EDTA was transformed into ferrous-EDTA (Fe (II)-EDTA) at cathodes, which was reused as electron acceptors after re-oxidation to Fe (III)-EDTA with a trickling filter-type oxidation column. The MFC operation using a pre-sedimented municipal wastewater revealed that the observed current density of the MFC using Fe (III)-EDTA reached 144 – 192 mA/m² that was much higher than that of the control using dissolved oxygen electron acceptors. The higher current density was attributed to the higher density of electron acceptors in the catholyte. The average coulombic efficiency of the MFC using Fe (III)-EDTA was 8.2%. When a conventional reagent-based pH control was applied, the electricity production of the MFC was deteriorated because of both the low temperature and the salt accumulation in catholyte derived from acid for pH control. On the contrary, the dialysis-based pH control successfully prevented the salt accumulation and maintained the higher current density. Thus, the introduction of Fe (III)-EDTA electron acceptors and the dialysis-based pH control system for catholyte was thought to be useful for operating the double-chamber MFC without any noble catalyst.

Keywords: dialysis, double-chamber microbial fuel cell, Fe (III)-EDTA, oxidation column, pH control

INTRODUCTION

A microbial fuel cell (MFC) is defined as a system that converts chemical energy of organic matter to electrical energy by catabolic activities of exoelectrogenic bacteria belonging to phyla Proteobacteria, Firmicutes, and others [1]. The exoelectrogenic bacteria have extracellular electron transfer mechanisms [2]. Therefore, they can catabolize organic compounds in wastewater and release electrons on their cell membranes, which are harvested with anodes in MFCs. The electrons harvested are transported to cathodes via an external circuit. Electron acceptors like molecular oxygen receive electrons at cathodes as follows:

The protons in equation (1) are produced by the microbial catabolic activities at anodes. When the composition of organic compound (electron donor) is expressed as C_aH_bO_c, the microbial catabolism at anodes is formulated as follows:

The MFC performance is influenced by many factors like electrode materials, pH buffer, electrolyte, and proton exchange systems among others through ohmic loss, activation loss, bacterial metabolic loss, and concentration loss [3,4]. Moreover, it was pointed out that the cathodic reaction (reaction (1)) was rate-determining for many MFCs [5]. To enhance the cathodic reaction, noble catalysts like platinum are introduced into cathodes for enhancing the reaction (1)

Corresponding author: Naoyuki Kishimoto, E-mail: naoyuki@rins.ryukoku.ac.jp

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[3] and single-chamber MFCs with air cathodes are widely used for avoiding concentration polarization of molecular oxygen near cathodes [6]. Although the MFC performance can be improved by these countermeasures, a few problems still remain, namely the high cost and short lifetime of catalysts and the low physical strength of air cathode. On the former problem, non-platinum and economical catalysts have been developed [7,8], though their lifetimes need to be further investigated. On the latter problem, air cathodes are usually composed of cation-exchange membranes and carbon-based porous cathodes, and are installed into a side of anodic chamber of MFC. Since the outside of air cathode is exposed to the air and the inside is contacted with water, the air cathode receives water pressure from the inside to the outside. Accordingly, it is difficult to scale up the MFC with air cathodes, because a larger pressure load may damage the air cathode.

A double-chamber MFC may be a countermeasure against the water pressure load problem. Since both sides of cathode in a double-chamber MFC are contacted with water, namely anolyte (wastewater) and catholyte, water pressure from the anolyte balances that from the catholyte. However, the solubility of molecular oxygen in water is low. Therefore, oxygen supply to cathodes usually restricts the MFC performance. Although an introduction of a substitute electron acceptor like ferricyanide can enhance the cathodic reaction and improve the MFC performance [9], it is difficult to use ferricyanide for a practical application due to its toxicity and slow re-oxidation rate by oxygen [5]. Instead of the harmful ferricyanide, Aelterman *et al.* [10] introduced ferric-chelate compounds with the ligand of ethylenediaminetetraacetic acid (Fe (III)-EDTA), nitrilotriacetic acid (Fe (III)-NTA), succinate (Fe (III) succinate), or citrate (Fe (III) citrate) into the catholyte. Although the ferric-chelate compounds tested showed higher open circuit voltages than the control, the re-oxidation characteristics of their reduced form, namely ferrous-chelate compounds, by aeration were different from each other: the highest in Fe (III)-EDTA and the lowest in Fe (III) citrate and Fe (III) succinate. As a result, Fe (III)-EDTA generated the highest continuous current of the four. Santana-Casiano *et al.* [11] reported that the addition of EDTA enhanced the oxidation rate of ferrous ion (Fe^{2+}) by oxygen, though other organic ligands like ethylenedioxidiethylene-dinitrilotetraacetic acid (EGTA), cysteine, and others did not show such an effect. Thus, EDTA seems to be a suitable ligand to chelating ferric ion (Fe^{3+}) as an electron acceptor.

In consideration of the aforementioned problems and previous researches on iron-chelate compounds, a double-

chamber MFC using Fe (III)-EDTA as an electron acceptor was used in this research. When Fe (III)-EDTA is used, it will act as a one-electron acceptor as is inferred from the corresponding redox couple of the MFC electrode reaction [3].

The product of Fe (II)-EDTA in reaction (3) should be re-oxidized into Fe (III)-EDTA by molecular oxygen for reuse. The overall oxidation reaction from Fe (II)-EDTA to Fe (III)-EDTA will be expressed as equation (4) according to the analogy of Fe^{2+} oxidation by molecular oxygen [12].

In the MFC system developed, the used catholyte was exposed to the air using a trickling filter-type oxidation column to cut down the aeration power for oxygen supply. When Fe (III)-EDTA is used as the electron acceptor, the cathodic reaction (reaction (3)) does not consume any proton. However, protons are consumed at the re-oxidation step of Fe (II)-EDTA to Fe (III)-EDTA (reaction (4)) by combined with hydroxide ion. Accordingly, it is expected to increase the catholyte pH during the operation of the MFC. Thus, a pH control system should be introduced to the MFC system for regulating the catholyte pH. Two pH control systems, a reagent-based system and a dialysis-based system, were introduced and their efficacies were discussed in this research.

MATERIALS AND METHODS

Experimental Apparatus

Figure 1 shows the structures of MFC unit and dialysis cell. The MFC unit had a flow cell structure. The inside of the flow cell was a cathodic chamber and the outside was an anodic chamber. Each side of the cathodic chamber was separated from the anodic chamber with a cation-exchange membrane (Nafion N117, DuPont, Wilmington, DE, USA) that was sandwiched with two carbon cloths for anode and cathode (Torayca CO6151B, Toray, Tokyo, Japan). The projected anode area was equal to the projected cathode area of 200 cm^2 . The spacer and covers of the MFC unit were made of polyvinylchloride plate with 5-mm thickness. The MFC unit was installed into an anodic chamber as shown in Fig. 2. The effective volumes of cathodic cell and anodic chamber were 70 mL and 867 mL, respectively.

The dialysis cell had two cells: a catholyte cell and an acid cell. Both cells were separated with a cation-exchange mem-

Fig. 1 Longitudinal sections of (a) MFC unit and (b) dialysis unit.

brane (Nafion NE-1110, DuPont, Wilmington, DE, USA), whose effective area was 32.2 cm². The spacer and the cover were made of 5-mm silicon rubber sheet and 5-mm acrylic resin plate, respectively. The effective volume of each cell was 16.1 mL.

The experimental setup was illustrated in **Fig. 2**. The MFC system was composed of the MFC unit, the anodic chamber, a catholyte reservoir, a trickling filter-type oxidation column, and a pH control system for catholyte. The catholyte reservoir stored 800 mL of Fe (III)-EDTA chelate solution containing 5 mM of iron (III) chloride and 10 mM of disodium ethylenediaminetetraacetate (Na₂EDTA). The catholyte pH was set to 7 by adding sodium hydroxide, because some precipitates were sometimes observed at a higher pH and a deterioration of the MFC performance was apprehended by using acidic catholyte [13] due to damage to exoelectrogenic bacteria by the acidic pH [14,15]. The oxidation column (trickling filter) was made of an acrylic pipe (26 mm in inner diameter and 1,000 mm in length), whose bottom was covered with a polyethylene plastic net with 5-mm apertures. The column was filled with 63 g of cylindrical media with a gear-shaped cross section made of high-density polyethylene with 5 mm diameter and 5 mm length (Dainippon Plastics,

Osaka, Japan). The apparent volume of the packed bed was 314 mL. Two pH control systems were used in this study, namely a reagent-based system and a dialysis-based system. The former was composed of a pH controller (FD-02, TGK, Tokyo, Japan), an acid reservoir storing 7-N sulfuric acid, and a peristaltic pump (MP-1000, EYELA, Tokyo, Japan) for adding sulfuric acid to the catholyte reservoir. The latter was composed of a pH controller (FD-02, TGK, Tokyo, Japan), the dialysis cell, an acid reservoir storing 20-mM hydrochloric acid (HCl), a peristaltic pump (SMP-23, EYELA, Tokyo, Japan) for pumping the catholyte and the 20-mM HCl to the dialysis cell, and an electromagnetic cock with three connectors.

Confirmation of Oxidation of Fe (II)-EDTA Using the Oxidation Column

When Fe (III)-EDTA are used as electron acceptors, they are transformed into Fe (II)-EDTA at the cathodes, which should be re-oxidized into Fe (III)-EDTA with the trickling filter-type oxidation column for reutilization. Therefore, the oxidation ability of the oxidation column from Fe (II)-EDTA to Fe (III)-EDTA was investigated as follows: 5 mM of Fe (II)-EDTA solution was prepared by dissolving iron (II)

(a) MFC with a reagent-based pH control system

(b) MFC with a dialysis-based pH control system

Fig. 2 Experimental setup of MFC systems with (a) a reagent-based and (b) a dialysis-based pH control system. The “P” and “T” symbolize a peristaltic pump and an electro-magnetic cock, respectively.

sulfate and Na_2EDTA into deionized water. The solution was adjusted to pH 7 using sulfuric acid and sodium hydroxide. Then, the Fe (II)-EDTA solution was fed into the oxidation

column described in Experimental Apparatus section at the sprinkling rate of 1.0 – 8.0 mL/min, which was equivalent to the volumetric hydraulic loading of 4.6 – 36.7 $\text{m}^3/(\text{m}^3 \cdot \text{d})$. The

effluent from the oxidation column was not circulated and was sampled for the absorbance measurement at 400 nm with a spectrophotometer (UV-1600, Shimadzu, Kyoto, Japan). In this experiment the following equations were established.

$$C_{\text{Fe}} = C_{\text{Fe(II)}} + C_{\text{Fe(III)}} \quad (5)$$

$$A = \varepsilon_{\text{Fe(II)}} C_{\text{Fe(II)}} + \varepsilon_{\text{Fe(III)}} C_{\text{Fe(III)}} \quad (6)$$

C_{Fe} : initial Fe (II)-EDTA concentration (= 5 mM)

$C_{\text{Fe(II)}}$: Fe (II)-EDTA concentration in effluent [mM]

$C_{\text{Fe(III)}}$: Fe (III)-EDTA concentration in effluent [mM]

A: absorbance of effluent at 400 nm [1/cm]

$\varepsilon_{\text{Fe(II)}}$: molar extinction coefficient of Fe (II)-EDTA [L/(mmol·cm)]

$\varepsilon_{\text{Fe(III)}}$: molar extinction coefficient of Fe (III)-EDTA [L/(mmol·cm)]

Finally, $C_{\text{Fe(III)}}$ can be determined by solving equations (5) and (6) as follows:

$$C_{\text{Fe(III)}} = \frac{\varepsilon_{\text{Fe(II)}} C_{\text{Fe}} - A}{\varepsilon_{\text{Fe(II)}} - \varepsilon_{\text{Fe(III)}}} \quad (7)$$

The molar extinction coefficients obtained by the preliminary spectrophotometric observations were 0.0333 L/(mmol·cm) for Fe (II)-EDTA and 0.1680 L/(mmol·cm) for Fe (III)-EDTA. The oxidation rate of Fe (II)-EDTA to Fe (III)-EDTA was calculated from the following equation.

$$R_{\text{Ox}} = \frac{C_{\text{Fe(III)}} Q}{1000} \quad (8)$$

R_{Ox} : oxidation rate of Fe (II)-EDTA with the oxidation column [mmol/min]

Q: sprinkling rate to the oxidation column [mL/min]

Experimental Procedure for MFC Operation

Two series of experiments were performed in this study. The objective of the first series (Run 1) was to elucidate the efficacy of Fe (III)-EDTA electron acceptor on the MFC performance. The second series (Run 2) aimed to clarify the effect of the dialysis-based pH control system.

In the first series, two sets of MFC systems (Run 1-Fe and 1-C) were simultaneously operated. Both systems were equipped with the same reagent-based pH control system (Fig. 2 (a)). The Fe (III)-EDTA solution was used for Run 1-Fe, but tap water instead of the Fe (III)-EDTA solution was used for Run 1-C as a control. The operational conditions except catholyte were the same for both runs. Pre-sedimented

municipal wastewater containing toilet flushing, grey water, and a restaurant wastewater from Ryukoku University was flowed into the anodic chamber at a hydraulic retention time of 4 h. The catholyte was circulated between the MFC unit and the catholyte reservoir via the trickling filter at a flow rate of 1.4 – 1.5 mL/min. The threshold of the pH controller was set at pH 7.0. Before experimental runs started, the MFC systems were operated for 35 days using tap water as catholyte for acclimation. Then, the catholyte was replaced by the Fe (III)-EDTA solution for Run 1-Fe and new tap water for Run 1-C.

Two sets of MFC systems were also used in the second series (Run 2-R and 2-D). The MFC system configuration for Run 2-R was the same as that for Run 1-Fe (Fig. 2 (a)), whereas the MFC system with the dialysis-based pH control system was used in Run 2-D (Fig. 2 (b)). The operation program of the dialysis system was as follows: When the catholyte pH was more than 7.0, the line [A]–[B] of the electromagnetic cock shown in Fig. 2 (b) was opened and the catholyte and the diluted HCl was supplied to the dialysis cell with the peristaltic pump. In the dialysis cell, protons in the diluted HCl were diffused into the catholyte through the cation-exchange membrane by the concentration-driven diffusion. When the catholyte pH dropped off to less than 7.0, the peristaltic pump was switched off and the line [B] – [C] of the electromagnetic cock was opened. As a result, the diluted HCl in the dialysis cell was discharged into the acid reservoir by gravity. Before experimental runs started, the MFC systems were operated for 18 days using Fe (III)-EDTA as the electron acceptor and the reagent-based pH control system for acclimation. Then, the dialysis-based pH control system was introduced into Run 2-D and the catholyte for both systems was replaced by new Fe (III)-EDTA solution.

Analytical Procedure

Each MFC unit was connected to a 5-Ω cement resistor and the terminal voltage was continuously monitored with a data logger (GL-220, Graphtec, Yokohama, Japan). The electric current through the external circuit was evaluated from the terminal voltage by Ohm's law. The current density was calculated as the electric current divided by the projected anode area. The coulombic efficiency was evaluated as follows:

$$CE = \frac{\alpha \times I}{\Delta COD \times Q \times F} \times 100 \quad (9)$$

CE: coulombic efficiency [%]

α : conversion factor from electrons to COD (= 8 mg-COD/

Table 1 Water quality of pre-sedimented influent wastewater.

Index	Run 1	Run 2
BOD	317 ± 111 mg/L	315 ± 80 mg/L
D-BOD	201 ± 43 mg/L	219 ± 67 mg/L
COD	570 ± 181 mg/L	633 ± 434 mg/L
D-COD	397 ± 64 mg/L	300 ± 135 mg/L
D-N	38.5 ± 13.0 mg/L	43.1 ± 21.0 mg/L
NH ₃ -N	31.5 ± 9.3 mg/L	38.2 ± 22.9 mg/L
NO _x -N	0.0 ± 0.0 mg/L	0.0 ± 0.0 mg/L
D-P	9.1 ± 1.6 mg/L	10.1 ± 3.8 mg/L
PO ₄ -P	8.5 ± 2.1 mg/L	9.3 ± 3.5 mg/L
SS	192 ± 21 mg/L	53.7 ± 36.1 mg/L
pH	7.3 ± 0.4	7.0 ± 0.4
Water temperature	25.2 ± 3.4°C	12.8 ± 1.9°C

Average ± sample standard deviation

mmol-electron)

I: observed current [mA] Δ COD: difference of dissolved COD in influent and in effluent [mg-COD/L]*Q*: flow rate of wastewater (= 6.0×10^{-5} L/s)*F*: Faraday's constant (= 96,485 mC/mmol)

Samples of influent to and effluent from the anodic chamber were analyzed about three times a week. Chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD), total nitrogen (T-N), ammonia nitrogen (NH₃-N), nitrite and nitrate nitrogen (NO_x-N), total phosphorus (T-P), orthophosphate (PO₄-P), and suspended solids (SS) concentrations were determined according to the Standard Methods [16]. Iron concentration in catholyte was measured by inductively coupled plasma spectrometry (Optima 5300 DV, Perkin Elmer, Waltham, MA, USA) after acidifying water samples with nitric acid. Water temperature and pH were monitored with a temperature data logger (TM-947SD, T&D, Matsumoto, Japan) and a pH meter (B-212, Horiba, Kyoto, Japan), respectively. **Table 1** summarizes water quality of influent wastewater. Electrical conductivity (EC) of catholyte was measured with an EC meter (B-173, Horiba, Kyoto, Japan) at Run 2. The significance of the difference in water quality of effluent between experimental runs was checked by the paired *t*-test using water quality data sampled at the same time.

RESULTS AND DISCUSSION

Oxidation of Fe (II)-EDTA Using the Oxidation Column

Figure 3 shows dependencies of Fe (III)-EDTA concentration in effluent from the oxidation column and Fe (II)-EDTA oxidation rate on the sprinkling rate. The Fe (III)-EDTA was detected by passing the Fe (II)-EDTA solution through the oxidation column. Thus, it was inferred that the Fe (II)-EDTA was oxidized by oxygen in the air as previously reported [10,11].

The Fe (III)-EDTA concentration in the effluent decreased with the increase in the sprinkling rate, though the Fe (II)-EDTA oxidation rate increased with the sprinkling rate. However, the slope of the graph of the Fe (II)-EDTA oxidation rate in **Fig. 3** gradually decreased over the sprinkling rate. This means that the oxidation efficiency, namely the oxidation rate per sprinkling rate, was decreased with the increase in sprinkling rate. In a trickling filter, oxygen is dissolved through an interface between thin water films on filter media and the air. Accordingly, the oxygen dissolution flux depends on the interfacial area and is independent of the thickness of water films. Logan *et al.* [17] reported that the thickness of thin water film on the filter media was proportional to the 0.5 power of hydraulic loading that was proportional to the sprinkling rate. Therefore, the increase in sprinkling rate decreases both specific interfacial area of water film on the filter media and hydraulic retention time in the oxidation column, and results in lowering oxidation efficiency through decreasing oxygen supply per water volume in the oxidation column. As a result of this oxidation test, a

Fig. 3 Dependencies of Fe (III)-EDTA concentration in effluent from the oxidation column and Fe (II)-EDTA oxidation rate on the trickling rate. The solution containing 5 mM Fe (II)-EDTA was sprinkled into the oxidation column. Arrows denote the corresponding vertical axis.

Fig. 4 Changes in current densities over time. The catholyte used was a solution containing 5-mM FeCl₃ and 10-mM Na₂EDTA at pH 7 for Run 1-Fe and a tap water at pH 7 for Run 1-C.

Table 2 Water quality, current density, and coulombic efficiency at Runs 1-Fe and 1-C during the first 15 days of operation.

Index	Influent	Run 1-Fe	Run 1-C
BOD	300 ± 51 mg/L	246 ± 47 mg/L	268 ± 61 mg/L
COD	515 ± 79 mg/L	435 ± 73 mg/L	488 ± 91 mg/L
D-COD	425 ± 68 mg/L	368 ± 81 mg/L	360 ± 72 mg/L
D-N	39.1 ± 6.2 mg/L	33.8 ± 9.2 mg/L	31.4 ± 7.9 mg/L
NH ₃ -N	32.8 ± 7.3 mg/L	29.9 ± 4.7 mg/L	29.0 ± 7.4 mg/L
D-P	9.6 ± 1.9 mg/L	8.1 ± 2.0 mg/L	8.1 ± 2.6 mg/L
PO ₄ -P	9.0 ± 2.0 mg/L	7.5 ± 1.8 mg/L	7.7 ± 2.0 mg/L
Current density	–	169 ± 14 mA/m ²	4.2 ± 1.9 mA/m ²
Coulombic efficiency	–	8.2%	0.2%

Average ± sample standard deviation

low-circulation flow rate of 1.4 – 1.5 mL/min was used in the following MFC operation.

Applicability of Fe (III)-EDTA Chelate Solution

Changes in current density observed are depicted in **Fig. 4**. The current density at Run 1-Fe was in the range of 144 – 192 mA/m² during the first 15 days of operation, whereas that at Run 1-C was less than 10 mA/m². Thus, Fe (III)-EDTA contributed to enhance the cathodic reaction, which improved the total performance of MFC. At Run 1-C the main electron acceptor was dissolved oxygen that was supplied from the air in the trickling filter. Oxygen receives electrons at cathodes as reaction (1). Since the saturated oxygen concentration at 25°C was 8.5 mg/L (0.266 mM) [18], oxygen-saturated water contains 1.06 mM-electron equivalent of electron acceptor. At Run 1-Fe Fe (III)-EDTA was used as electron acceptor. It receives an electron as reaction (3). Since the Fe (III)-EDTA concentration in the catholyte was 5 mM, the catholyte contained 5 mM-electron equivalent of electron acceptor. In addition to Fe (III)-EDTA, dissolved oxygen also acted as electron acceptor. Accordingly, the electron acceptor concentration of catholyte at Run 1-Fe was about 5 – 6 times higher than that at Run 1-C. The higher concentration of electron acceptor was inferred to accelerate the diffusion-controlled rate of the cathodic reaction and enhanced the MFC performance. The similar enhancement of MFC performances by Fe (III)-EDTA was observed by Aelterman *et al.* [10].

The current density observed at Run 1-Fe tended to decrease since about 15 days of elapsed time and finally dropped to 20 mA/m² (**Fig. 4**). It is known that the MFC performance is strongly affected by water temperature. No successful operation of a MFC was observed at a low temperature of 15°C, whereas the MFC functioned well at 22°C or higher after a lag phase of less than 60 h [19]. In this study

water temperature was kept over 20°C during the operation as shown in **Table 1**. Accordingly, water temperature was not a causation of the current density drop after 15 days of operation. Instead of temperature effect, it was observed that the color of catholyte at Run 1-Fe changed from light yellow to orange during the operation and the viscosity of catholyte seemed to be increased. The reagent-based pH control system was used at Run 1, which intermittently added 7-N sulfuric acid to the catholyte for pH control. In the catholyte, protons supplied by H₂SO₄ addition were consumed in the oxidation column by combining with hydroxide ions produced through equation (4). However, sulfate ions were not consumed at all and were not discharged from the catholyte, because the catholyte was separated from anolyte with a cation-exchange membrane that was unable to permeate anions like sulfate ion. Accordingly, it was inferred that the accumulation of sulfate ions caused the viscosity increase of catholyte and the current density drop with the extended operation.

Table 2 summarizes the water qualities of influent wastewater and effluent, current densities, and coulombic efficiencies at Runs 1-Fe and 1-C during the first 15 days of operation. The D-COD removal efficiency showed only 13 – 15%, probably due to the small ratio of anode area to anodic chamber volume (231 cm²/L) and short hydraulic retention time (4 h). The paired *t*-test revealed that the difference in effluent water quality between Run 1-Fe and Run 1-C was statistically insignificant under the significance level of 5% (*n* = 6). The *CE* at Run 1-Fe was estimated to be 8.2%, whereas that at Run 1-C was only 0.2%. He *et al.* observed the *CE* of 0.7 – 8.1% for an upflow MFC treating a sucrose-containing artificial wastewater and reported that methanogenic activity accounted for 35 – 58% of D-COD removal [20]. Although methanogenic activity was not measured in this research, anaerobic bacteria like methanogenic ones were inferred to

Fig. 5 Changes in current densities over time. The catholyte pH control was performed with a reagent-based system for Run 2-R and a dialysis-based system for Run 2-D. The catholyte for both runs was the same as that used in Run 1-Fe.

mainly contribute to the D-COD removal at Runs 1-Fe and 1-C.

Efficacy of Dialysis-Based pH Control

Figure 5 shows the current density observed at Run 2. The observed current density at Run 2-D increased after the elapsed time of 7 days. This current density change indicated that the acclimation of MFCs required the preliminary operation of 25 days instead of 18 days. Although the MFC system at Run 2-R was the same as that at Run 1-Fe, the observed current density at Run 2-R was much smaller than that at Run 1-Fe. The water temperature was kept around 15°C or less as shown in **Table 1**. Therefore, the inactivation of exoelectrogenic bacteria by the low temperature [19] was inferred to result in the low current density. Despite the low temperature, the MFC system with the dialysis-based pH control (Run 2-D) was superior in current density to that with the reagent-based pH control (Run 2-R). The observed current density after 10 days of operation was 39.8 ± 7.8 mA/m² at Run 2-D and 9.3 ± 6.3 mA/m² at Run 2-R (average $\pm$ sample standard deviation). **Figure 6** depicts the observed EC of catholytes during the operation. The catholyte EC

at Run 2-R increased steadily during the operation due to sulfate accumulation and finally reached 6.9 mS/cm that was 2.3-times higher than the initial EC. It was reported that the oxidation rate of Fe (II)-EDTA by oxygen was lowered with the increase in ionic strength [11]. Moreover, the oxidation of Fe (II)-EDTA by oxygen is a pure chemical reaction, whose rate usually dropped with lowering temperature. Accordingly, the sulfate accumulation and low temperature synergistically lowered the current density at Run 2-R. Contrary to Run 2-R, the catholyte EC at Run 2-D did not increase during the operation, which showed that the dialysis system successfully regulated the catholyte pH without salt accumulation.

Despite the successful pH control with the dialysis-based system, a slight decrease in the catholyte EC was observed at Run 2-D (**Fig. 6**). Therefore, it was apprehended that part of iron was lost by the diffusion-driven discharge from catholyte to anolyte via the cation-exchange membrane. The initial and final iron concentrations in catholyte at Run 2-D were 279 and 257 mg/L, respectively. The decreasing rate of iron concentration was 8%, whereas the decreasing rate of catholyte EC was 23%. Accordingly, the decrease in catho-

Fig. 6 Changes in electrical conductivities of catholyte over time. The catholyte pH control was performed with a reagent-based system for Run 2-R and a dialysis-based system for Run 2-D. The catholyte for both runs was the same as that used in Run 1-Fe.

lyte EC did not necessarily accompany the iron loss. Since EDTA is a typical aminocarboxylic ligand containing two tertiary amino groups and four carboxyl groups, it can form chelate compounds with ferric ions as follows:

where K is a stability constant [21]. Based on these equilibriums, more than 99.9% of ferric ions in the catholyte formed Fe (III)-EDTA chelates in this study (pH 7) and more than 99.9% of Fe (III)-EDTA chelates was estimated to be an anionic form of $[\text{Fe} \cdot \text{EDTA}]^{-}$. Therefore, it was natural that iron was retained in the catholyte. **Figure 7** shows the concept of cation behaviors in the MFC system.

The catholyte contacted with acid solution (20 mM HCl) in the dialysis cell and wastewater (anolyte) in the MFC through cation-exchange membranes. Accordingly, cations transported through the cation exchange membranes by concentration-driven diffusion. Since both the wastewater and the catholyte showed pH around 7, the diffusion of protons between them could be almost ignored. Instead, protons were supplied from the acid solution to the catholyte because of higher proton concentration in the acid solution. The protons supplied to the catholyte were finally transformed into water by combining hydroxide ions that were supplied from the oxidation column by reaction (4). When protons in the acid solution were diffused into the catholyte, other cations should be supplied to the acid solution for the conservation of charge. Such a cation supply was caused by diffusive transport of cations from the catholyte to the acid solution, because concentrations of cations (except proton in the acid solution) were equal to or lower than those in the catholyte. The cations transported into the acid solution were basically supplied from the wastewater by the diffusive mass transfer. Finally, two possible mechanisms were inferred to cause the

Fig. 7 Behaviors of cations in the MFC system with the dialysis-based pH control. M^{n+} depicts a cation except proton, such as sodium, potassium, calcium, and magnesium ions. The dashed arrow means the diffusive mass transfer through the cation-exchange membrane.

slight decrease in EC in catholyte: the penetration of water from anolyte to catholyte and the diffusive mass transfer of cations. The EC of influent wastewater (anolyte) was in the range of 0.5 – 0.6 mS/cm that was lower than the EC of catholyte (3.0 mS/cm). Accordingly, the former process was caused by osmotic pressure. Since Na_2EDTA was used as the EDTA source in this study, the catholyte initially contained 20 mM of sodium ion (Na^+) that was much higher than the Na^+ concentration in wastewater (anolyte) and 20-mM HCl solution. Accordingly, Na^+ was transported to the wastewater and 20-mM HCl solution by diffusion and other cations except Na^+ was supplied to the catholyte in compensation for the Na^+ loss. Since the equivalent conductivity of Na^+ is lower than that of other cations like ammonium, potassium, calcium, and magnesium ions [22], the latter process gave a pressure to decrease the EC to the catholyte.

The D-COD in the effluent from the anodic chamber was 220 ± 95 mg/L for Run 2-R and 240 ± 105 mg/L for Run 2-D (average $\pm$ sample standard deviation). The paired *t*-test revealed that the difference in D-COD between both runs was statistically insignificant under the significance level of 5% ($n = 13$). The average D-COD removal efficiencies were 27% for Run 2-R and 20% for Run 2-D and the average *CEs* were only 0.3% for Run 2-R and 0.9% for Run 2-D. As aforementioned, the inactivation of exoelectrogenic bacteria by low temperatures was thought to result in the low *CE*.

CONCLUSIONS

A double-chamber MFC using Fe (III)-EDTA chelates as electron acceptors was developed and a dialysis-based system was introduced to the catholyte pH control of MFC in this research. In the developed MFC system Fe (III)-EDTA chelates were transformed into Fe (II)-EDTA chelates at cathodes, which were reused as electron acceptors after re-oxidation to Fe (III)-EDTA with a trickling filter-type oxidation column.

It was proved that Fe (III)-EDTA functioned well as an electron acceptor and was reusable by passing through the oxidation column. When the MFC system was applied to a pre-sedimented municipal wastewater containing BOD of 300 mg/L and D-COD of 425 mg/L on average, the observed current density of the MFC using ferric-EDTA electron acceptors reached 144 – 192 mA/m² that was much higher than that of the control using dissolved oxygen electron acceptors (less than 10 mA/m²). The higher current density was attributed to the higher density of electron acceptors in the catholyte. The average coulombic efficiency (*CE*) of the MFC using Fe (III)-EDTA electron acceptors was 8.2%, whereas the *CE* of the control was only 0.2%. However, the D-COD removal efficiency remained 13 – 15%, probably due to the small ratio of anodic area to anodic chamber volume (231 cm²/L) and short hydraulic retention time (4 h).

The MFC performance using a dialysis-based pH control system was compared with that using a reagent-based pH control system. Since water temperature during the operation was low, around 15°C or less, the average current density of the MFC using the dialysis-based pH control system remained 39.8 mA/m². However, this current density was higher than that of the control using the reagent-based pH control system (9.3 mA/m²). The low current density using the reagent-based system was attributed to both the low temperature and the accumulation of sulfate ions in the catholyte, which came from sulfuric acid used for pH control. Such a salt accumulation was prevented by introducing the dialysis-based system, though the EC of catholyte slightly decreased due to osmotic pressure-driven water penetration from anolyte to catholyte and diffusive mass transfer of cations through the cation-exchange membranes. Consequently, the introduction of ferric-EDTA as electron acceptors and the dialysis-based pH control system for catholyte was thought to be useful for operating the double-chamber MFC without any noble catalyst like platinum.

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