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Preliminary Evaluation of a Microbial Fuel Cell Treating Artificial Dialysis Wastewater using Graphene Oxide

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Abstract. Artificial dialysis wastewater (ADWW) generally contains 800–2,200 mg L\textsuperscript{-1} of organic matter. Prior to its discharge to the sewage system, ADWW must be treated in order to reduce organic matter to less than 600 mg L\textsuperscript{-1}. This study assesses the applicability of a microbial fuel cell (MFC) to the reduction of organic matter in ADWW as an alternative pre-treatment system to aeration. In the MFC, conductive floccular aggregates microbially produced from graphene oxide (GO-flocs) were applied as an anode material in the MFC. The GO-flocs were obtained by anaerobic incubation of graphene oxide (GO) with microorganisms in ADWW at 28 °C for a minimum of 10 days. During incubation, GO in the mixture was transformed into black conductive floccular aggregates having 0.12 mS cm\textsuperscript{-1}, suggesting the microbial reduction of GO to the reduced form. The produced GO-flocs were then used as the anode material in a cylindrical MFC, which was filled with ADWW and covered with a floating, platinum (Pt)-coated carbon cathode. The MFC was polarized via an external resistance of 10 Ω and applied for 120 days by replacing half of the supernatant of the MFC with fresh ADWW, every 6–9 days. As a result, the MFC achieved a 128 mg L\textsuperscript{-1} d\textsuperscript{-1} chemical oxygen demand (COD Cr) removal rate. For example, the MFC contained 1,500 mg-COD Cr L\textsuperscript{-1} just after replacement, with this concentration being reduced to 1,000 mg-COD Cr L\textsuperscript{-1} after 6–9 days of incubation. At the same time, the MFC showed an average power density of 28 mW m\textsuperscript{-2} and a maximum power density of 291 mW m\textsuperscript{-2}. These results suggest that a MFC packed with GO-flocs can be used as an alternative biotreatment system, replacing the energy-intensive aeration process.

INTRODUCTION

The number of dialysis patients in Japan is estimated at approximately 300,000 [1]. This is responsible for the production of artificial dialysis wastewater (ADWW) at a rate of 1 m\textsuperscript{3} person\textsuperscript{-1} d\textsuperscript{-1} [2]. ADWW is generally nutrient-rich, containing organic matter such as acetate and glucose. Using biochemical oxygen demand (BOD) as a biological index to quantify organic matter, 800–2,000 mg L\textsuperscript{-1} of BOD is generally contained in ADWW [3]. This value is much higher than BOD in urban sewage (100–200 mg L\textsuperscript{-1}). In Japan, ADWW must be treated before discharging it into the sewage system, in order to reduce its BOD concentration to less than 600 mg L\textsuperscript{-1} to prevent any damage to sewer pipes. In general, ADWW is pre-treated by aeration to enhance microbial oxidization of organic matter. However, the aeration process requires 0.3 kWh m\textsuperscript{3} of electric power, approximately twice the amount used in other general wastewater treatment processes [4][5]. Conversely, operation of standard activated sludge processes was estimated to discharge at 0.13–0.41 t-CO\textsubscript{2} m\textsuperscript{-3} [6]. Therefore, an alternative process, which consumes less energy, is required. The
The present study focuses on the microbial fuel cell (MFC) as an optimum process for achieving reduction of organic matter without aeration.

MFC is a technology that uses microorganisms as catalysts to oxidize organic compounds and generates an electric current [7]. Currently, MFC generally comprises one or two chambers, which have a platinum (Pt)-coated carbon cathode in one or two dimensions. In the anodic chamber, electrons produced during microbial oxidation are carried to the cathode via external resistance and are utilized in the reduction of oxygen, which is supplied to the cathode from the atmosphere [8]. Therefore, organic compounds in wastewater can be oxidized efficiently without aeration. Over the last decade, this type of MFC has been applied to common wastewater treatments, such as domestic water, confectionary wastewater, olive mill wastewater, chocolate industry wastewater and brewery wastewater [9]-[13]. In the fed-batch process, these MFCs removed 65–96% of 1,000–5,670 mg L\(^{-1}\) of organic compounds, measured via chemical oxygen demand (COD), after 3–7 days of incubation. In addition, these MFCs that can generate 187–1,500 mW m\(^{-2}\) of electric power density per cathode projected area, using 100–1,000 \(\Omega\) of external resistance. In terms of the maximum power density (\(P_{\text{max}}\)), 205–483 mW m\(^{-2}\) were recorded in these batch MFCs. However, there is no research regarding the application of MFC to the treatment of ADWW.

The aim of this study is to carry out a preliminary evaluation of the performance of organic compound removal in ADWW by MFC. As an anode in MFC, we used conductive floccular aggregates microbially produced from graphene oxide (GO). GO has been reported to be transformed microbiologically to a reduced form by natural microbial communities [14], providing a higher electricity production than conventional carbon anodes [15] [16]. In this study, a MFC using conductive floccular aggregates microbially produced from graphene oxide (GO-flocs) as anodes was established for the treatment of ADWW. The MFC was evaluated for the removal of COD\(_{Cr}\) and electricity generation in semi-batch mode operation.

**MATERIALS AND METHODS**

**Preparation and Microbial Reduction of GO**

Based on the methodology of a previous study [15], 7.9 g (dry wt.) of GO (SEC Carbon, Kyoto, Japan) was prepared from 10 g of graphite powder. The prepared GO was dispersed in sterilized MILLIQ\textsuperscript{®} water to give a concentration of 10 g L\(^{-1}\) and was stored at 4 °C until the day of its use. GO of 0.67 g L\(^{-1}\) was added to the ADWW in a 900 mL glass bottle. The mixture of GO and ADWW was incubated anaerobically at 28 °C over 10 days.

The transformation of GO to the conductive form in the ADWW was evaluated by measuring the change of electrical conductivity in the mixture. Electrical conductivity was measured by 4-terminal sensing using 4 platinum wires on a glass slide covered with samples, as reported in previous research [16]. The mixture of ADWW and GO was placed on a partition (0.3 mm thick, 1 cm\(^2\)) glass slide and measured for current at voltage in the range from -0.1 to 0.1 mV, with 0.5 mV sec\(^{-1}\) of scan rate.

**MFC Operation**

Figure 1 shows the configuration of the MFC used in this study. The MFC has a cylindrical body made of acrylic (120 mL capacity), 3.5 cm in diameter and 12 cm in height. The MFC was of the air-cathode single-chamber type, filled with ADWW and covered with a floating, Pt-coated, carbon cathode. The GO-flocs, which was obtained through the incubation of 900 mL of 0.67 g L\(^{-1}\) GO and ADWW mixture, was introduced in the anode chamber as the anode material. The MFC was then filled with ADWW and covered with a floating, Pt-coated, air cathode (9 cm\(^2\) in projected area), which was prepared according to the methodology of a previous study [17]. The MFC was maintained in a semi-batch mode by half-replacement of the anodic chamber with fresh ADWW every 6–9 days. The MFC was polarized for 120 days by connecting the anode and the cathode via an external resistance of 10 \(\Omega\). The voltage in the MFC was recorded every 60 min with the use of a data logger (T&D Corporation, Nagano, Japan). Power density curves were obtained by changing the external resistance from 1 \(\Omega\) to 30,000 \(\Omega\), 1 day after refreshing half of the ADWW. The power was normalized by the projected surface area of the cathode.
Chemical Analysis (CODCr, Ammonia, Nitrate)

To determine the amount of organic matter in ADWW before and after MFC treatment, we chemically oxidized the ADWW using chromium and quantified the amount of chromium consumed. The value was generally defined as COD and CODCr, particularly for the value determined by using chromium as the oxidant. We measured CODCr via the colorimetric method, in accordance with the standard methods for wastewater (5220 D) [18]. The digestion solution and the sulfuric acid reagent were added to the ADWW sample and were heated for 2 h at 150 °C. Following this, the samples were cooled to room temperature and measured at 600 nm.

Ammonium (NH4+) was determined by colorimetry, according to the indophenol blue method (JIS K7230). Phenol–sodium nitriprusside solution and sodium hypochlorite solution were added to an ADWW sample and measured at 635 nm.

Nitrate (NO3-) and nitrite (NO2-) were also determined colorimetrically (Roche, Schweiz, Basel). Sulfanilamide and N-(1-naphthyl)-ethylendiamine dihydrochloride were added to an ADWW sample and measured at 540 nm in order to determine nitrite content. Nicotinamide adenine dinucleotide phosphate and flavine adenine dinucleotide were dissolved in a potassium phosphate buffer. Nitrate reductase, sulfanilamide and N-(1-naphthyl)-ethylendiamine dihydrochloride were also added and measured at 540 nm for the determination of both nitrite and nitrate concentrations. Nitrate was determined by subtraction of the nitrate concentration value from the total concentration of nitrite and nitrate.

The absorbencies of CODCr, ammonia, and nitrate were measured by GeneQuant1300 (General electric company, CT, Fairfield).

Coulombic Efficiency

The Coulombic efficiency (CE) was calculated according to Liu and Logan [19], as EC = Cp/CTi × 100%, where Cp represents the total Coulombs, which was calculated by integrating the current over time. CTi is the theoretical amount of Coulombs that can be produced from ADWW, calculated as:

\[ C_{Ti} = \frac{Fb_iS_i\nu}{M_i} \]  

where F is Faraday’s constant (98485 C per mol of electrons), b_i is the number of moles of electrons produced per mole of oxygen (b = 4), S_i (g L^-1) is the CODCr concentration, \( \nu \) (L) is the liquid volume and M_i is the molecular weight of oxygen (32).
RESULTS AND DISCUSSION

Microbial Reduction of GO

GO in the ADWW was initially dispersed in the whole mixture, turning the solution brown. After 10 days of incubation, the GO in the mixture turned from brown to black. The conductivity of floccular aggregates in the ADWW was 0.12 mS cm⁻¹. Conversely, the ADWW culture without supplemental GO, and the mixture of ADWW and GO before incubation, did not indicate conductivity (Figure 2). These results show that the GO was microbially transformed to the conductive form. The change in color and conductivity of the microbial culture supplemented with GO has previously been observed in the process of microbial GO reduction [16][20][21]. As with previous studies, the production of GO-flocs can be considered to be the microbially reduced form of GO. The GO-flocs are similar in Figure 2 to the reduced GO (rGO) that can be found in a river sediment microcosm [14], in pure cultures of *Shewanella* spp. [20][21], in baker's yeast [22] and in *Escherichia coli* [23]. Recently, we observed the formation of rGO into a block with different inocula within 10 days [16]. These results indicate that the figure of rGO, floccular aggregates or block was variable and depended on the microbial source and incubation time.

![Figure 2](image_url)

**FIGURE 2.** Electrical conductivity of ADWW incubated for 21 days (A), the mixture of GO and ADWW before incubation (B), and floccular aggregates in ADWW after incubation (C).

MFC Operation

Figure 3 shows the performance of the cylindrical MFC packed with GO-flocs. The COD₅₀ of ADWW in the MFC initially had a concentration of 1,500 mg L⁻¹ prior to polarization, however after 7 days of polarization it decreased to 1,000 mg-COD₅₀ L⁻¹ (Figure 3A). After refreshing half of the ADWW in the MFC, the COD₅₀ recovered to 2,000 mg L⁻¹ and then decreased to 500 mg L⁻¹. COD₅₀ removal and recovery by refreshment of ADWW were repeatedly observed, however the COD₅₀ removal rate was variable. Overall, 89% of 1170 mg-COD₅₀ L⁻¹ was removed within 6–9 days. The average COD₅₀ removal rate was 128 ± 54 mg L⁻¹ d⁻¹, following 120 days of polarization. At the same time, the concentration of NH₄⁺ also decreased and was recovered with refreshment (Figure 3B). The removal rate of NH₄⁺ was 2.9 mg L⁻¹ d⁻¹, NO₃⁻ and NO₂⁻, oxidized forms of NH₄⁺, were not detected during the operation.

The polarized MFC, using 10 Ω of external resistance, generated 10 mW m⁻² of the electric power density on day 1 (Figure 3C). Similar to COD₅₀ removal and recovery, the electric power density decreased to 0.1 mW m⁻² and recovered from the refreshment of ADWW. The correspondence of changes in COD₅₀ and electricity clearly indicated that the electricity was generated by the degradation of organic substances in the ADWW within the MFC. Figure 3D shows the changes of the maximum power density (Pₘₐₓ) over the 120 days of polarization. The Pₘₐₓ of the MFC was initially 262 mW m⁻², which gradually increased to 291 mW m⁻² over 30 days (Figure 3D). The Pₘₐₓ slowly declined between the 40th and the 120th day. During the term, the original cathode was exchanged with a new one after 70 days.
Following the cathode exchange, electricity production temporarily recovered, but then gradually decreased once more. After 92 days, the conducting wires of the anode collector broke due to corrosion. The corrosion possibly caused the decline of electricity generation from 40 days up until this point. Following the exchange of the anode collector, the $P_{\text{max}}$ slightly recovered to $87 \text{ mW m}^{-2}$, but was kept 3-times lower than the value of the highest $P_{\text{max}}$. Figure 3E shows the power density curves of the MFC after 0 days, 30 days, and 82 days. After 30 days, at $291 \text{ mW m}^{-2}$ of $P_{\text{max}}$, $990 \text{ mA m}^{-2}$ was obtained at $0.294 \text{ V}$, using $330 \Omega$ of external resistance.

In the MFC, electricity was generated immediately after polarization. Either the immediate rise or shortening of the lag time for electricity generation was also observed in the soil microbial fuel cell with GO [15] and in electrochemical cultivation using GO [16]. These results suggest that the cultivation of ADWW with GO before polarization resulted in the pre-enrichment of exoelectrogenic bacteria, as previously demonstrated in other study [15]. The reason why electricity decreased in the latter operation is not definitively known. The following factors are possibly responsible for negatively effecting electricity generation: corrosion of the anode collector, growth of biofilm, which may have inhibited electron transfer in the GO-flocs, or the sinking of electrons rather competitive metabolism such as methanogenesis than anode-respiration. The highest $P_{\text{max}}$ of this MFC was $291 \text{ mW m}^{-2}$, which was in the range of $205–483 \text{ mW m}^{-2}$. This range has been found in other MFC-treated wastewater, such as brewery wastewater [11] [12] and confectionery wastewater [9].

**FIGURE 3.** The performance of MFC ADWW treatment over a period of 120 days: Changes of COD$_{\text{Cr}}$ (A), NH$_4^+$ (B), power generation (C), maximum power density (D) and power density curves (E) obtained from the MFC are shown. The small arrows indicate the half-replacement of the anodic chamber with fresh ADWW.
Coulombic efficiency in the MFC

CE was calculated by measuring the change in the concentration of COD\textsubscript{Cr} and the accumulated number of electrons recovered as electricity in every term, from refreshment to following 6–9 days of polarization. On average, the CE was 31 ± 20% for the 120 days of polarization, however values ranging from 12–69% were obtained between 0–7 days and 35–41 days, respectively (Figure 4B). The CE seemed to reflect the changes of COD\textsubscript{Cr} removal rate (Figure 4A), rather than electricity generation (Figure 3C and Figure 3D). Briefly, a high COD\textsubscript{Cr} removal rate provided a low CE. This suggested that a high COD\textsubscript{Cr} removal rate was achieved without being coupled with the recovery of electrons in the anode.

Correlation of MFC performance with COD\textsubscript{Cr} concentration

Figure 5 shows the COD removal rate at different COD concentrations in the MFC used in this study, as well as those used in previous studies [9]-[10]. The COD removal rate showed a strong, positive correlation (R\textsuperscript{2} = 0.85) with the COD concentrations. Such a positive correlation has been previously reported in a MFC which was used to treat beer brewery wastewater [22]. However, the correlation was not significant between the COD\textsubscript{Cr} removal rate and the COD\textsubscript{Cr} concentration (R\textsuperscript{2} = 0.36) when considering only the data obtained in this study. This was probably caused by the MFC changes in the initial and latter stages of the experiment, likely due to corrosion of the anode. The correlations of P\textsubscript{max} and CE with COD concentration were also examined, but showed no statistically significant relationship (data not shown). As shown in previous studies, the ion strength of the anolyte, rather than the COD concentration, influences electricity generation and CE [22].

![COD\textsubscript{Cr} removal rate and Coulombic efficiency](A and B)

**FIGURE 4.** COD\textsubscript{Cr} removal rate (A) and Coulombic efficiency (B) at every half refreshment of ADWW in MFC: CE was calculated when the ADWW contained over 1000 mg-COD\textsubscript{Cr} L\textsuperscript{-1}. 
CONCLUSION

This study evaluated MFC treatment for ADWW. In the preliminary evaluation, the COD Cr removal rate, the electricity generation rate and the CE were in a similar range to that observed in MFCs treating other sources of wastewater. The MFC removed organic matter in ADWW at 130 ± 54 mg L$^{-1}$ d$^{-1}$ of CODCr removal rate. This indicates that an enlarged MFC in this configuration can effectively result in the removal of COD from 1 m$^3$ of ADWW, including 1200 mg-COD L$^{-1}$ over 4.6 days, and therefore allow discharge to sewage systems. Currently, the system can save the energy needed for aeration but possibly require more energy for other processes due to longer retention time. To establish a low energy system, the configuration of MFC should be modified to decrease the retention time.

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