

Remediation of Sediment Deposited near Sewage Outlet with Solar Cell-Combined Sediment Microbial Fuel Cells

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Abstract- It has been reported that solar cell-combined sediment microbial fuel cell (SC-SMFC) can be an alternative option for remediating sediment. Near a sewage outlet, huge amount of sediment accumulation causes many environmental problems, such as malodor and the restriction of benthos inhabitation. This study aims to employ SC-SMFC for remediating sediment deposited near a sewage outlet. Particularly, we aim to determine the remediation range of sediment from the anode of SC-SMFC. SC-SMFC was applied into the sediment deposited on the riverbank of a tidal river, and the distribution of sediment quality from the anode was examined at 14 weeks after the employment of SC-SMFC. Decreases in hydrogen sulfide, phosphate, manganese, and ammonium ion concentrations were found, indicating the sediment remediation owing the SC-SMFC application. A larger decrease in each ion concentration was found near the anode. From the ion distributions, the sediment located between 0 and 1 m from the anode was strongly influenced by the SC-SMFC application, which was approximately 6.7-fold longer than that obtained from the laboratory experiment. At in-situ, water current that can transport substances to the anode and the biodiversity of microorganisms that can produce much of electrons may partly contribute to the increasing SC-SMFC performance, leading to the long range of sediment remediation. Furthermore, it is newly found out that ammonium and manganese ions are efficiently removed from sediment via the anode oxidation during the SC-SMFC application.

Keywords- Solar Cell; Sediment Microbial Fuel Cell; Sediment Quality; Remediation Range; Hydrogen Sulfide, Ammonium

I. INTRODUCTION

Municipal sewage amount increases in proportion to the population growths and urban development. Because conventional combined sewer overflows cannot treat such large amounts of increased sewage, a significant amount is sluiced into rivers. As a result, huge amount of sediment deposits on the riverbanks. On one of the riverbanks in Hiroshima prefecture (Fig. 1, Eba, Hiroshima, Japan), over 1m of sediment layer has been formed. It has been reported that organic matter decomposition releases large amounts of reduced substances (e.g., hydrogen sulfide (H₂S), organic acids, and nutrient salts) within sediment, deteriorating not only the sediment quality but also bottom water quality due to diffusion [1-2]. Hence, large amounts of these substances are released owing to excess decomposition of organic matter, causing environmental problems, such as malodor and the restriction of benthos inhabitation. Therefore, sediment remediation is required for restoring both sediment quality and benthos inhabitation.



Fig. 1 Location of the field experiment in this study (Eba, Hiroshima, Japan).

Recently, Sediment microbial fuel cell (SMFC)-based technologies have received notable attention for improving both water and sediment environments. An increasing number of studies have found a decrease in the amount and a variation in the state of the organic matter present in the sediment-applied SMFC, and a positive increase of the redox potential (ORP) of sediment when using SMFC [3-5]. Furthermore, SMFC has been shown to be effective in protecting against the deterioration of water quality via ion diffusion from sediment [6]. Touch et al. [7] has demonstrated that the employment of SMFC can effectively remove H₂S from sediment and fix phosphate within the sediment. Moreover, it has been pointed out that the application of SMFC into sediment can improve the benthos inhabitation in highly reduced sediment [8]. The authors demonstrated that the oxidation of reduced substances at the anode of SMFC plays an important role in improving the sediment

quality and the benthic habitat environment. Therefore, it is expected that the employment of SMFC into the sediment deposited near a sewage outlet can improve the sediment quality, leading to the restoration of benthos inhabitation.

An attempt has been made [9], aimed at increasing the SMFC efficiency in improving sediment and water quality after increasing the SMFC current with addition of external power supply. The authors demonstrated that the increasing current could obtain a higher efficiency of SMFC in sediment remediation. For instance, an increase in sediment ORP was higher when a potentiostat-combined SMFC was applied, in comparison with SMFC alone. Touch et al. [7] looked into the potential of using a solar cell as the external power supply of SMFC, i.e. SC-SMFC. The authors reported that solar cell could be used as the external power supply of SMFC, and the SC-SMFC efficiency was 2-fold higher compared with the SMFC efficiency.

In this study, SC-SMFC is applied into the sediment deposited near a sewage outlet. In our previous study [7], removal of H_2S , fixation of phosphate (PO_4^{3-}), and the remediation range of sediment from the anode were already examined through the laboratory experiments. In this study, a further investigation on the removal of ammonium ion (NH_4^+) is conducted. As laboratory (close) conditions differ from field (open) conditions, the remediation range of sediment from the anode of SC-SMFC is also examined. This study may be useful for researchers in designing a highly effective SC-SMFC for practical uses.

II. MATERIALS AND METHODS

A. The Construction of SC-SMFC System and Its Installation

The SC-SMFC system comprised of nine anodes and two cathodes (Fig. 2). An anode was made up of carbon fibers with a surface area of 0.09 m^2 . Note that the surface area refers to the surface area of carbon cloth (News Company, PL200-E) that was used to make the carbon fibers. The anode was mixed with sediment at field, and it was then placed in a plastic-net bag. The bag was then buried in the sediment layer (0 to 0.2 m) at intervals of 1 m, as shown in Fig. 3a. Cu-electrical leads were used to connect all anodes. A surface area of 0.18 m^2 of the carbon cloth was broken into carbon fibers, and the carbon fibers were then placed between two wooden boards to make a cathode (1 m in length and 0.15 m in height), as shown in Fig. 2b. The cathodes were fixed to the PVC-pipes that were inserted in the riverbed. It should be noted here that the cathodes exposed to the air during the low water level of the spring tides (Fig. 2b). This means that the system cannot operate (no electrical current) during the low water level of the spring tides. Following Nagatsu et al. [10], the carbon cloth was heated to $500\text{ }^\circ\text{C}$ for 1 h to improve its performance before being used as the electrode material. A reference electrode (Ag/AgCl, sat. KCl) (Toyo Co., TRE-7) was fixed to a cathode (Fig. 3a) for measuring the electrode potential.

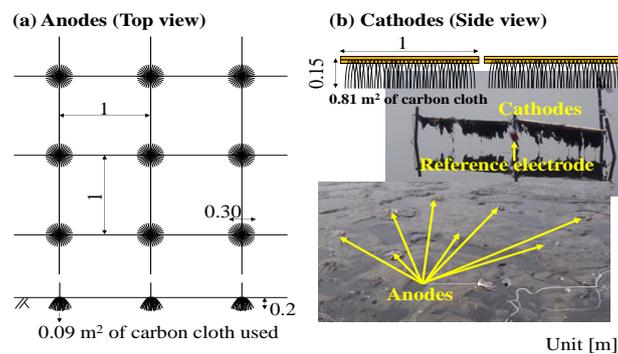


Fig. 2 Top view of anodes (a) and side view of cathodes (b) of the SC-SMFC system.

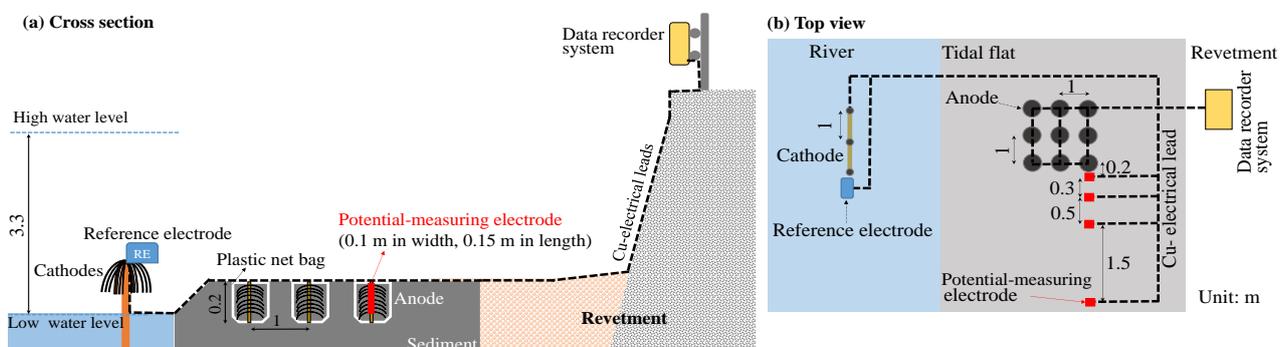


Fig. 3 Installation of the SC-SMFC system: Cross section (a) and Top view (b).

Four sheets of 0.1 m × 0.15 m-heated carbon cloth were also inserted into the sediment layer at 0.2, 0.5, 1, 2.5 m from an anode (Fig. 3b). This would be able to measure the potential distribution in the sediment during the electron removal via SC-SMFC.

B. The System Operations and Analyses

After the installation of anodes and cathodes, all anodes were connected in parallel, and the terminal of the paralleled-anodes was connected to the positive terminal of four-paralleled-solar cells (Tamiya, 1.5 V-500 mA). Similarly, the terminal of the paralleled-cathodes was connected to the negative terminal of the paralleled-solar cells. The addition of the solar cells into the SMFC system, i.e. SC-SMFC, was to increase the electrical current of the system. An external resistance was loaded between the anodes and the solar cells for controlling the system current.

The paralleled-anodes were also connected to the reference electrode for measuring the anode potential (Fig. 4). To examine the remediation range of sediment, the potential distribution in the sediment was measured by connecting the potential-measuring electrodes to the reference electrode. To measure the system current, the voltage of the two ends of the external resistance was recorded. The current was calculated using the recorded voltage based on Ohm's law, $I = U/R_{ex}$, where U (V) is the voltage, I (A) is the current, and R_{ex} (Ω) is the external resistance. The voltage was recorded every 30 min using a voltage recorder (T&D Corp., VR-71).

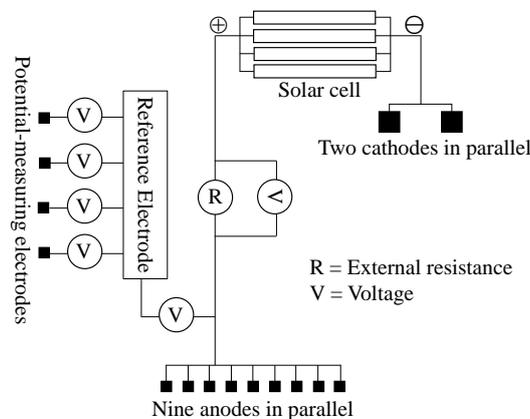


Fig. 4 Circuits for measurements of the anode potential and the system current.

The experiment started from July 23, 2017, and electrons were transferred from the sediment to water via SC-SMFC with a maximum current of 160 mA until October 24, 2017 (without loading an external resistance into the system). And then, a 10 Ω of external resistance was loaded into the system between the anodes and the solar cells. On November 05, 2017, the sediments near the potential-measuring electrodes were collected and analyzed for evaluating the sediment remediation. The collected sediments were transported to the laboratory for measuring the concentration of ions, such as manganese (Mn) ion and nutrient salts, present in the sediment pore water, except the concentration of H_2S . The H_2S concentration was measured at field using a H_2S detective tube (Gastec, No. 211M). This was for protecting the volatilization of H_2S during the transportation of the sediment to the laboratory. The collected sediment was placed in 50 mL-centrifuge tubes. The tubes were then centrifuged at a speed of 6000 rpm for 10 min to extract the sediment pore water (AS ONE, CN2060). This rotation speed was chosen in order to directly measure the pore water quality without filtration. The filtration of pore water may largely influence on the pore water quality. Finally, the ion concentration was measured using a digital water quality analyzer (Kyoritsu Chemical-Check Lab. Corp., A9000). It should be noted here that no pre-treatment of the sediment pore water was conducted, and the average value of duplicate samples was used.

III. RESULTS AND DISCUSSION

A. Improvement of the Reduction Level of Sediment via SC-SMFC

The reduction level of sediment is commonly evaluated based on the ORP of the sediment. However, the sediment ORP cannot be continuously measured using an ORP meter. Instead, the anode potential is used to understand the reduction level of sediment in this study. Fig. 5 shows the temporal changes of the anode potential after the application of SC-SMFC. Note that, after the experiment started until September 18, 2017, electrons were transferred from the sediment to water with a maximum current (I_{max}) of 160 mA. And then, a 10 Ω of external resistance was loaded into the system, resulting in a decrease of I_{max} to 120 mA. This was for a temporal measurement of the system current in order to examine the relation between the anode potential and the system current. As known, solar cell only works during the daytime, the minimum anode potential (P_{min} , the potential during the night time) refers to the anode potential without current generation, i.e. the reduction level of sediment.

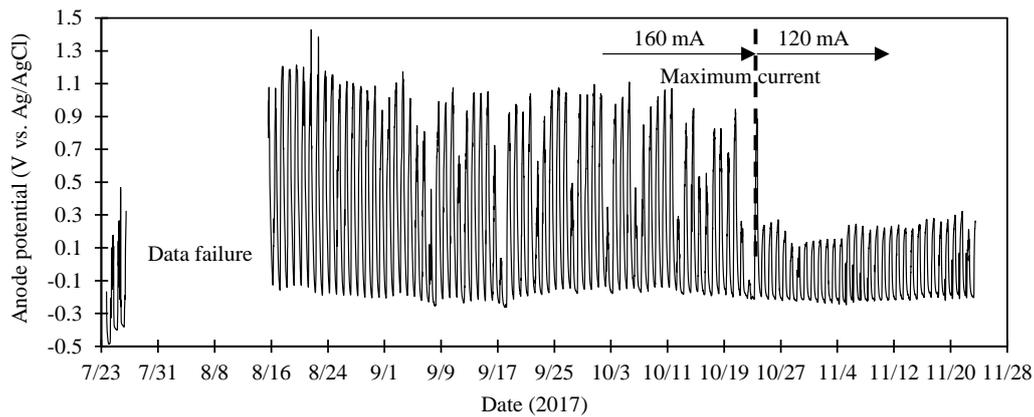


Fig. 5 Temporal changes of the anode potential after the application of SC-SMFC. The potential was measured with an error of ± 0.002 V.

During $I_{max} = 160$ mA, P_{min} temporally increased from -0.49 V, reaching -0.13 V on August 16, 2017. Generally, the oxidation of electron donors (some of reduced substances) causes an increase of electron acceptors (oxidants). This increases the sediment ORP, as following to the Nernst equation. More detailed information concerning the increasing sediment ORP by electricity generation can be also found in the reports by Touch et al. [11], Choi et al. [12], and Sturm et al. [13]. Thus, the increase in P_{min} during the SC-SMFC application indicates that the reduced level of sediment is improved by the SC-SMFC application.

Unfortunately, P_{min} started to decrease from August 16, reaching -0.26 V on September 18, 2017. During the summer season, anaerobic decomposition of organic matter is advanced according to an increase in temperature, leading to a stronger reduction level of sediment. It can be understood that the I_{max} of 160 mA is still not enough for improving the reduction level of the sediment during the summer season, i.e. the amount of electron transferred < the amount of electron released. After September 18, 2017, P_{min} started to increase and reached -0.15 V on October 11, 2017. The increase in P_{min} indicates the improvement of the reduction level of sediment. This may be partly due to a decrease in the decomposition rate of organic matter owing to a decrease in temperature from the summer season to the fall season. Therefore, the I_{max} of 160 mA is enough to increase the reduction level of sediment from -0.46 V to -0.13 V, i.e. the amount of electron transferred > the amount of electron released. It should be noted here that the decrease in P_{min} from October 11, 2017 may be attributed to a decrease in the SC-SMFC performance, i.e. the system current. It was confirmed that P_{min} decreased from -0.15 to -0.22 when the system current was decreased from 160 to 120 mA (Fig. 5).

B. The Remediation Range Based on the Potential Distribution During the SC-SMFC Application

During the oxidation of reduced substances at the anode, electrons are transferred to the cathode via the anode. Consequently, the anode potential increases when the amount of electron oxidized is larger than that of electron transported to the anode. At a higher electrical current, a larger amount of electrons are oxidized at the anode. However, as the electrons transport to the anode is lower comparing with the electrons oxidized, consequently, the anode potential increases. This means that the anode potential increases with an increase in current (Fig. 6). It can be said that the increase in electrode potential refers to the amount of electrons transferred from the sediment to water (sediment remediation).

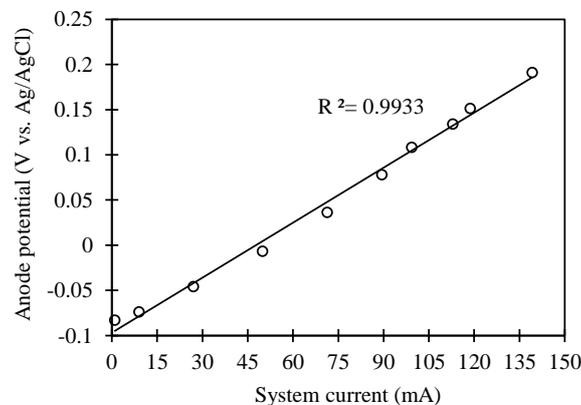


Fig. 6 Increase in the anode potential with an increase in the system current.

Fig. 7 depicts the relations between the anode potential and the potential increases of the electrodes located at different distances from the anode. Again, the minimum of the anode potential refers to the sediment potential without current

generation, and the increase in the anode potential refers to the electrons transferred from the sediment to water. Moreover, the increase in the potential of potential-measuring electrode refers to the electrons transferred from the sediment that the electrode was placed.

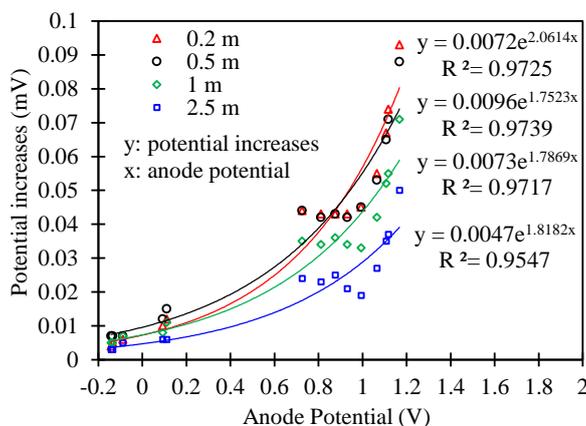


Fig. 7 Relations between the anode potential and the potential increases of electrodes located at different distances from the anode.

In Fig. 7, the potential of the potential-measuring electrodes increased along with an increase in the anode potential, a larger increase in the potential was found with the electrode located near the anode. It can be understood that the electrons in the sediment located 2.5 m from the anode are transferred during the application of SC-SMFC. As the relation between the anode potential and the potential increases of each potential-measuring electrode were different, the amount of electrons transferred from the sediment that the electrode placed was also different. In other words, the distribution of potential was formed in the sediment. As sediment remediation is in proportional to the transferring amount of electrons from the sediment, it is predicted that the distribution of sediment remediation is formed corresponding to the distribution of electron transferred.

C. Sediment Remediation via SC-SMFC

Fig. 8 shows the distributions of the ion concentration in the sediment pore water. In a laboratory scale, it has been reported that H_2S and PO_4^{3-} concentrations decrease after the application of SC-SMFC [7]. The authors demonstrated that H_2S decreased owing to the oxidation of H_2S at the anode, and PO_4^{3-} decreased via the fixation of PO_4^{3-} by Fe^{2+} and Ca^{2+} ions dissociated from metal complexes during the application of SC-SMFC. In this study, i.e. in a field scale, H_2S and PO_4^{3-} concentrations also decreased towards the anode (Fig. 8). The H_2S concentration in the sediment located at over 2 m from the anode was 300 mg/L, decreased to 200 mg/L in the sediment located 1 m from the anode, and to 35 mg/L in the sediment located 0.15 m from the anode. The PO_4^{3-} concentration was 19.3 mg/L, decreased to 17.8 mg/L in the sediment located 1 m from the anode, and to 8 mg/L in the sediment located 0.15 m from the anode. These findings further strengthen that SC-SMFC is a highly effective method for improving sediment quality, i.e. removal of H_2S and fixation of PO_4^{3-} . From the distributions of H_2S and PO_4^{3-} concentrations, it can be said that the sediment in a range of 0–1 m from the anode was strongly influenced by the SC-SMFC application. Interestingly, this remediation range (1 m from the anode) was 6.7 fold longer than that suggested from the laboratory experiment results (0.15 m from the anode) [7]. It is thought that field conditions, such as water current and the biodiversity of microorganisms, play an important role in enhancing the sediment remediation.

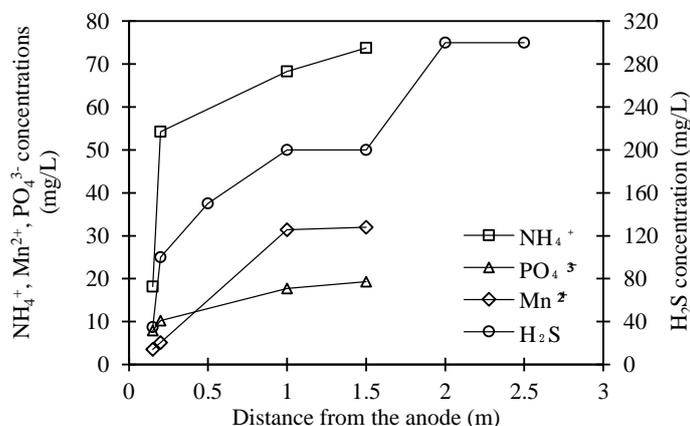


Fig. 8 Distributions of the ion concentration in the sediment pore water. 0 refers to the center of the anode. Mn^{2+} , NH_4^+ , H_2S , and PO_4^{3-} were measured with an error of ± 0.05 mg/L ($n=2$), ± 0.02 mg/L ($n=2$), ± 0.01 mg/L ($n=2$), and ± 0.02 mg/L ($n=2$), respectively.

Another purpose of this study was to examine the removal of ammonium ion (NH_4^+) via the application of SC-SMFC. Previously, it has been reported that NH_4^+ can be removed via the application of SMFC [14]. The authors reported that the activation of microorganisms and chemical reactions involved the removal of NH_4^+ . In this study, decreases in NH_4^+ were also observed, and NH_4^+ concentration decreased towards the anode (Fig. 8). Remarkably, a larger decrease in NH_4^+ was observed between 0.15 and 0.20 m from the anode. The NH_4^+ concentration was about 54.3 mg/L in the sediment located 0.2 m from the anode, decreased to 18.2 mg/L in the sediment located 0.15 m from the anode. It is thought that the oxidation of NH_4^+ at the anode (Eqs. 1-3) greatly involves in the large decreases in NH_4^+ .



The redox potential of Eqs. (1), (2), and (3) are 0.167, 0.148, and -0.473 V vs. Ag/AgCl, respectively. The potential was calculated at the temperature of 25 °C. Although redox potential depends on temperature, variation in the potential owing to changes in temperature is too small (10 °C-changes in temperature cause only 6 mV-changes in potential), so that the temperature dependence was not discussed in this study. As can be seen in Fig. 7, most of the anode potential was over than 0.11 V during the current generation by SC-SMFC. In addition to the oxidation of NH_4^+ via Eq. 3, it is thought that the oxidation of NH_4^+ via Eqs. 1 and 2 occurs during the application of SC-SMFC. Comparing with the use of SMFC alone, SC-SMFC can make a higher redox potential, contributing to the oxidation of NH_4^+ via Eqs. (1) and (2). In other words, SC-SMFC can be an alternative method for efficiently removing NH_4^+ from sediment. Furthermore, it was also found that SC-SMFC can effectively remove Mn ion from the sediment. The Mn concentration was about 32.4 mg/L in the sediment located 1 m from the anode, decreased to 3.6 mg/L in the sediment located 0.15 m from the anode (Fig. 8).

IV. CONCLUSIONS

SC-SMFC was employed to the sediment deposited near a sewage outlet to examine the remediation range of sediment and the removal of NH_4^+ via SC-SMFC. In addition to our previous laboratory results, the results obtained from this study further strengthen that SC-SMFC is a highly effective method for improving the reduction level of sediment, removal of H_2S from sediment, and fixation of PO_4^{3-} within sediment. Moreover, it is newly found out that SC-SMFC can be an alternative method to effectively remove NH_4^+ and Mn ions from sediment. Based on the ion distributions in the sediment pore water, the sediment in a range of 0–1 m from the anode was strongly influenced by the SC-SMFC application, which was approximately 6.7 fold longer than that suggested from the previous laboratory experiment (0.15 m). At in-situ, water current that can transport substances to the anode and the biodiversity of microorganisms that can produce much of electrons may partly contribute to the increasing SC-SMFC performance, leading to the long range of sediment remediation.

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