



Changes in the State of Organic Matter Present in Sediment by Different Methods of Electrokinetic Treatment

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Abstract During sedimentation, organic matter is absorbed on metal ions or clay minerals (soil particles), affording metal complexes that are difficult to use as organic materials. Hence, it is critical to separate the organic matter from metal or clay mineral complexes, possibly leading to the effective use of sediment and agriculture soils. Previously, a solar cell-combined sediment microbial fuel cell, constituting one of electrokinetic treatments, was applied into the sediment. As a result, metal complexes in the sediment were found to be dissociated, leading to changes in the state of organic matter present in the sediment. In this study, a new perspective into the changes in the state of organic matter by different methods of electrokinetic treatment was reported. In laboratory experiments, the sediment was subjected to different methods of electrokinetic treatment. Positive current was conducted for the transfer of electrons from the sediment to water, i.e., electron recovery. On other hand, negative current was conducted for the transfer of electrons into the sediment, i.e., electron supply. Thermogravimetric analysis (TG-DTA) and Fourier infrared (FTIR) spectral analysis of each sediment were carried out at the end of experiments. TG-DTA results revealed that the mass loss on ignition increases compared to the control sediment due to electron recovery, indicative of the release of organic matter. However, a difference was not observed with electron supply. FTIR results suggested that changes in the state of organic matter are the same for electron recovery and electron supply, i.e., release of O-H hydroxyl and C=O carboxylic acid groups were confirmed. Notably, by supplying electrons after electron recovery, the losses of O-H hydroxyl and C=C aromatic groups from the sediment were confirmed. Clearly, different states of organic matter were obtained by changing the method of electrokinetic treatment.

Keywords sediment, electrokinetic treatment, organic matter state, TG-DTA, FTIR

INTRODUCTION

Abnormal weather leads to the flow of large amounts of wastewater into wastewater treatment plants. As conventional wastewater treatment plants cannot treat such large amounts of increased wastewater, a significant amount is discharged into local water bodies. During sedimentation, organic matter present in the wastewater is absorbed on metal ions or clay minerals (soil particles) to form metal complexes, accumulating in the water bodies. Previously, several studies have reported that the excess accumulation of organic matter in water bodies leads to the deterioration of the aquatic environment (Martin, 2009; Wright et al., 2012).

The sediment is highly reduced because of the excess decomposition of organic matter. The oxidation reduction potential is extremely low (approximately -200 mV vs SHE for littoral sediments); hence, it is possible to recover electricity from the sediment. Numerous studies have reported the generation of electricity from the sediment by using sediment microbial fuel cells

“SMFCs” (Hong et al., 2008; Touch et al., 2014). Furthermore, the sediment can be a useful natural resource due to the presence of organic compounds. Unfortunately, as a metal complex, organic matter is considered to be barely decomposed organic matter, making it difficult to use as an organic material. Therefore, it is critical to separate organic matter from metal or clay mineral complexes to possibly improve the potential use of sediment.

From the viewpoint of using organic compounds, several methods have been proposed for changing organic compounds into useful products. For instance, Zhang et al. (2016) have carried out alkaline treatment involving the addition of steel slag into waste-activated sludge and reported better performance for the hydrolysis and acidification of sludge. The authors have revealed that alkaline treatment leads to the increased production of volatile fatty acids and high enzyme activities. Li et al. (2013) have demonstrated that alkaline post-treatment leads to the increased production of volatile fatty acids and polysaccharides in the sludge. Song and Jiang (2011) have reported that heating the sediment prior to use as a fuel in SMFCs affords a high power density of SMFCs. Furthermore, the application of SMFCs into the sediment has been reported to alter the organic matter state in the sediment (Hong et al., 2010).

In our previous studies, electrokinetic treatment has been reported to decrease the sediment pH, which can dissociate metal complexes. This dissociation in turn can lead to the release of ferric ions in the sediment pore water (Touch et al., 2015) and change the ignition characteristics of the sediment (Touch et al., 2017a). In addition, the application of a solar cell-combined SMFC (SC-SMFC) into the sediment can dissociate metal complexes present in the sediment (Touch et al., 2018). Interestingly, the state of the dissociated organic matter was different according to different application methods of SC-SMFC. As such, this study aims to examine the details of changes in the state of organic matter in response to different methods of electrokinetic treatment.

OBJECTIVE

The objective was to examine changes in the state of organic matter based on thermogravimetric analysis (TG-DTA) and Fourier infrared (FTIR) spectral analysis after making positive current flow (transfer electrons from the sediment to water) and negative current flow (transfer electrons into the sediment) in sediment.

MATERIALS AND METHODS

Experimental Device and Materials

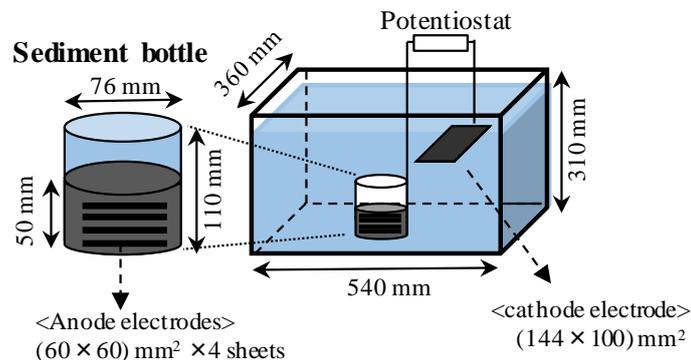


Fig. 1 Experimental device used in this study

Figure 1 shows the experimental device, comprising a cylindrical bottle with an inner diameter of 76 mm and a height of 110 mm. The wet sediment was placed till a height of 50 mm from the bottle bottom, and tap water was loaded on the sediment. The sediment was collected from the seafloor of the Fukuyama inner harbor (Fukuyama, Hiroshima, Japan). Approximately 30 cm of the

deposited sediment on the seafloor was collected and transported to the laboratory. The sediment was passed through a 2 mm-mesh sieve, which was placed in a room at 25 °C ± 2 °C before being used in the experiments. The pH, redox potential (ORP), and water content of the sediment were 6.92, -416 mV vs. Ag/AgCl (-218 mV vs. SHE), and 530%, respectively. The pH and ORP were measured using a digital pH/ORP meter (Horiba, D-50). Mass loss on ignition (LOI) at 600 °C for 4 h was approximately 288 mg/g.

In the sediment layer, four sheets of carbon cloth (News Company, PL200-E), i.e., anode, were installed at intervals of 10 mm from the bottle bottom. This installation ensured the homogenous electron flow in the sediment layer. One sheet of the anode electrode exhibited a surface area of 3600 mm². After installing the anode, the sediment bottle was placed in a container (360 mm in width, 540 mm in length, and 310 mm in height) that was filled by tap water. The pH, ORP, electrical conductivity (EC), and dissolved oxygen (DO) concentration of tap water were 7.78, 302 mV, 13.63 mS/m, and 8.49 mg/L, respectively. The EC and DO concentrations were measured using an EC meter (Horiba, D-74) and a DO meter (WTW, FDO925), respectively.

In the container, carbon cloth with a surface area of 14400 mm² (100 mm in width and 144 mm in length), i.e., cathode, was horizontally submerged in the container close to the water surface. Notably, the carbon cloth was heated at 500 °C for 1 h to improve its performance before being used as the electrode material following Nagatsu et al. (2014).

Operations and Analyses

The experiments were conducted under various operations (Fig. 2). Four days after placing the sediment bottle in the container, the anode and cathode were connected to a potentiostat (Hokuto Denko, HSV-110) for making electrical current flow (Fig. 1). A Ni-wire (Nilaco, NI311477) was used for the connections.

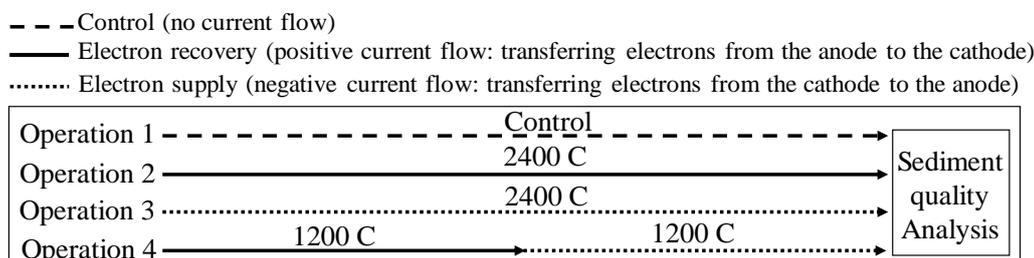


Fig. 2 Operation conditions for changing the state of organic matter

Three methods of electrokinetic treatment were conducted (Fig. 2). First (Operation 2), a positive current (electron recovery) was made for transferring electrons (electrical charge of 2400 C) from the anode (sediment) to the cathode (water). Second (Operation 3), a negative current (electron supply) was made for transferring electrons (electrical charge of 2400 C) from the cathode to the anode. Third (Operation 4), an electrical charge of 1200 C was supplied into the sediment after recovering an electrical charge of 1200 C from the sediment. In each operation, electrical current was fixed at 1 mA by the potentiostat. This current was chosen on the basis of our previous study (Touch et al., 2015). Operation 1 refers to the sediment without the current flow (control sediment).

At the end of the experiment, the sediment was collected from the bottle, followed by drying in the oven at 50 °C for 5 days. To examine the state of organic matter present in each sediment, TG-DTA and FTIR analyses were conducted using a Shimadzu-DTG 60H analyzer and a Shimadzu IRAffinity-1S (DRS-8000), respectively. It should be noted that the dried sediment was passed through a 75µm-mesh sieve prior to use in analyses. In TG-DTA, a 30 mg sample of the dried sediment passed through a 75µm-mesh sieve was heated to 800°C at a scan rate of 5 °C/min and under a steady nitrogen flow of 40 mL/min.

RESULTS AND DISCUSSION

Variations in the Mass Loss on Ignition (LOI) of the Sediment

Previously, Cuypers et al. (2002) have demonstrated that the state of organic matter could be evaluated on the basis of the ignition behavior of the sediment. Notably, labile and rather simple organic matter (e.g., fatty acids, peptides, and carbohydrates) predominantly burned at 290-310 °C. On the other hand, humified organic matter (e.g., humic and fulvic acids) predominantly burned at 370-390 °C and 530-540 °C. The burning temperature increased with the increased humification of the organic matter.

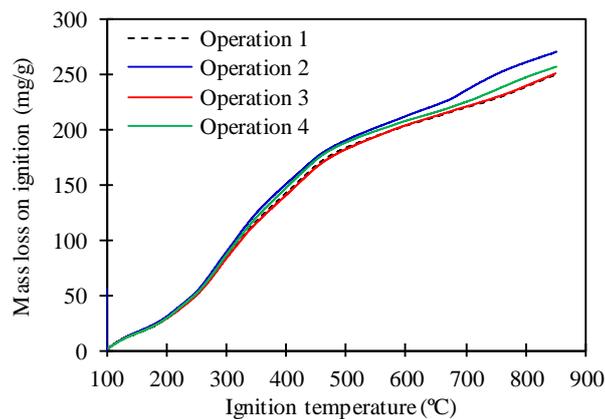


Fig. 3 Mass loss on ignition of the sediment at the end of each operation

Figure 3 shows the LOI of the sediment at the end of each operation. By the comparison to the control sediment (Operation 1), electron recovery (Operation 2) caused a large increase in the LOI at a temperature greater than 300 °C. Conversely, a difference was not found in the case of electron supply (Operation 3). As there was no re-supply of organic matter into the sediment, the dissociation of metal complexes was thought to contribute to the increased LOI. This was in good agreement with our previous report (Touch et al., 2018).

Interestingly, the electron supply after electron recovery (Operation 4) caused an increase in the LOI; however, the increase was less than those observed in Operation 2 at 500-850 °C. Touch et al. (2017b) have reported that approximately 99% of organic matter is burned at 500 °C based on the losses in the content of carbon in the sediment. Hence, from the results obtained in Operation 4, the electron recovery causes to the dissociation of metal complexes, leading to the release of metal and organic compounds. The electron supply after the electron recovery immobilized the released metal compounds, while it did not affect the released organic compounds. The immobilization of metal compounds may be partly related to the increase in hydroxyl ions owing to the electron supply (details can be found in the report by Yuan and Weng, 2003). The combination of electron recovery and electron supply can lead to the effective separation of the organic matter from metal complexes.

Variations in the State of Organic Matter Present in the Sediment

Figure 4 shows the spectral difference between the treated and the control sediment. The difference equaled to the spectra of the control sediment minus the spectra of the treated sediment. Hence, negative absorbance reveals the release of a substance in the sediment, while positive absorbance reveals the loss of a substance from the sediment.

In Operations 2 and 3, negative absorbance was confirmed at 3300-3700 cm^{-1} and 1600 cm^{-1} (Fig. 4). These operations predominantly exhibited the same change of spectra, i.e., release of O-H hydroxyl (3300-3700 cm^{-1}) and C=O carboxylic acid (around 1600 cm^{-1}) groups. Both electron

recovery and electron supply predominantly exhibited the same effects on the change in the state of organic matter in the sediment.

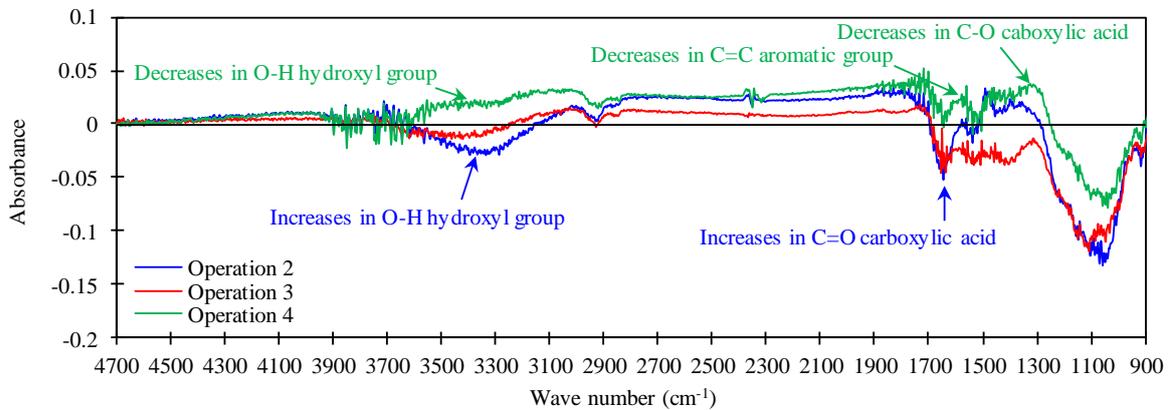


Fig. 4 Spectral difference between the treated and the control sediment

Conversely, losses of the O-H hydroxyl group and C=C aromatic group from the sediment were confirmed in Operation 4. In addition, the loss of C-O carboxylic acid group (around 1400 cm^{-1}) was observed, indicating that the state of organic matter is effectively changed in Operation 4. This further establishes that the combination of electron recovery and electron supply can effectively separate organic matter from metal complexes. The decrease in the O-H hydroxyl group in Operation 4 may be partly related to the immobilization of metal compounds owing to the electron supply, which is consistent with the suggestion from Fig. 3.

CONCLUSION

In this study, laboratory experiments were conducted to examine changes in the state of organic matter owing to the application of different methods of electrokinetic treatment, i.e., electron recovery, electron supply, and a combination of electron recovery and electron supply. Both electron recovery and electron supply can dissociate metal complexes present in the sediment, leading to the increase in the LOI of the sediment. However, electron recovery was more effective for the dissociation of metal complexes. Based on the FTIR results, this dissociation released the O-H hydroxyl group and organic compounds. By conducting electron supply after electron recovery, the loss of the O-H hydroxyl group and the decrease in LOI greater than 500 °C were confirmed, indicative of the immobilization of metal compounds owing to the electron supply. Furthermore, changes in the state of various organic matter were confirmed. Hence, different states of organic matter can be obtained by changing the method of making the flow of electrical current in the sediment. The combination of electron recovery and electron supply can effectively separate organic matter from metal complexes.

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REFERENCES

- Cuypers, C., Grotenhuis, T., Nierop, K. G. J., Franco, E. M., de Jager, A. and Rulkens, W. 2002. Amorphous and condensed organic matter domains, The effect of persulfate oxidation on the composition of soil/sediment organic matter. *Chemosphere*, 48, 919-931.

- Hong, S.W., Kim, H.S. and Chung, T.H. 2010. Alteration of sediment organic matter in sediment microbial fuel cells. *Environ. Pollut.*, 158, 185-191.
- Hong, S.W., Kim, H.S., Choi, Y.S. and Chung, T.H. 2008. Field experiments on bioelectricity production from lake sediment. *Bull. Korean Chem. Soc.*, 29, 2189-2194.
- Li, H., Zou, S., Li, C. and Jin, Y. 2013. Alkaline post-treatment for improved sludge anaerobic digestion. *Bioresour. Technol.*, 140, 187-191.
- Martin, W.R. 2009. Chemical processes in estuarine sediments. In John H.S., Karl K.T. and Steve A.P. (Eds.) *Environ. Ocean Sci.*, Elsevier, 539-550.
- Nagatsu, Y., Tachiuchi, K., Touch, N. and Hibino, T. 2014. Factors for improving the performance of sediment microbial fuel cell. *J. Jpn. Soc. Civ. Eng., Ser. B2 (Coast. Eng.)*, 70 (2), 1066-1070 (in Japanese).
- Song, T.S. and Jiang, H.L. 2011. Effects of sediment pretreatment on the performance of sediment microbial fuel cells. *Bioresour. Technol.*, 102, 10465-10470.
- Touch, N., Hibino, T., Nagatsu, Y. and Tachiuchi, K. 2014. Characteristics of electricity generation and biodegradation in tidal river sludge-used microbial fuel cells. *Bioresour. Technol.*, 158, 225-230.
- Touch, N., Hibino, T., Takata, H. and Yamaji, S. 2017b. Loss on ignition-based indices for evaluating organic matter characteristics of littoral sediments. *Pedosphere*, 27 (5), 978-984.
- Touch, N., Kinjo, N., Hibino, T. and Takata, H. 2017a. Effects of electron recovery from sediment on sediment and water environments. In *Proc. 2017 SICEAS Conf.*, 46-57.
- Touch, N., Kinjo, N., Tachiuchi, K., Nakashita, S. and Hibino, T. 2015. Development of a method for improving reduced environment of the sludge deposited in estuarine regions. *J. Jpn. Soc. Civ. Eng., Ser. B1 (Hydraul. Eng.)*, 71, 697-702 (in Japanese).
- Touch, N., Takata, H., Yamaji, S. and Hibino, T. 2018. Changing organic matter characteristics of littoral sediment by solar cell-combined sediment microbial fuel cell. *Int. J. Environ. Sci., Dev.*, 9 (3), 62-66.
- Wright, J.J., Konwar, K.M. and Hallam, S.J. 2012. Microbial ecology of expanding oxygen minimum zones. *Nat. Rev. Microbiol.*, 10, 381-394.
- Yuan, C. and Weng, C.H. 2003. Sludge dewatering by electrokinetic technique, Effect of processing time and potential gradient. *Adv. Environ. Res.*, 7 (3), 727-732.
- Zhang, Y., Zhang, C., Zhang, X., Feng, L., Li, Y. and Zhou, Q. 2016. Waste activated sludge hydrolysis and acidification, A comparison between sodium hydroxide and steel slag addition. *J. Environ. Sci.*, 48, 200-208.