# Removal and Changes of Sediment Organic Matter and Electricity Generation by Sediment Microbial Fuel Cells and Amorphous Ferric Hydroxide

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Sediment microbial fuel cell (SMFC) could reduce the total organic carbon (TOC) and dissolved organic carbon (DOC) of sediment, change the proportion of biopolymer (BP), fulvic acid (FA) and humic acid (HA), as well as generate electricity. After start-up of 15 days, the maximum voltage and power density of 0.679 V and 4.03 W $m^{-3}$ were achieved. Fe(III) addition affected electricity generation slightly. The combined application of Fe(III) addition and SMFC employment led to the highest removal rate (50.2 % of TOC and 74.6 % of DOC). Fe(III) addition could promote the removal of complex and high molecular-weight organic matter such as HA. The combined application of SMFC and Fe(III) addition offered a more efficient method to solve sediment pollution problems.

*Key words:*

sediment microbial fuel cell (SMFC), electricity generation, organic removal, Fe(III) addition

## Introduction

Sediments play an important role in determining the quality of lakes, rivers and oceans as they can act as either a source or sink for pollutants. Once the input pollution is controlled, sediments as a secondary source of pollution can release the accumulated pollutants to overlying water.[1] The organic matter content of sediments can also affect the structure of macroinvertebrate assemblages.[2] To date, traditional sediments remediation methods include monitored natural recovery, in-situ treatment, and ex-situ treatment.[3] The traditional methods are either expensive or not environmentally friendly, so it is crucial to find a cost-effective and environmentally friendly way to solve the contaminated sediments problem.

Microbial fuel cell (MFC) technology is considered an environmentally friendly and promising approach for converting wastewater or solid waste into electricity.[4–6] Recently, some studies have shown that sediment microbial fuel cell (SMFC) can alter the properties and enhance the removal of organic matter in sediment.[7–9] Wang[9] developed a three-dimensional floating biocathode to dispose river sediments, and concluded that the sediment organic matter content near the anode was removed by 29 %. Hong[7] found that sediment organic matter around the electrodes became more humified, aromatic, and polydispersed, and had a higher average molecular weight, along with its partial degradation and electricity generation compared to that of the original sediment. Sajana[10] studied the performance of SMFC by adding cellulose in freshwater and demonstrated effective cellulose degradation from aquaculture pond sediment and maintained the oxidized sediment top layer favourable for aquaculture. Zhou[11] improved the SMFC performance by amendment of colloidal iron oxyhydroxide into sediments and concluded that high Fe(II) concentration in pore water of sediments led to high power production. Song[12] found that the addition of biomass in appropriate proportions can enhance output power in SMFC.

However, mass transfer limitations for electron donors to reach the anode and a low rate of oxygen reduction in cathodes were major limitations for power production.[13] In freshwater environments, the maximum power densities in SMFC with felt graphite[14] and carbon paper[15] as cathode were 4 mW $m^{-2}$ and 2 mW $m^{-2}$ respectively. Song[13] constructed SMFC with granule activated carbon cathode and stainless steel anode and obtained 3.5 mW $m^{-2}$ maximum power density, and further increased to 11.2 mW $m^{-2}$ by adding cellulose. Jiang[16] built MFC with graphite fiber brush and enhanced TCOD removal rate from 11.3 % to 19.2 % for raw sludge.

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The reason why graphite fiber brush was considered as cathode is that graphite fiber brush can increase the oxygen transfer rate to cathode surface and form a biofilm (biocathode), which accelerates the oxygen reduction reaction.[9] Besides, the low conductivity of freshwater SMFC had a negative effect on power output.[17–18] Microorganisms can also anaerobically degrade organic matter in polluted aquatic sediments with alternative electron acceptors.[19–22] The electrodes in SMFC and amorphous ferric hydroxide were considered as electron acceptors, respectively.

In this study, a new SMFC configuration was built with self-made graphite fiber brush anode and cathode in order to increase the contact area of anode and sediment, and reduce the mass transfer limitations. The power output, the changes in properties, and the removal of organic matter in sediment were compared, and it was tested if the optimal results could be obtained by the combined application of amorphous ferric hydroxide addition and SMFC employment. The work demonstrated that SMFC can enhance removal of organic matter in sediments, and amorphous ferric hydroxide as alternative electron acceptor can improve the operation results, which offers a more efficient method to solve sediment pollution problems.

## Materials and methods

### Sediment and freshwater sampling

The sediment and freshwater sampling were taken from the downstream of Ashi River (45°49′29″N, 126°42′59″E), a tributary entering Songhua River, located in the Heilongjiang Province, China. The large gravels were removed from the sediment samples. These sediment samples were sieved through a 0.5 cm sieve to remove coarse debris, and mechanically homogenized. All sediment and freshwater samples were stored in a refrigerator at 4 °C prior to use. The sediment total organic carbon (TOC) and dissolved organic carbon (DOC) were measured as 67.9 and 4.58 g $kg^{-1}$ dry sediment. The chemical oxygen demand (COD) and ammonia nitrogen ($NH_3$-N) of freshwater were measured as 43.9 mg $L^{-1}$ and 0.4 mg $L^{-1}$, respectively.

### SMFCs construction and operation

Four bioreactors served this experiment. BR1 was applied to imitate the natural degradation without addition of electron acceptor. In BR2, amorphous ferric hydroxide with 9 g wet weight was mixed and homogenized with sediments.[23] BR3 and BR4 were operated with an electrode serving as the electron acceptor through operation of SMFC. Amorphous ferric hydroxide with the same amount as that added to sediment in BR2 was added to the sediment in BR4.

The SMFC was of columnar shape and made of plexiglas, with an inner diameter of 20 cm and height of 30 cm. The materials of anode and cathode electrodes were a graphite fiber brush and titanium wires. The bottom of each container was filled with wet sediment, and the anode was buried in the sediment in order to ensure a sufficient contact area of anode and sediment. The total height of the sediment containing the anode was 10 cm, and the effective volume of anode was 3140 mL. The top of each bioreactor was filled with freshwater, and the cathode was submerged just below the water surface and anchored by an iron wire to the container edge. The total height of water containing the cathode was 15 cm, and the effective volume of the cathode was 4710 mL. The size of the bioreactor without operation of SMFC was the same as that with SMFC. The compositions of the mineral salts medium in the overlying water was (g $L^{-1}$): $KHPO_4 \cdot 3H_2O$, 0.0001; $KH_2PO_4$, 0.0002; $NH_4Cl$, 0.0115; $MgCl_2 \cdot 6H_2O$, 0.1; $CaCl_2 \cdot 2H_2O$, 0.1; and $FeCl_2 \cdot 4H_2O$, 0.02.[23]

### Fractionation of organic matter from sediment

The chemical fractionation of sediments based on differences in solubility in alkaline and acid solutions was performed according to the procedure recommended by the International Humic Substances Society.[7] The sediment organic matters fractionated from the sediment samples were classified into three factions: fulvic acid (FA), humic acid (HA) and biopolymer (BP). The organic carbon content of each fraction was quantified as total organic carbon (TOC) concentration. Dissolved organic carbon (DOC) from sediment was measured as follows: dry sediment and distilled water were mixed according to the mass ratio of 1:5; then shocked for 1 h and centrifuged for 10 minutes, the TOC value of the liquid supernatant was the DOC value of the sediment.[7]

### Analytical methods

The anode and cathode were connected to an external resistor (1000 Ω), and the SMFC voltages were recorded using a data acquisition system (12-bit A/D-conversion chips, US) connected to a computer. The external resistor ranged 10 to 9999 Ω to determine the maximum power density as a function of changing electric current. The anode potential was measured by a reference electrode (Ag/AgCl, +195 mV vs. standard hydrogen electrode (SHE)). Voltage was converted to power den-

sity $P$ (W m$^{-3}$) via the equation $P = U \cdot I/V_a$, where $U$ is voltage (V), $I$ is current (A), and $V_a$ is the effective volume of anode.

The organic carbon content in the sediments were quantified as total organic carbon (TOC) and dissolved organic carbon (DOC) concentration, which were measured using a TOC-5000 Total Organic Carbon Analyzer (Shimadzu Co., Tokyo, Japan). The COD and $NH_3$-N analysis was via Standard Methods.

## Results and discussion

### Voltage and power density generation by SMFC

One period (60 d) operational results of SMFC with two different conditions (with or without adding amorphous ferric hydroxide) are shown in Fig. 1. The curves of power density and current measured on the tenth day are shown in Fig. 2.

In the initial 15 days, the voltage increased and reached the maximum values of 0.664 and 0.679 V, corresponding to adding and not adding amorphous ferric hydroxide. Sajana[10] operated the SMFC with

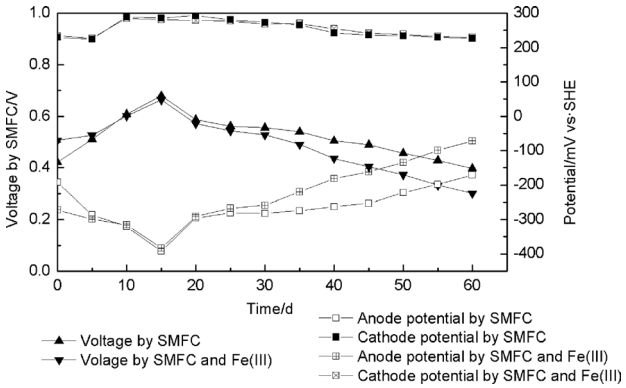


Fig. 1 – *Voltage and electrode potential in SMFCs under adding and not adding amorphous ferric hydroxide into the sediment conditions*

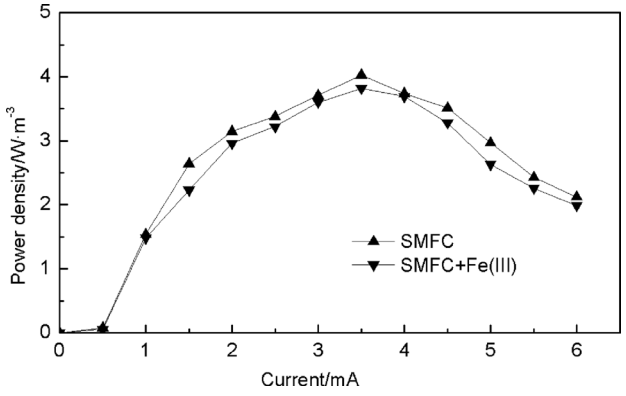


Fig. 2 – *Power density changed with current in SMFCs under adding and not adding amorphous ferric hydroxide into the sediment conditions*

the presence of cellulose and obtained the maximum voltage of 0.976 V. Higher voltage produced by SMFC was related to the biodegradable organic matter concentration in sediment. After 15 days, the voltage began to decrease gradually until the end. As known, both amorphous ferric hydroxide and the anode of SMFC can serve as electron acceptors, but the voltage values of the two bioreactors did not show much difference. Therefore, anode of SMFC is easier to be used by microorganisms than amorphous ferric hydroxide serving as electron acceptor.

Anode and cathode potentials of SMFCs were monitored during this experiment. After the initial instable 15 days, the anode potential of SMFC began to increase from –392 to –171 mV, and the cathode potential changed slightly. Adding amorphous ferric hydroxide into the sediment did not affect the trend. The initial increasing voltage was caused by the decreased anode potential, which resulted from the exoelectrogens enrichment on the anode. The decreasing voltage after 15 days was due to the gradually reduced organic matter in sediment.

The current was zero under open-circuit conditions, so the power density was also zero. Power density increased gradually with the increased current when the current changed from 0 to 3.5 mA (Fig. 2). After that, the power density decreased with the increased current, which was caused by the polarization of SMFC. A similar power density generation trend was reported by Sajana.[10] The maximum values of power density were 3.82 and 4.03 W m$^{-3}$ under conditions of addition and non-addition of amorphous ferric hydroxide into the sediment, respectively. Adding alternative electron acceptors into the sediment of SMFC slightly affected the electricity generation, which was similar to Zhou's study.[11] Zhou[11] found that only amending amorphous bulk ferric oxyhydroxide into sediment did not affect SMFC operation. However, amendment of the mixed solution including soluble ferric citrate and colloidal iron oxyhydroxide can improve SMFC operation, which was unrelated to organic matter removal.

### Organic matter degradation by SMFC

The sediments from BR1~BR4 were collected at 0, 15, 30, 45, and 60 days. The surface sediment samples (1 cm down from the interface) were discarded, and the others from different depths were mechanically homogenized for analysis. The TOC and DOC removal rates of sediment by SMFC under various conditions are illustrated in Fig. 3.

The TOC and DOC degradation in four bioreactors showed similar curves. Both SMFC and

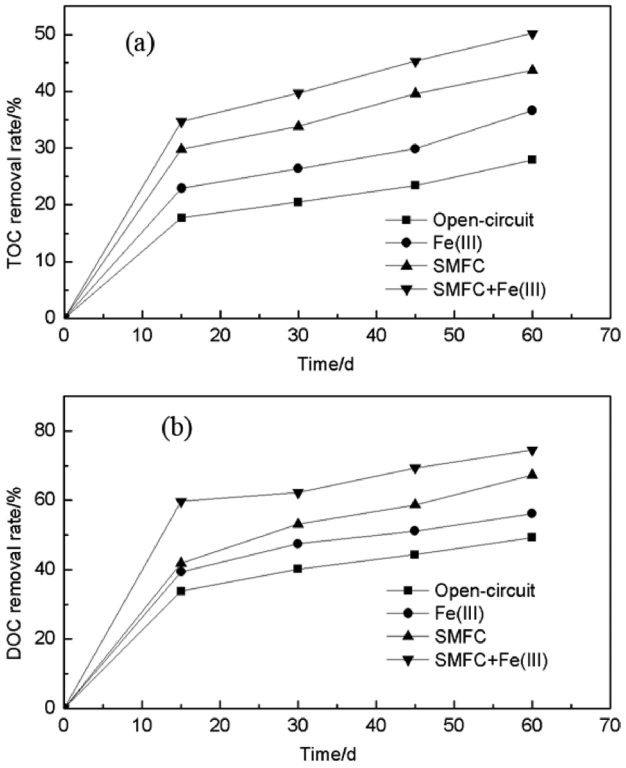


Fig. 3 – *TOC (a) and DOC (b) removal rate by SMFC under different conditions during 60 days*

Fe(III) addition could promote the organic matter degradation, since microorganisms used the anode of SMFC and Fe(III) as electron acceptors to degrade organic matter. The removal rate was considered as two ranges of fast and slow degradation. The main reduction of TOC and DOC concentrations occurred mainly within the initial 15 days of the experiment. The combined application of Fe(III) addition and SMFC employment led to the highest removal rate (50.2 % of TOC and 74.6 % of DOC after 60 days). The employment of SMFC could obtain higher removal efficiencies than only Fe(III) addition, which indicated that the deployment of electrode as electron acceptor in SMFC was better than Fe(III) amendment. These results were the same as those of Yan's study applying SMFC and Fe(III) to degrade PAHs in sediment.[23]

DOC contains carbohydrate, simple amino acid, micromolecular protein, and some humic acid and fulvic acid. By comparing Fig. 3 (a) and (b), the DOC in the sediment is much more degraded than the TOC, as DOC is easier to be used by microorganisms. The microorganisms first used DOC in the sediment, then began to decompose the insoluble organic matter into dissolved low molecular weight organic matter. After 60 days, the DOC still existed in the sediment, which was due to the mass transfer limitation of anode and the decomposition of insoluble organic matter.

## Changes in properties of sediment organic matter

The sediments from BR3 and BR4 were collected at 0, 15, 30, 45, and 60 days; and the sediment from BR1 and BR2 (open-circuit) were collected only at 60 days as control. The surface sediment samples (1 cm down from the interface) were discarded, and the others from different depths were mechanically homogenized for fractionation. Changes in organic carbon content of each fractionated sediment under SMFC employment and SMFC with Fe(III) amendment conditions are illustrated in Fig. 4.

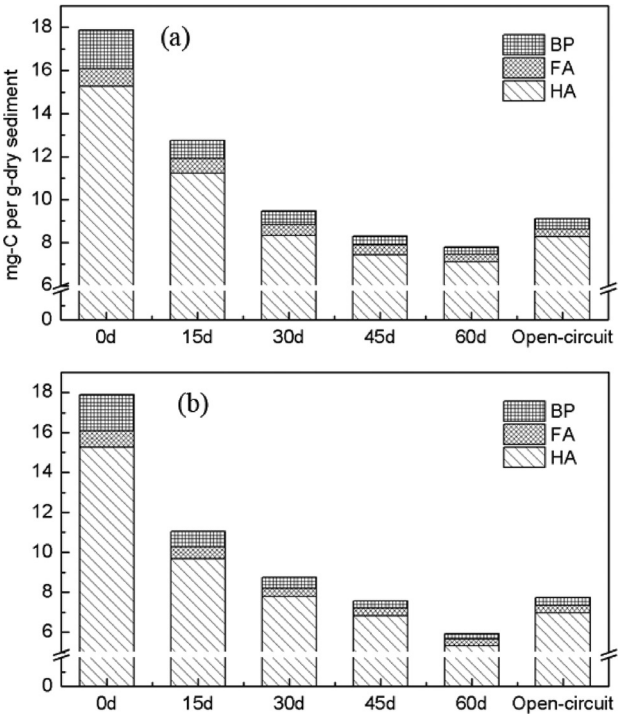


Fig. 4 – *Changes in TOC of each fractionated sediment under SMFC employment condition (a) and SMFC employment and Fe(III) amendment condition (b)*

All fractionated sediments decreased under the two conditions during the experiment. In the first 15 days, the decrease was more notable, which was consistent with the electricity generation and TOC variation trend. Approximately 82 %, 58 % and 53 % of BP, FA and HA was removed after 60 days in SMFC (Fig. 4(a)). The highest BP removal rate suggested that low molecular-weight matter of sediment can be more susceptible to microbial utilization than complex matter such as HA, which was consistent with the study of Hong,[7] while higher removal efficiency was obtained in this study. On the other hand, approximately 73 %, 55 % and 46 % of BP, FA and HA was removed after 60 days under open-circuit conditions. It is clear that SMFC em-

ployment can improve the removal of BP, FA and HA and organic matter was utilized by microorganisms for electricity generation.

As shown in Fig. 4(b), approximately 85 %, 63 % and 65 % of BP, FA and HA was removed after 60 days in SMFC with Fe(III) amendment, which was higher than only employment of SMFC, especially for the removal of HA. Therefore, microorganisms are prone to use Fe(III) as electron acceptor to degrade highly complex, larger, and high molecular-weight organic matter of sediment.

## Conclusions

The conclusions are as follows:

(1) SMFC employment generated maximum 0.679 V voltage and 4.03 W $m^{-3}$ power density, and Fe(III) addition in sediment affected the electricity generation of SMFC slightly.

(2) The combined application of Fe(III) addition and SMFC employment led to the highest removal rate after one period operation: 50.2 % of TOC and 74.6 % of DOC.

(3) SMFC employment can improve the removal of BP, FA and HA, and low molecular-weight matter of sediment such as BP is more susceptible to microbial utilization than complex matter such as HA, and Fe(III) as electron acceptor can promote HA degradation obviously.

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