Alternation of Sediment Characteristics during Sediment Microbial Fuel Cells Amended Biochar

Xunan Yang\textsuperscript{1,2,3} and Shanshan Chen\textsuperscript{1,}\textsuperscript{*}

1. Fujian Provincial Key Laboratory of Soil Environmental Health and Regulation, College of Resources and Environment, Fujian Agriculture and Forestry University, Fuzhou 350002, China.
2. Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Institute of Microbiology, Guangzhou, China.
3. State Key Laboratory of Applied Microbiology Southern China, Guangzhou, China.

Email: chenss@fafu.edu.cn

Abstract. Sediment microbial fuel cells (SMFCs) are considered as a new technology in sediment remediation, while biochars can promote interspecies electron transfer in bioelectrochemical systems. We conducted the SMFCs amended with biochars to investigate their effects on sediment characteristics. Results showed that the anode of SMFCs could oxidize the chemical oxidizable matter in sediments (by 4\%-16\%) correlating with the maximum power density ($r=0.982$, $p<0.01$) and then changed the chemical characteristics of the sediments. The reducible metal (Mn, Fe, Co, Ni and Zn) species increased after SMFCs performed, which might lead to releases of metals that bound to the oxidable fraction. On the other hand, the loosely-sorbed, redox-sensitive, and organic phosphorus decreased (1.6-40, 3.5-40, and 277-923 μg/g, respectively), as well as the refractory Al-phosphorus increased (2.8–58 μg/g), implied that the mobility of phosphorus was inhibited. As the high stable biochar, the ratio of recalcitrant carbon to total organic carbon did not change significantly in sediments while the ratio of recalcitrant nitrogen increased (2\%-19\%), suggesting that low quality of organic matter (C/N=24-32) were retained after remediation. The work took insight to sediment characteristic alternations under SMFC operation, which gave information on the element pool related to pollutants and the risk of the application of SMFCs.

1. Introduction

High-speed urbanization and associated human activities have led to a dramatic alternation on urban river ecosystems [1]. Although the pollution sources have been controlled by the governments, the organic pollution in sediments is still a serious problem [2].

Sediment microbial fuel cells (SMFCs) have been considered as bioelectrochemical technologies that can remove organic contaminants from sediment through stimulating the microbial metabolism involved in scavenging electricity [3]. Different from that in seawater environment, the SMFCs in freshwater sediment are usually short of ionic conductivity. Therefore, biochar, which could potentially help overcome the mass and electron transport barrier in SMFCs, was considered to be useful for sediment amendments [4]. The primary study has demonstrated that biochar reduced the charge transfer resistances of SMFCs, which improved the SMFC power generation by 2–10 times and enhanced the total organic carbon (TOC) removal rate by 1.7–10 times relative to those without biochar amendments [4]. However, most researches mainly focused on the advantages of SMFCs on organic carbon removal and power generation [3]. The alternations of sediment characteristics usually be ignored, which should be the comprehensive assessment on in situ remediation practices. This
study aims to investigate the alternations of sediment characteristics, including chemical oxidizable matter (COM$_{Cr}$), labile and recalcitrant pools of carbon (C) and nitrogen (N), and speciation of phosphorus (P) and metals, as well as the microbial community, during SMFCs-created redox processes.

2. Materials and Methods

2.1. Preparation of Sediment and Biochar
Surface sediments (0–15 cm) were collected from the Pearl River (23°6'36"N, 113°18'21"E) in China. The biochar, that derived from a coconut shell (pieces in 5 cm) were heat-treated in nitrogen at 400, 700, 800, and 900°C for 1.5 h, then milled and sieved through 0.3-mm sieve.

2.2. Setup of SMFCs
A 10 g biochar sample was mixed with 170 g (wet weight) of the sediment and placed in the beaker. River water from the Pearl River was added to the beaker and maintained 2 cm. The anodes in each cell were graphite plates (1×1 cm, 0.3 cm thick) and buried 2 cm deep in sediment. The cathodes were graphite felt (5×5 cm, 0.3 cm thick) and fixed horizontally 5 cm above the sediment surface. An external resistance (1000Ω) connected the anode and cathode using titanium wires (Figure 1). The SMFCs were placed in the dark and maintained at 25°C.

![Figure 1. Schematic of the structure of SMFC.](image)

While running the SMFCs, the voltages across the external resistances were recorded using a data acquisition system and divided by the resistance values to obtain the currents. The recovered current (Q) was calculated through integrating the current during the experiment period. The maximum power density (P$_{max}$) was measured and calculated according to Logan et al. [5].

2.3. Chemical and Microbial Analysis
The chemical oxidizable matter (COM$_{Cr}$) was determined via the potassium dichromate dilution heat colorimetric method. The forms of phosphorus (P) were extracted and determined according to Rydin’s method [6]. The forms of metals were extracted and determined according to BCR method [7]. The labile and recalcitrant pools of carbon (C) and nitrogen (N) were measured according to the Cheng’s method [8]. The DNA extraction, MiSeq sequencing of 16S rRNA gene and data analysis followed the description in the reference [9].
3. Results and Discussion

3.1. Shift of Redox Conditions

Remediation of the organic contaminants in sediments achieved great concerns recently. However, during the remediation process, the basic physical and chemical properties of the sediment would be alternative and lead to potential changes for total chemicals, which should be also paid attention to. Generally, polluted sediments tend to be anaerobic with low redox potential and most of the elements exist in a reduced state, such as ammonium, Fe(II) and sulfide. The content of these reductive substances represents the redox condition of the sediments.

As the primary study, the SMFC performances were positively correlated to the pyrolytic temperature of the biochar, because of the amendment of high pyrolytic biochar could create a low resistivity of sediment. In this study, with the SMFC process, the COM\text{Cr} decreased with the increase of SMFC performances (P\text{max} and Q) (Table 1), which exhibited significant correlations (p<0.01, Table 1). The results implied that the sediment became more oxidative after SMFCs performed. As the redox conditions in sediment had been changed, the forms of elements pool would be followed.

| Table 1. Correlations of chemical oxidizable matter reduction and SMFC performances |
|------------------------------------|
| COM\text{Cr} | P\text{max} | Q |
| COM\text{Cr} | 1 | 0.98 | 0.96 |
| P\text{max} | 1 | 0.99 |
| Q | 1 |

3.2. Shifts of Phosphorus and Metal Fraction

Sediment generally acts as net sinks for P and metals, as well as supports the trophic status and ecological risk of the water. In general, different P and metals forms in sediments are measured using different sequential extraction schemes. For P, together with dissolved P and interacting P (Loosely sorbed-P, Ls-P), and redox-sensitive P forms (P adsorbed to the surface of Fe and Mn, BD-P) have been known to supply internal loading [10]. In this study, low alternation of Ls-P and BD-P had been observed after SMFC performed, and also for the Ca-P which fractions are generally recognized as a refractory sedimentary P incorporated into the crystal structure of Ca minerals [11] (Figure 2).

![Figure 2](image-url)  
**Figure 2.** The alternations of various phosphorus fractions

The pool of organic P (Or-P) found dramatic decreases with increasing SMFC performance (Figure 2), indicating that this pool was labile and attributed to the enhancement of organic contaminate oxidation. It was surprising to note that the content of residual P (Res-P) in sediment decreased after the construction of SMFC (Figure 2), which implying that SMFC could be a potential technology for
treating the recalcitrant P in sediments. As the results, the total P in sediment decreased and meant that P release to water during SMFC remediation need to be considered.

In this study, the fraction distributions of heavy metals could be divided into two groups, Cr and Pb were abundant in the oxidizable and residual fractions, while Mn, Co, Ni and Zn were abundant in exchangeable and reducible fractions which fractions are considered higher potential mobility [12]. However, similar behaviors were observed between these two groups. With the decrease of oxidizable fraction, reducible fraction was increasing responding to the pyrolytic temperature of the biochar and SMFC performance (Figure 3), which indicated that more metals were trend to bond to amorphous iron and manganese oxides and hydroxides attributed to the oxidation effects of the anode. The results implied that the ecological risk of metals decreased with the SMFCs performance.

**Figure 3.** The alternations of various metal fractions

3.3. *Shifts of Microbial Community and Pools of C and N*

It is worth to notice that limited scale of anode could oxidize a wide range of sediments, which is attributed by the bacteria, specialized in electrode respiratory metabolism. During the 12 days process, the microbial community had significantly altered, in which genera *Fusibacter, Anaerorhabdus, Geobacter, Thiobacillus* and *Anaerovorax* increased more than 1% (Table 2). These five groups of
bacteria were detected in many previous MFC studies, and most of them were known for their abilities to oxidize various hydrocarbons and sulfur [13, 14]. The increase of these bacteria could enhance the oxidation effects in sediment and thus altered the physical and chemical properties discussed above, such as the decrease of TOC and Or-P.

Table 2. The most increasing genera during SMFC performed

| Phylum              | Genus         | Day 0    | Day 12  |
|---------------------|---------------|----------|---------|
| Firmicutes          | Fusibacter    | 0.11%    | 8.11%   |
| Bacteroidetes       | Anaerorhabdus | 0.03%    | 4.82%   |
| Deltaproteobacteria | Geobacter     | 0.62%    | 4.34%   |
| Betaproteobacteria  | Thiobacillus  | 0.38%    | 1.41%   |
| Firmicutes          | Anaerovorax   | 0.03%    | 1.25%   |

As the functional bacteria came active, high degradation of TOC had been observed [4]. In this study, we took insight of the fraction shifts of C and N. The ratio of recalcitrant C to total organic C did not change significantly in sediments, which might be attributed to the high stability of biochar. In contrast, the ratio of recalcitrant N increased (2%–19%), suggesting that low quality of organic matter (C/N=24–32) were retained after remediation.

4. Conclusions

The alternations of sediment characteristic were observed with the SMFCs running. Firstly, electroactive bacteria, which have the ability to oxidize reductive compounds in anaerobic sediments, were stimulated by SMFCs amended with biochar. The labile organic C and N were degraded. Meanwhile, organic and residual P fractions were transferred, which could remove the total P in sediment, but also increase the risk of P pollution in water. In addition, the metals became more stable as the increase of SMFCs performance. These findings could serve as the supporting information on the utilization of SMFCs, including the remediation options and risk management.

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