To improve the performance of sediment microbial fuel cell through amending colloidal iron oxyhydroxide into freshwater sediments

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HIGHLIGHTS

- Amendment of conductive magnetite in sediments did not have effect on SMFC operation.
- Amendment of colloidal iron oxyhydroxide into sediments improved SMFC performance.
- Enhanced voltage production was not due to organic matter removal in sediments.
- High Fe(II) concentration in pore water of sediments led to high power production.
- This amendment way was especially for sediments with low amount of organic matters.

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ABSTRACT

Effects of iron oxide amendment into freshwater sediments on performance of sediment microbial fuel cell (SMFC) were investigated. It was found that amending amorphous bulk ferric oxyhydroxide, and crystalline goethite and magnetite did not affect SMFC operation. However, amendment of the mixed solution including soluble ferric citrate and colloidal iron oxyhydroxide, stably improved SMFC performance with voltage outputs up to threefolds higher than those without amendment. The enhanced voltage production corresponded to lower anode potential, but was not related to organic matter removal in sediments. Further experiments demonstrated that colloidal iron oxyhydroxide instead of soluble ferric iron played an important role in voltage production through maintaining high-concentration ferrous iron in pore water of sediments as electron shuttle and for chemical oxidation on the anode. Thus, colloidal iron oxyhydroxide amendment was a promising strategy to improve power production from SMFC employed in sediments especially with low content of organic matters.

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1. Introduction

A sediment microbial fuel cell (SMFC) is a type of microbial fuel cell (MFC) with an anode electrode embedded in anaerobic sediments and a cathode electrode suspended in the aerobic water column above the anode electrode (Reimers et al., 2001). Anode-respiring microorganisms in sediments transfer electrons produced during the oxidation of organic or inorganic matter to the anode electrode, while oxygen is reduced in the water column by accepting electrons from the cathode electrode. As a result, an electric current is generated. Owing to their unique characteristics, SMFCs could be used as power sources for instruments deployed in marine and lake environments for long-term monitoring with low maintenance requirement (Donovan et al., 2013; Zhang et al., 2011). In addition, SMFCs could also be explored as a new technology for the removal of organic pollutants from sediments (Hong et al., 2010; Yan et al., 2012).

Due to various limiting factors such as substrate mass transfer limitation in sediments and low electric conductivity especially in fresh water, internal resistances in SMFC were generally higher than those in chamber MFC (He et al., 2007; Logan et al., 2006; Song et al., 2010), which then led to a low voltage and power output from SMFC. Several attempts have been made to improve SMFC performance through optimizing external resistance (Song et al., 2010), improving sediment conductivity (Babu and Mohan, 2012), modifying electrode materials, and altering electrode configurations and assembly (An et al., 2013; Hong et al., 2009a; Karra et al., 2013).

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It was also reported that addition of electron donors like glucose or cellulose to sediments improved SMFC performance through increasing substrate availability for anode-respiring microorganisms (He et al., 2007; Rezaei et al., 2008). As microbial anode respiration occurs under anoxic condition, the penetration of oxygen leads to aerobic oxidation of substrate in sediments, and often inhibits the activity of anode-respiring microorganisms with a low power output from SMFC (Karra et al., 2013). However, the effect of alternative electron acceptors other than oxygen in sediments on SMFC operation was unknown.

In freshwater sediments, ferric compounds exist abundantly as electron acceptors, and the reduction of ferric to ferrous is also an important biogeochemical process in freshwater sediments (Lovley and Phillips, 1986; Roden, 2012). Most iron in nature combines with oxygen as iron oxide minerals (Kato et al., 2010). Iron oxides occur in sediments as a spectrum of phases, ranging from amorphous minerals to crystals, such as goethite (α-FeOOH) and magnetite (Fe_3O_4) (Cornell and Schwertmann, 2003). Crystalline iron oxides are typically abundant relative to amorphous forms in sediments (Roden, 2012).

The existence of ferric compounds could encourage the oxidation of organic matters in sediments via iron reduction pathway. Compared to crystalline iron oxides, soluble and amorphous ferric ion are more liable to be reduced by dissimilatory iron-reducing bacteria due to higher surface areas and solubility (Lovley and Phillips, 1986; Roden, 2012). Thus, amendment of soluble and amorphous ferric iron to sediments with SMFC employment might also increase the growth pressure for those anode-reducing microbes colonizing on the anode, as iron-reducing and anode-reducing processes would probably compete for limited carbon substrate in sediments. In fact, it was previously reported that ferric amendment did not significantly improve power density, as microbes in MFC used ferric rather than the anode as electron acceptor (Liu et al., 2011).

On the other hand, most crystalline iron oxides are (semi)conductive, for example, goethite and magnetite are semi-conductive and conductive, respectively. Those particles of (semi)conductive iron oxides might serve as electron conduits between bacterial cells and distant electron acceptors such as the electrodes in electrochemical cells (Kato et al., 2010). Moreover, three-dimensional conductive networks established with (semi)conductive iron oxide minerals were suggested to exist even in sediment environments at local niche (Nielsen et al., 2010). Due to respiratory interactions of bacteria with iron compounds, the supplementation with semi-conductive/conductive iron oxide minerals might result in enhanced performance of MFC (Kato et al., 2010; Nakamura et al., 2013).

Therefore, effects of iron amendment to sediments on SMFC performance depended on the form of iron compounds. It seemed reasonable to speculate that addition of conductive iron oxides rather than soluble or amorphous ferric was able to improve power production from SMFC. To test this hypothesis, lab-scale SMFCs were constructed with sediment samples taken from one freshwater lake. Then, four kinds of ferric compounds including amorphous minerals, goethite, and magnetite were amended to sediments, respectively, and SMFCs were operated for over two months. This study would be helpful in developing practical strategies for long-term enhancement of power production from SMFC.

2. Methods

2.1. Sediment sampling

Surface sediment samples were collected from Taihu Lake (31°10′N, 120°24′E), a typical eutrophic shallow freshwater lake in China. These sediment samples were sieved through a 0.5 cm sieve to remove coarse debris and mechanically homogenized, and then stored in a refrigerator at 4 °C prior to analysis and experiments. The total nitrogen and the total phosphorus of the sediment were measured to be 1.43 g kg⁻¹ sediment and 0.76 g kg⁻¹ sediment, respectively.

2.2. Iron oxide preparation

Amorphous bulk ferric oxyhydroxide was prepared by neutralizing a 0.4 M solution of $FeCl_3$ to pH 7 with NaOH (Lovley and Phillips, 1986). To prepare goethite, a 0.4 M $FeCl_3$ solution was adjusted to pH 12 with NaOH and left for 1 week at room temperature, followed by incubation at 90 °C for 16 h (Lovley and Phillips, 1986). Magnetite was synthesized through using $FeCl_2$ and $FeCl_3$ with a 0.5 M ratio of Fe(II)/Fe(III) at pH 11–12 as described in detail elsewhere (Kang et al., 1996). After synthesis, iron oxides prepared above were cleared of remaining ions through centrifugation at 1000g for 20 min and resuspension in Milli-Q water until the chloride concentration in the supernatant dropped below 1 mM.

To prepare colloidal iron oxyhydroxide, 4.19 g of ferric citrate was dissolved in 100 mL Milli-Q water and adjusted to pH 8.0 by addition of a 32% NaOH solution under vigorous stirring (Leibl et al., 1999). At pH 8.0, stirring was continued for 30 min. At this stage, the solution contained both soluble ferric ion and colloidal iron oxyhydroxide, and was called as SC solution. The proportion of soluble ferric iron content to the total iron in SC solution reached up to 98%. The SC solution was prepared easily and used for the phase I of experiments. In addition, colloidal iron oxyhydroxide was cleared of remaining ions in the SC solution for the phase II of experiments. To remove soluble ferric ion in SC solution, SC solution was firstly subject to high-speed centrifugation at 36,000g for 60 min. The supernatant was then discarded, and the precipitate was resuspended in Milli-Q water. These centrifugation and resuspension steps were repeated until the supernatant remained colorless after centrifugation, and residual colloidal iron oxyhydroxide was suspended in Milli-Q water.

All synthesized iron compounds were stored at 4 °C in the dark under an anoxic environment filled with nitrogen. Characteristics of the particles were identified by transmission electron microscopy (TEM) and X-ray diffraction (XRD). For TEM analysis, dried samples were diluted and sonicated, and then one drop was transferred onto a 3 mm holey carbon-coated Cu grid, and characterized using a JEM-200CX TEM (JEOL) equipped with a Gatan CCD camera. XRD (Rigaku, Ultima IV with D/teX Ultra) analysis was applied with random powder specimens from 2° to 80° in steps of 0.02° to confirm the phase of iron compounds. In addition, energy dispersive spectroscopy (EDS) element components of particles were also examined through a field emission scanning electron microscope (HITACHI S-4800, Japan) and a HORIBA EMAX Energy EX-350 Energy Dispersive X-ray Microanalyzer.

2.3. Measurement of iron reduction rate

Iron reduction rates with various iron oxides prepared above as electron acceptors were measured. 2.0 g (wet weight) of sediments was added to 40 mL of sterile basal medium in 100-mL serum bottles. The composition of basal medium included (g L⁻¹): NaHCO₃, 2.5; CaCl₂·2H₂O, 0.1; KCl, 0.1; NH₄Cl, 1.5; NaH₂PO₄·H₂O, 0.6; NaCl, 0.1; MgCl₂·6H₂O, 0.1; MgSO₄·7H₂O, 0.1; MnCl₂·4H₂O, 0.005; NaMoO₄·2H₂O, 0.001; and yeast extract, 0.05. Iron oxide with a concentration of 40 mM was added into the serum bottles as the sole electron acceptor. Glucose with a concentration of 10 mM was added to serve as organic carbon resource. The pH of liquid medium in bottles was adjusted to 7.0. After bubbled with nitrogen for 10 min, the bottles were sealed with rubber stopper and