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Arsenic mitigation in paddy soils by using microbial fuel cells☆

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ABSTRACT

Arsenic (As) behavior in paddy soils couples with the redox process of iron (Fe) minerals. When soil is flooded, Fe oxides are transformed to soluble ferrous ions by accepting the electrons from Fe reducers. This process can significantly affect the fate of As in paddy fields. In this study, we show a novel technique to manipulate the Fe redox processes in paddy soils by deploying soil microbial fuel cells (sMFC). The results showed that the sMFC bioanode can significantly decrease the release of Fe and As into soil porewater. Iron and As contents around sMFC anode were 65.0% and 47.0% of the control respectively at day 50. The observed phenomenon would be explained by a competition for organic substrate between sMFC bioanode and the iron- and arsenic-reducing bacteria in the soils. In the vicinity of bioanode, organic matter removal efficiencies were 10.3% and 14.0% higher than the control for lost on ignition carbon and total organic carbon respectively. Sequencing of the 16S rRNA genes suggested that the influence of bioanodes on bulk soil bacterial community structure was minimal. Moreover, during the experiment a maximum current and power density of 0.31 mA and 12.0 mWm^{-2} were obtained, respectively. This study shows a novel way to limit the release of Fe and As in soils porewater and simultaneously generate electricity.

1. Introduction

Rice paddy soils are rich in iron (Fe) oxides, which serve as a potent repository for many soil contaminants, especially arsenic (As) (Li et al., 2011; Wang et al., 2009). When paddy soil becomes anoxic, bacteria oxidize organic matter (OM) to carbon dioxide (CO_2) and use soluble and insoluble electron acceptors such as sulfate, nitrate, arsenate (As(V)) and Fe (oxy)hydroxides as the final electron acceptors (Lovley et al., 2004; Lovley and Phillips, 1986; Qiao et al., 2017a, 2017b). The transfer of electrons to Fe (oxy)hydroxide by iron reducing bacteria (IRB) is prevalent in flooded paddy soils and this results in the dissolution of Fe and consequent release of As(V), which can then be reduced to arsenite (As(III)) by As(V)-reducing and dissimilatory As(V)-reducing microorganisms (Qiao et al., 2017b; Roden et al., 2010; Shelobolina et al., 2003). In addition, the direct reduction of As(V) to As(III) from the surface of metal oxides can also enhance the release of As into the soil porewater (Qiao et al., 2017b; Takahashi et al., 2004). The reduction of Fe(III) and As(V) in turn increases As bioavailability and subsequent uptake of As by rice plants via the silicon pathway (Seyfferth et al., 2014, 2017, 2018; Williams et al., 2006; Zhu et al., 2008). The increased bioavailability of As in flooded paddy soil is a major concern because rice is consumed worldwide and the chronic consumption of As tinted rice expose individuals to this harmful carcinogen (Barragan et al., 2011; Chaney et al., 2016; Vithanage et al., 2017; Zhu et al., 2008). Hence there is an urgent need to develop ways to limit As bioavailability in paddy soil.

The redox cycles occurring in paddy fields give rise to electricity upon implantation of soil microbial fuel cells (sMFC) (Chen et al., 2012; De Schamphelaire et al., 2010; Kaku et al., 2008). A simultaneous outcome is that sMFCs are environmentally friendly bioelectrochemical systems that have the capacity to remove

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pollutants (Li and Yu, 2015). In sMFCs, exoelectrogens oxidize organic substrates and transfers electrons to the bioanode (Logan, 2008; Rezaei et al., 2007). The electrons are then transferred to the cathode across an external circuit, where they reduce oxygen (Logan et al., 2006). Thus the bioanode of the sMFC is able to work as a continuous sink for electrons produced during the oxidation of organic substrates and in the same way influence soil redox chemistry and microbiology (Huang et al., 2011; Logan, 2009).

Previous studies have shown that the sMFC can immobilize and even extract metal ions by changing their redox state or via electrokinetic processes. It has been demonstrated that sMFC can facilitate the reduction of carcinogenic and mutagenic substance such Cr(VI) and U(VI) to the less harmful species (e.g. Cr(III) and U(IV)) in the cathode chamber (Wang et al., 2015a). Similarly, the bioanode has also been used to for the *in situ* bioremediation of U(VI) (Gregory and Lovley, 2005). Chen et al. (2015) demonstrated that the sMFC can be used to produce sufficient energy to extract zinc and cadmium removal from paddy soils via electrokinetic transport to the cathode chamber. In addition to metal remediation, sMFC have also been utilized in nutrient (Martins et al., 2014; Xu et al., 2017; Yang et al., 2016; Zhang and Angelidaki, 2012) and OM (Morris and Jin, 2012; Song et al., 2010; Xun et al., 2016; Zhu et al., 2016) removal. The sMFC favors phosphate and nitrogen removal from overlying waters by increasing soil redox potential, Fe(III) concentration and overlying water pH (Martins et al., 2014; Yang et al., 2016). However, few studies have investigated the influence of the bioanode on bulk soil Fe oxides and the elements coupled with Fe cycle in contaminated paddy soils.

When the sMFC operates in paddy soils, the bioanode may change the bacterial community (Lu et al., 2014), acidify soils (Hong et al., 2009; Jang et al., 2004) and deplete bioaccessible organic substrate (Morris and Jin, 2012; Song et al., 2010; Xun et al., 2016; Zhu et al., 2016). Recent studies have provided evidence that Fe containing mineral reduction in flooded soils might also be influenced by the buried bioanode (Touch et al., 2017; Yang et al., 2016). However, it is still unknown whether the bioanode can affect the behaviors of Fe and soil trace elements, especially As bound with Fe mineral, in paddy soils, which have great significance in both plant nutrition and food safety. Given that the bioanode may affect Fe mineral behavior and can stimulate dissolved organic carbon (DOC) removal (Xu, 2015), we tried to manipulate redox processes in As-contaminated paddy soils by deploying sMFCs and observing changes in soil porewater total Fe and As concentration over time. Additionally, the effect of the bioanode on the bacterial community and paddy soil physiochemical properties at various distances away were also elucidated.

2. Methods

2.1. Paddy soil samples

Subsurface paddy soil (from the upper ~15 cm) was collected from an arsenic-contaminated paddy field in Shangyu, Zhejiang, China (N29.159 E119.957) and transported directly to the lab. The soil contained 140 mg As kg^{-1} due to contamination from nearby mining activities. Samples were air dried at room temperature and sieved to less than 2 mm to remove all large particles and other large terrestrial deposits. Selective soil properties were determined and are presented in Table S1.

2.2. Soil microbial fuel cell assembly

Eight sMFCs, were assembled following the method previously described by Wang et al. (2015b) with few modifications. Four were replicate treatments (close circuit) and four replicate controls (open circuit). Each sMFC contained 1 kg (dry weight) of paddy soil. A light-proof columnar polyethylene terephthalate container (10 cm diameter × 15 cm depth) was used to construct each sMFC. Soil porewater was sampled through 3 valve ports (Top: 1 cm below the soil water inter phase, Middle: ~2 cm above the bioanode and Bottom: adjacent to the bioanode) by using a self-made sampler with 0.45 μm hollow fiber membrane. Both the anode and cathode of the sMFC were prepared from circular carbon felt (Sanye Carbon Co., Ltd, Beijing, China) with a geometric surface area of 50.2 cm^2. A data logger (USB-6225, National Instrument, Austin, USA) was used to monitor the voltage between the anode and cathode continuously across a 500 Ohm resistor.

In each sMFC container, a 1 cm depth of soil was added and then the anode was placed on the surface of the soil layer. The remaining soil sample was then used to bury the anode. Then deionized water was used to flood the paddy soil to stimulate the natural conditions leaving 500 ml of overlying water. Additional water was added daily to each sMFC to compensate for water lost due to evaporation. The cathode was installed in the overlaying water in aerobic conditions. All of the cells were incubated in the dark for 60 days at 28 °C.

2.3. Chemical analysis

Total As and Fe concentrations in soil porewater were determined by inductively coupled plasma emission spectrometry (ICPMS, NexlON™ 350x, Pekin Elmer, USA) and atomic absorption spectrometry (AAS, PinAAcle™ 900,PerkinElmer, USA), respectively, from day 0–50 at 10 days intervals. The soil from top, middle and bottom layers were collected on day 60 from both the sMFC and the control. The samples were homogenized and the content of total organic carbon (TOC) and loss on ignition (LOI) carbon was determined. LOI carbon refers to the organic matter estimated based on the weight loss on ignition (LOI) method (Santisteban et al., 2004; Zhao et al., 2016).

TOC and DOC (porewater) content were determined with a TOC analyzer (Shimadzu TOC-VCPH, Japan). LOI carbon content was determined by heating 10 g of soil at 550 °C for 4 h in a muffle furnace. Prior to heating at 550 °C samples were dried at 105 °C for 12 h and weighed. The decrease in mass after ignition of soil at 550 °C from mass obtained at 105 °C was assumed as LOI carbon (Santisteban et al., 2004).

Soil pH and redox potentials (*E*h) were measured using a HACH 440d Multi-Meter (Hach, USA) and a combined Pt and Ag/AgCl electrode, respectively. The *E*h of the soil was measured approximately 0.5 cm above the bioanode and was allowed to stabilize for 1 h before recording. The pH was determined from a soil slurry made by mixing dry soil with deionized water at a ratio of 1:2.5.

2.4. Bacterial community analysis

The bacterial communities of all the sMFC were characterized at the end of the experiment by 16S rRNA gene targeted Illumina sequencing. Briefly, 0.25 g of soil was carefully sampled from the top and middle location within each replicates sMFC. Whereas in the anode location, 0.25 g of attached soil and biofilm were carefully scraped from the anode with a sterile razor and the genomic DNA was immediately extracted from the samples using Powersoil DNA isolation Kit (MoBio Laboratories, Carlsbad, CA, USA) according to the manufacturer's instructions. The DNA concentration was quantified by a spectrophotometer (Qubit 2.0 Fluorometer, Thermo Scientific, USA) and was stored at - 80 °C until sequencing. Next generation sequencing library preparations and Illumina MiSeq2500 PE250 platforms sequencing were conducted at GENEWIZ, Inc. (Suzhou, China). Details for Illumina sequencing,