Arsenite removal from aqueous solution by a microbial fuel cell–zerovalent iron hybrid process

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ABSTRACT

Conventional zerovalent iron (ZVI) technology has low arsenic removal efficiency because of the slow ZVI corrosion rate. In this study, microbial fuel cell (MFC)–zerovalent iron (MFC–ZVI) hybrid process has been constructed and used to remove arsenite (As(III)) from aqueous solutions. Our results indicate that the ZVI corrosion directly utilizes the low-voltage electricity generated by MFC in the hybrid process and both the ZVI corrosion rate and arsenic removal efficiency are therefore substantially increased. The resultant water qualities are compliant with the recommended standards of EPA and WHO. Compared to the ZVI process alone, the H_2O_2 generation rate and output are dramatically improved in MFC–ZVI hybrid process. Strong oxidants derived from H_2O_2 can rapidly oxidize As(III) into arsenate (As(V)), which helps to improve the As(III) removal efficiency. The distribution analysis of As and Fe indicates that the As/Fe molar ratio of the flocs in solution is much higher in the MFC–ZVI hybrid process. This phenomenon results from the different arsenic species and hydrous ferric oxides species in these two processes. In addition, the electrosorption effect in the MFC–ZVI hybrid process also contributed to the arsenic removal by concentrating As(V) in the vicinity of the iron electrode.

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1. Introduction

Arsenic contamination of water has been a worldwide concern due to the toxicity and carcinogenicity of various arsenic species [1–3]. The predominant species in natural water are inorganic arsenate (As(V)) and arsenite (As(III)). As(III) exists not only in groundwater, but also widely in surface water and sediment [4–7]. Compared to As(V), As(III) is more mobile and 25–60 times higher in toxicity. The concentrated As(III) in sediment is released continuously into surface water due to the presence of a reducing environment, which renders the task of As(III) removal protracted and arduous [4,8]. Conventional techniques for arsenic removal, e.g., coagulation, precipitation and adsorption, are generally less effective for As(III) than for As(V) [3,9,10]. Therefore, studies on As(III) removal are becoming a focus in arsenic pollution research especially in drinking water treatment.

For efficient arsenic removal, oxidation of As(III) to As(V) has been suggested [9,11,12]. Arsenic removal by zerovalent iron (ZVI) technology, a facile and economical process, can simultaneously oxidize and remove As(III) [11,13–15]. The ZVI corrosion process in water releases Fe^{2+} ions, which undergo a series of oxydrolysis and finally generate many types of hydrous ferric oxides (HFOs). During this process, arsenic can be removed by means of adsorption and coprecipitation [16]. The newly formed HFOs are generally considered more effective for the pollutant removal as compared to the iron coagulants added directly [10,17]. Moreover, when the Fe^{2+} released from the ZVI process is further oxidized to Fe^{3+} by O_2, oxidants (H_2O_2, $\bullet OH$) are also generated at the same time. These oxidants can oxidize As(III) to As(V), and the latter is usually more easily removed by adsorption [3,14]. The ZVI corrosion rate directly determines the generation rates of both HFOs and oxidants, and therefore affects the arsenic removal efficiency in the ZVI process. According to the electrolytic theory, the ZVI will not corrode unless an electric current goes through the electrolyte in the system. The corrosion rate depends on the potential difference between the cathode and the anode as well as the conductivity of the electrolyte solution [18]. Since the potential differences between different sites on the ZVI surface are small, the ZVI corrosion rate is therefore quite slow. As a consequence, the arsenic removal efficiency is seriously restricted.

A microbial fuel cell (MFC) is a device that uses bacteria as the catalysts to oxidize organic and inorganic matter in the environment to produce electricity [19–22]. Sediment microbial fuel cell

(SMFC) and benthic microbial fuel cell (BMFC) are the types that generate modest levels of electrical power in sediment or seafloor environments by a mechanism analogous to the coupled biogeochemical reactions that transfer electrons from organic carbon through redox intermediates to oxygen [23,24]. Due to the limitation of the theoretical electrogenesis voltage of the MFC (on the order of 1.1 V) and the possible losses, the maximum open circuit voltage of MFC is typically less than 0.8 V [19,25]. Even in the latest microbial reverse-electrodialysis cell (MRC), the maximum voltage generated is around 1.2–1.3 V [26]. Stacking MFCs in series can improve the voltage output [27,28]. However, the advantage gained by increasing the number of series-stacked MFCs may be offset by the concomitant electric energy loss [29]. The inferior capability of power generation in the MFCs seriously restricts their applications. Currently, MFCs are mainly used to power miniwatt devices under particular circumstances. One example exploited the voltage difference between the cathode in oxygen rich water and the anode in anaerobic substrate sludge by means of BMFC to power sensors in the ocean [30].

When the MFC is coupled with other instruments or technologies, direct utilization of the generated electricity without electricity collection is possible because of the specific structure of the MFC and its electricity generation characteristics [31]. For example, the MFC can be used to treat the wastewater containing NO_3^-, CrO_4^{2-}, Cu^{2+}, etc. [32–34]. Modified MFC can also be used in seawater desalination, in which the potential difference generated in the MFC was directly used to separate the anions from cations in seawater [35,36]. These novel ways of MFC utilization not only make full use of the electrons and electricity generated in the MFC, but also expand its range of application.

The marriage of the MFC and ZVI technologies would potentially provide an efficient way of utilizing the low electricity generated by the MFCs for driving the ZVI corrosion process. To the best of our knowledge, no study on the MFC–ZVI hybrid process has been reported.

In this paper, we provide proof of concept of the MFC–ZVI hybrid system for As(III) removal from aqueous solutions. The unique characteristics of this hybrid system as compared to the ZVI process are discussed. The underlying mechanism in the As(III) removal process is investigated in terms of the As(III) removal efficiency, the production of HFOs and H_2O_2 and the distribution profiles of the arsenic and iron in the process.

2. Materials and methods

2.1. Construction and operation of the MFC

A single-chamber MFC, 125 cm³ in volume of slab geometry, 5 cm × 5 cm × 5 cm, was used in this work. Carbon paper containing a Pt catalyst (0.5 mg cm⁻²) on the water-facing side (4 cm × 4 cm (16 cm²), Feichilvneng Co., Beijing, China), as the air cathode, was connected to the external circuit by a copper mesh (100 mesh, Hiway Co., Beijing, China). Non-wet-proofed carbon felt (4 cm × 4 cm (16 cm²), 3 mm thick, Beijing Evergrow Resources Co., Ltd., China) was used as the anodes. The MFC was inoculated with anaerobic sludge (collected from Xiaojiahe Wastewater Treatment Plant in Beijing, China, 50% v/v) and fed with a synthetic medium. The medium composition was as follows (per liter): glucose, 800 mg; $NaH_2PO_4 \cdot 2H_2O$, 5620 mg; $Na_2HPO_4 \cdot 12H_2O$, 6150 mg; NH_4Cl, 310 mg; KCl, 130 mg; a mineral solution of 12.5 mL [37]. The MFC was operated at a room temperature of 25 ± 3 °C. The performance of the working MFC was characterized by polarization curves and power density curves. Polarization curves were obtained using an adjustable external resistance.

Power and current were calculated based on the following equations:

$$P = I \times E \tag{1}$$

$$I = \frac{E}{R_{ext}} \tag{2}$$

where P is the generated power; E is the measured cell voltage; R_{ext} is the external resistance, and I is the produced current. The online recorded produced current and power were normalized by the surface area of the used anode. Columbic efficiency (CE) can be calculated as follows [38].

$$CE = \frac{C_P}{C_T} \times 100 \tag{3}$$

where C_P is obtained by integrating the current variation over time and C_T is the theoretical amount of coulombs that can be produced from the carbon source (i.e., glucose).

2.2. Arsenite removal experiment

The chemicals were of analytical reagent grade and used without further purification. The test solution containing 300 µg/L arsenic was prepared by adding a proper amount of As_2O_3 into the tapwater obtained from Peking University. The pH value of the test solution is 8.0. Its compositions are shown in Table S1 in Supporting information. Other solutions were prepared using Milli-Q (18.2 MΩ cm) water.

Arsenite removal was conducted using the MFC–ZVI hybrid process and the ZVI process, respectively. The ZVI process was composed of a beaker (250 mL) and two electrodes. Anode was made of high purity iron (2.5 cm × 2.5 cm (6.25 cm²), 5 mm thick, Mengtai Co., Beijing, China) and cathode was made of carbon felt (2.5 × 2.5 cm (6.25 cm²), 3 mm thick, Beijing Evergrow Resources Co., Ltd., China). The distance between the two electrodes immersed in water was 0.7 cm. Before the experiment, high purity iron electrode was polished by a sand paper and rinsed in 1 N H_2SO_4 followed by deionized water. This process should be repeated if the electrode is used again. During the experiments, air was pumped (2 W, Hibive Co., Hangzhou, China) into the cathode region at a flux of about 500 mL/min. The distance between the two electrodes, specific surface area of anode, cathode material and other parameters of the ZVI process may affect the arsenic removal efficiency. For the objective of the study is to provide a proof of the concept of the MFC–ZVI hybrid system for As(III) removal from aqueous solutions, these parameters were kept constant in this study. The MFC–ZVI hybrid process was set up by coupling the MFC with the ZVI process and its schematic is shown in (Fig. 1). The cathode of the MFC was connected to the high purity iron anode of the ZVI process, while the anode of the MFC was connected to the carbon felt cathode of the ZVI process. The current going through the MFC–ZVI hybrid process was obtained by measuring the voltage over a 10 Ω resistance connected into the circuit (Eq. (2)).

200 mL test solution was used in each test. The air pump was started as soon as the entire circuit was completed. Samples were taken by syringes at regular intervals for the analysis of As(III) and total arsenic (As(tot)). Each test was repeated three times, and the average was used for data analysis.

2.3. H_2O_2 and Fe(tot) determination

Fe(II) generated by ZVI corrosion can react with H_2O_2, which results in the consumption of H_2O_2 and the production of HFOs. In order to get the accurate amount of H_2O_2 and total Fe (Fe(tot)) generated in both processes, a specific experiment was conducted by adding 5 µM 2,2'-bipyridyl (BPY) into the reaction system to