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Spontaneous thallium (I) oxidation with electricity generation in single-chamber microbial fuel cells

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HIGHLIGHTS

- Tl(I) is oxidized to Tl(III) spontaneously in microbial fuel cells (MFCs).
- The maximum power density of 457.8 ± 15.2 mW m^{-2} is obtained.
- Tl(III) precipitates naturally, realizing total Tl removals from groundwater.
- Enriched *Rhodococcus* and newly appearing *Acidovorax* contribute to Tl(I) oxidation.
- Electricigens as *Ochrobactrum* and *Aquamicrobium* are also accumulated.

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ABSTRACT

Pollution of highly toxic thallium (Tl) attracts worldwide attention and development of promising removal technologies will be of strong interest. Herein, spontaneous Tl(I) oxidation was realized with electricity generation in microbial fuel cells (MFCs). Over 67.2 ± 2.3% of Tl(I) was removed during 72 h operation with initial Tl(I) concentration of 100 μg L^{-1} in MFCs, and maximum power density of 457.8 ± 15.2 mW m^{-2} was achieved. Electrochemical tests suggested the adverse effects of Tl(I) addition in power outputs. The oxidation product was less mobile Tl(III), which could precipitate naturally in a wide pH range. High-throughput 16S rRNA gene sequencing implied the potential ability of enriched *Rhodococcus* and newly appearing *Acidovorax* to implement the process of Tl(I) oxidation while accumulated electricigens as *Ochrobactrum* and *Aquamicrobium* were responsible for electricity generation. This work initiates an efficient and cost-effective method to deal with thallium pollution in environment.

1. Introduction

Thallium (Tl), a rare but widely distributed element, presents in nearly all mediums [1]. Its intensive applications in pest control, disease treatment [2] as well as growing demand in high-technology fields increases the risk of a much larger portion of Tl releasing into the environment [3]. Tl contamination in water and soil is widespread in the world and it has a serious impact on public health [4,5]. Compared with other heavy metals as Cd, Pb, Zn and Hg, Tl is much more toxic to mammals, as it can be absorbed through the skin or mucous membranes, then disperses in the whole body and accumulates in bones, finally infects the central nervous system [6]. The US Environmental Protection Agency (USEPA) lists thallium as a priority pollutant due to its high toxicity. There are two main oxidation states of Tl, i.e. Tl(I) and Tl(III) [7]. Tl(I) possesses much stronger mobility than Tl(III) as it acts similarly to K^+ and can be transported through cell membranes actively, drawing more attentions [8]. Over the past decades, numerous technologies have been employed for Tl(I) removal, mainly fitting into adsorption [9,10], with requirements of large amounts of adsorbents which are very expensive and difficult to regeneration or disposal. Moreover, Tl(III) tends to be hydrolyzed with predominant form of Tl $(OH)_3$, which is easier to be removed from aqueous solution, though it is more toxic than Tl(I) [11]. Oxidation of Tl(I) to Tl(III), with subsequent precipitation is also a promising strategy [12,13], while supplementary oxidants with complicated operations are frequently involved when chemical oxidations are conducted [14]. High costs of electrochemical oxidation also restrict its engineered applications though it can oxidize Tl(I) to Tl(III) [15]. A more efficient, green and simple way is urgently required for controlling Tl(I) contamination.

Microbial fuel cells (MFCs) are recognized promising devices which

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use microbes as catalysts to oxidize organic or inorganic matters to generate electricity simultaneously [16,17]. In the past decade, MFCs have become an attractive and continual expanding field and single-chamber air cathode MFCs are recognized as the most promising configuration to scale up for actual applications in the future [18,19]. Numerous pollutants have been successfully handled as substrates in MFCs with electricity generation [20,21]. Redox sensitive heavy metals with higher valences can also be electrochemically reduced, instead of commonly used oxygen, for detoxification in cathode chambers of MFCs, such as Cr, V, Cd, Ag and Zn [22,23]. As microbes can tolerate toxicities of heavy metals to a certain extent, treating heavy metals in the anode chambers of MFCs exhibits primary advantages with their accelerated removals due to biological and electrochemical oxidations taking place simultaneously. Successful V and As treatments have provided evidences, with specific functional microbial species [24,25]. Redox potential of the pair Tl(III)/Tl(I) ($E^{\Theta} = -1.26$ V) indicates the relatively easier oxidation of Tl(I) to Tl(III) for removal by weak oxidant or even through microbial metabolisms [26,27]. Actually, highly Tl-tolerant microbes are reported, which are potentially useful in the remediation of Tl-contaminated sites [28]. Thus Tl, one of the redox sensitive heavy metals, can also be handled in the anode chamber of MFCs with energy recovery, exhibiting economic and environmental benefits. Representative microbial communities may also be accumulated, while limited studies have been carried out on this aspect.

In this study, efficient Tl(I) oxidation was achieved in the anode chambers of MFCs with electricity generation simultaneously. The polarization curves and power outputs of MFCs with addition of Tl(I) were studied. Oxidation products and electrochemical characteristics of MFCs were also investigated to understand the oxidation process and evaluate the performance of MFCs deeply. The involved microbial communities have also been analyzed based on molecular bio-techniques. This study offers a new alternative to remediate Tl-contaminated environment efficiently.

2. Methods and materials

2.1. Experimental apparatuses and operations

Four cubic single-chamber air cathode MFCs were constructed (Fig. 1), as reported in our previous study, with an operative volume of 125 mL (5 cm × 5 cm × 5 cm) [29]. Carbon felt with 1 cm thickness, 3 cm length and width acted as anode. The cathode made of plain carbon paper with 0.5 mg cm^{-2} of Pt on one side was placed on the opposite site of the anode with a projected surface area of 9 cm^2. The anode and cathode were connected via an external resistor (100 Ω) using copper wires. The components (per liter) of the electrolyte were: $C_6H_{12}O_6$ (0.75 g); $NaH_2PO_4{\cdot}H_2O$ (4.97 g); $Na_2HPO_4{\cdot}H_2O$ (2.75 g); NH_4Cl (0.31 g); KCl (0.13 g); vitamin solution (1.25 mL) and 12.5 mL trace mineral element solution [24]. Glucose is a fermentable substrate and can support more diverse and complex bacterial communities, which was of particular importance during microbial treatment of contaminants with high toxicity [30]. All MFCs were divided into two groups equally, i.e. MFCs with addition of 100 μg L^{-1} Tl(I) in the form of $TlNO_3$ (MFC-Tl) and MFCs without Tl as control (MFC-C). The initial Tl(I) level was based on the average Tl concentration of 62 μg L^{-1} in the groundwater of Lanmuchang area (southwestern Guizhou Province, China) [31]. Another two abiotic fuel cells (AFC) without inoculation built with the same structure as the above MFCs, were also employed for comparison (AFC-Tl).

All MFCs were inoculated with 25 mL anaerobic sludge obtained from an anaerobic reactor in a wastewater treatment plant. Subsequently, the MFCs operated with respective anolyte in a 72 h batch mode until the voltage output of MFCs was reproducible in more cycles, which indicated the successful start-up of MFCs and also excluded the influence of adsorption by anodic electrode for Tl(I) removals. After that, the Tl(I) oxidation and the power outputs were evaluated in MFC-Tl in a typical cycle (72 h), compared with all control sets. Trials of AFC-Tl were also performed after the achievement of adsorption saturation of its anodic electrode for Tl(I). Then the exhausted anolyte in MFC-Tl was filtered through a suction filter with a 0.22 μm membrane to obtain the oxidation product for component analysis. Parts of Tl in bacterial cell and anodic electrode were separated according to Wang et al. [32] for element balance analysis. The richness, diversity and taxonomy of the involved microbes were also analyzed through high throughput sequencing after another 6 cycles' operation. All experiments were carried out at ambient temperature (22 ± 2 °C) and the two sets in each group operated under identical conditions. Each test was repeated three times and average results were

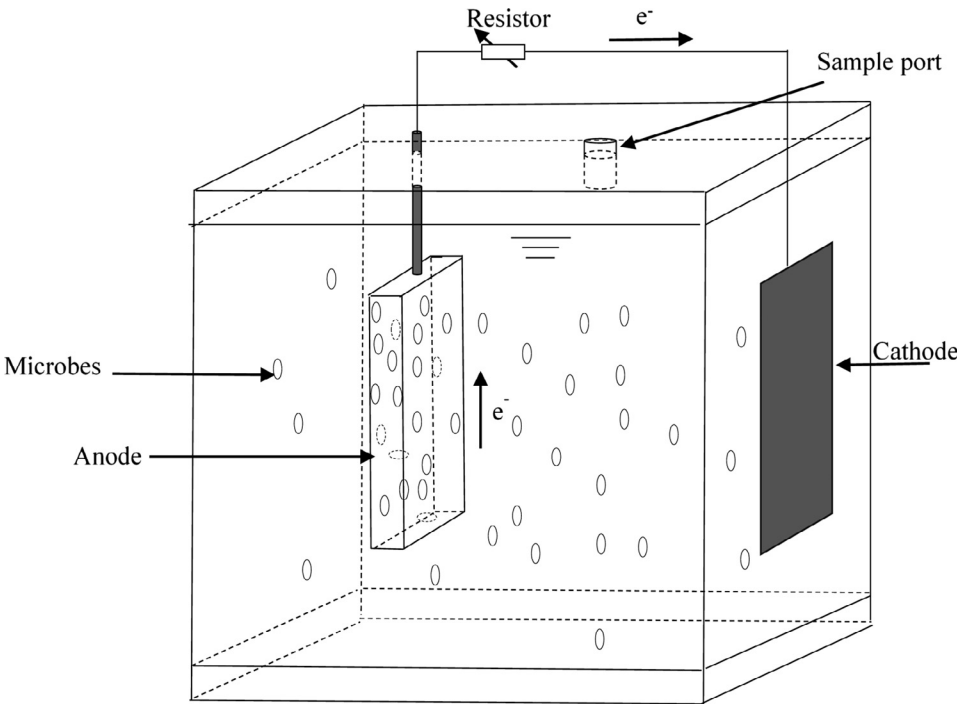

Fig. 1. The schematic diagram of MFCs employed in the present study.