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Mixed sulfate-reducing bacteria-enriched microbial fuel cells for the treatment of wastewater containing copper

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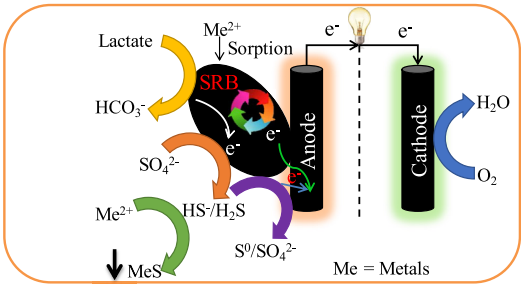
HIGHLIGHTS

- SRB enriched MFC system was developed for investigating heavy metal removal.
- Ten successive batches for voltage generation showed excellent reproducibility.
- Maximum copper tolerance concentration in the biological anodic chamber was 20 mg/L.
- Among SRB, *Desulfovibrio* (38.1%) was the most abundant genus at the anode.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) have been widely investigated for organic-based waste/substrate conversion to electricity. However, toxic compounds such as heavy metals are ubiquitous in organic waste and wastewater. In this work, a sulfate reducing bacteria (SRB)-enriched anode is used to study the impact of Cu^{2+} on MFC performance. This study demonstrates that MFC performance is slightly enhanced at concentrations of up to 20 mg/L of Cu^{2+}, owing to the stimulating effect of metals on biological reactions. Cu^{2+} removal involves the precipitation of metalloids out of the solution, as metal sulfide, after they react with the sulfide produced by SRB. Simultaneous power generation of 224.1 mW/m^2 at lactate COD/SO_4^{2-} mass ratio of 2.0 and Cu^{2+} of 20 mg/L, and high Cu^{2+} removal efficiency, at >98%, are demonstrated in the anodic chamber of a dual-chamber MFC. Consistent MFC performance at 20 mg/L of Cu^{2+} for ten successive cycles shows the excellent reproducibility of this system. In addition, total organic content and sulfate removal efficiencies greater than 85% and 70%, respectively, are achieved up to 20 mg/L of Cu^{2+} in 48 h batches. However, higher metal concentration and very low pH at <4.0 inhibit the SRB MFC system. Microbial community analysis reveals that *Desulfovibrio* is the most abundant SRB in anode biofilm at the genus level, at 38.1%. The experimental results demonstrate that biological treatment of low-concentration metal-containing wastewater with SRB in MFCs can be an attractive technique for the bioremediation of this type of medium with simultaneous energy generation.

1. Introduction

Tremendous micro and macro industrialization with heavy

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metals as an integral part of numerous activities has led to discharges of large amounts of metal-containing wastewater, which has caused severe environmental problems. Cu^{2+}-containing waste, in particular—from many metal industries (including hydrometallurgy and metal finishing), mining, electroplating, battery production and microelectronics—has been continuously increasing in the influent streams reaching wastewater treatment plants (Ma et al., 2014). Cu^{2+} is a toxic and non-biodegradable inorganic heavy metal pollutant that bioaccumulates in the food chain, creating lethal effects in many vital human organs and also in all other organisms (Gall et al., 2015). In addition, high sulfate content is prevalent in waste streams from metal-leaching operations. As a pollutant, sulfate corrodes metals and causes H_2S-altered toxicological effects. Extended exposure to it can also cause acute renal failure, hepatotoxicity, increases in hippocampus superoxide dismutase, neurological impairment, and shock (Hussain et al., 2016). Therefore, heavy metals including Cu^{2+} and sulfates must be treated efficiently before wastewater is discharged into the environment.

Many physical and chemical methods are available for treating wastewater containing metals (Wang and Chen, 2009), including chemical precipitation, electrochemical treatment, reverse osmosis, ion exchange, and evaporation recovery, which can be often futile or incur huge expenses, particularly if the metal concentrations is as low as 1–100 mg/L (Ahluwalia and Goyal, 2007). Moreover, the treatment of organics present in wastewater cannot be achieved by these techniques alone. Therefore, economical, effective, and eco-friendly processes are continuously sought to remove heavy metals from wastewater and ensure their presence in the environment is below permissible limits.

A microbial fuel cell (MFC) is a promising technology for directly generating electricity from organics; therefore, it has huge potential to treat wastewater economically and sustainably without involving fossil fuel-based energy (Logan and Regan, 2006; Rabaey and Verstraete, 2005). In earlier MFC studies, Cu^{2+} removal/recovery has been studied using dual-chamber MFCs in which Cu^{2+} was mainly removed in the cathodic chamber by cathode metal reduction and organic matter in the anodic chamber was used as a carbon source and an electron donor (Heijne et al., 2010; Pau et al., 2015; Tao et al., 2011). In those studies, however, the cathodic medium contained only Cu^{2+} without organic compounds, whereas many waste streams contain sulfates and organic substances in addition to heavy metals like textile, paper and pulp, acid mine drainage, and mining and mineral processing wastewater. Therefore, the use of the microbial section of MFCs can be more viable for the simultaneous removal of these pollutants up to certain limits.

Microbial communities in MFCs play a very important role in overall current generation and effective pollutant treatment (Hernández-Fernández et al., 2015). Sulfate-reducing bacteria (SRB) were recently tested for removing organics and generating power in MFCs, and the SRB were confirmed to have an electroactive nature with the ability to perform extracellular electron transfer (Kang et al., 2014). One of the most attractive approaches for the treatment of metallic waste is the precipitation of metal ions in the form of their respective sulfides, in which metal precipitation can be aided by biological sulfate reduction to S^{2-}, HS^-, H_2S, and other components. Such a technique offers attractive advantages over the conventional chemical precipitation methods. Thus, SRBs enriched MFCs can be cost-effective due to moderate operational condition, low sludge production, and high electric efficiency (Lovley, 2008). Removal of heavy metals by SRB is due to the formation of highly insoluble precipitates with biogenic sulfide. The solubility product of most metal sulfides is extremely low, where the solubility product constant of CuS is 1.27×10^{-36} (White and Gadd, 2000). This implies that small sulfide concentrations are required to effectively remove metals. The additional advantage associated with the biological sulfate reduction technique is the production of a low amount of secondary sludge for further disposal. Thus, it is known to be an efficient technique for removing heavy metals from wastewater at low initial concentrations (Cabrera et al., 2006).

The aim of the present work is to develop and investigate an MFC system to treat wastewater containing low concentrations of Cu^{2+}, using mixed SRB in an anodic chamber coupled with bioelectricity generation. The reproducibility of the MFC system is confirmed by running many consecutive cycles at a specific feed condition. The maximum tolerance concentration (MTC) for Cu^{2+} in the anodic chamber is determined, and the mechanism of Cu^{2+} removal with sulfate reduction and current generation is proposed. The tests are also designed to differentiate between sorption and other removal mechanisms of Cu^{2+} in the anodic chamber. Microbial community analysis by using the Illumina Miseq platform is also conducted to determine the shift toward SRB-dominant cultures.

2. Materials and methods

2.1. Inoculum and culture medium

Sludge was collected from the anaerobic section of a domestic wastewater treatment plant in Daegu, Republic of Korea. The sludge was sieved to remove larger foreign particles and was then used for the enrichment of SRBs. Briefly, 1-L glass bottles were seeded with sieved anaerobic sludge and Postgate's B medium after autoclaving at 121 °C and 15 psi for 20 min. The medium contained sodium sulfate and sodium lactate for sulfate and lactate sources, respectively. Sodium bromoethane sulfonate was also initially added to the medium to avoid methanogenic activity, which can consume the carbon (lactate) source. Enrichment was conducted in a shaking incubator at 130 rpm and 30 °C. 70% of the medium was decanted and was replaced weekly. The enriched medium after six cycles, with sulfate reduction and sulfide formation indicated by blackening of the media, was then transferred to the anodic chamber of the MFC for further experiments.

2.2. MFC setup and operation

The MFC was composed of two 0.2-L chambers separated by a 183 μm thick Nafion 117 proton exchange membrane. Treatment of the Nafion membrane was conducted for performance enhancement by 0.1 M H_2SO_4 solution, deionized water, 0.1 M H_2O_2 solution, and deionized water again, heating each at boiling point for 1 h. A 3.18 mm thick carbon felt (Alfa Aesar, Haverhill, USA) having length of 5 cm and a width of 5 cm was used as the anode electrode. A 1.0 mg/cm^2, 20 wt% platinum-coated carbon cloth (Fuel Cell Earth, Wakefield, USA) having dimensions of 5 cm × 5 cm was utilized as the cathode electrode. The anode and cathode electrodes were connected by a titanium wire through a 500 Ω resistor. The growth medium used in the anode contained per liter 500 mg (COD) of lactate, 500 mg of K_2HPO_4, 1000 mg of NH_4Cl, 60 mg of $FeSO_4 \cdot 7H_2O$, 100 mg of $MgSO_4 \cdot 7H_2O$, and 1 mL of trace mineral solution. A lactate COD/SO_4^{2-} mass ratio of 2.0 was used. It is important to mention here that lactate is used due to its superiority as an electron donor to many others such as ethanol, H_2, propionate, and acetate in terms of energy and biomass yield. Thus, lactate as the electron donor for SRB accelerates the start-up of the bioprocess. Moreover, complete oxidation of lactate by SRB produces 3 mol of bicarbonate alkalinity per mol of substrate, and sulfidogenic lactate oxidation yields some alkalinity even if the oxidation is incomplete, which is not the case with other substrates (Nagpal