Simultaneous removal of tetrathionate and copper from simulated acidic mining water in bioelectrochemical and electrochemical systems

Mira L.K. Sulonen*, Marika E. Kokko, Aino-Maija Lakaniemi, Jaakko A. Puhakka

Laboratory of Chemistry and Bioengineering, Tampere University of Technology, Tampere, Finland

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ABSTRACT

This study demonstrates (bio)electrochemical tetrathionate ($S_4O_6^{2-}$) degradation with simultaneous elemental copper recovery from simulated acidic mining water. The effect of applied external voltage on anodic tetrathionate removal, cathodic copper removal and current density was studied using two-chamber flow-through bioelectrochemical (MEC) and abiotic electrochemical (EC) systems. At low applied cell voltages (≤ 0.5 V), the highest tetrathionate removal rate (150–170 mg L^{-1} d^{-1}) and average current density (15–30 mA m^{-2}) was obtained with MEC. At applied external voltages above 0.75 V, abiotic EC provided the highest average current density (410–3600 mA m^{-2}). In bioelectrochemical systems, the current generation likely proceeds via intermediary reaction products (sulfide and/or thiosulfate), while in electrochemical system tetrathionate is oxidized directly on the electrode. The copper removal rates remained low (< 10 mg L^{-1} d^{-1}) in all systems at applied cell voltages below 0.5 V, but increased up to a maximum of 440 mg L^{-1} d^{-1} in MEC and to 450 mg L^{-1} d^{-1} in EC at applied cell voltage of 1.5 V. After seven days of operation at applied cell voltage of 1.5 V, copper removal efficiency was 99.9% in both MEC and EC and the average tetrathionate removal rates were 160 mg L^{-1} d^{-1} and 190 mg L^{-1} d^{-1}, respectively. This study shows that by applying external voltage, tetrathionate and copper can be efficiently removed from acidic waters with bioelectrochemical and electrochemical systems.

1. Introduction

Mining waters from sulfide mineral processing often contain metals and reduced inorganic sulfur compounds (RISCs), such as thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$). RISCs can be toxic to several organisms at concentrations above 0.5 g L^{-1} (Schwartz et al., 2006). Several sulfur oxidizing microorganisms, such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Sulfolobus metallicus*, oxidize RISCs aerobically, forming sulfuric acid (Johnson and Hallberg, 2008). The uncontrolled release of RISC containing mining waters can thus lead to oxygen depletion and acidification of the environment. The acidic waters can leach minerals, which further increases their metal concentrations and therefore also their toxicity. The guideline value for, for example, copper concentration in drinking water set by the World Health Organization (WHO) is 2 mg L^{-1} (WHO, 2011). According to the Code of Federal Regulations of United Sates, the copper concentration in effluents from ore mining operations should remain below 0.3 mg L^{-1} (EPA, 2011).

In electrochemical systems, chemical energy is converted to electrical energy via redox reactions. A substrate is oxidized in the anodic chamber and the electrons released are transferred from the anode electrode to the cathode via an electrical circuit. At the cathode, an electron acceptor receives the electrons from the cathode electrode and becomes reduced. In bioelectrochemical systems (BESs), the oxidation of the substrate or/and the reduction of the electron acceptor is catalyzed by microorganisms (Logan et al., 2006; Pandey et al., 2016). BESs producing electrical energy are called microbial fuel cells (MFCs), while in microbial electrolysis cells (MECs) external electrical energy is applied to realize the oxidation and reduction reactions.

Metals can be removed and recovered from water by reducing them at the cathode of an electrochemical system. Certain metals present in acidic solutions can be electrodeposited on to a surface of an electrode in pure elemental form (Chen, 2004). Electrochemical systems enable efficient and selective recovery of metals even from water streams with low metal concentrations (Janin et al., 2009). With BES, the electrical energy required for electrochemical metal recovery can be fully or partly driven from microbially mediated anodic oxidation of biodegradable substrates. In BESs, metal recovery was first demonstrated with copper (ter Heijne et al., 2010), and, thereafter, several other metals, such as zinc, silver, and vanadium, have been successfully recovered (Choi and Cui, 2012; Modin et al., 2012; Zhang et al., 2012).

Previous bioelectrochemical metal removal studies have been

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mainly conducted with neutral anodic solution and with organic compounds, such as acetate (ter Heijne et al., 2010; Choi and Cui, 2012; Modin et al., 2012) and glucose (Zhang et al., 2012), as the anodic electron donors. Recently, Ntagia et al. (2016) demonstrated copper removal in BES via biological hydrogen oxidation at neutral conditions. Water streams from processing of sulfide minerals usually contain no organic compounds. Therefore, to recover metals bioelectrochemically from such streams, an external organic substrate stream would be required. In addition, the anodic pH needs to be maintained close to neutral with a buffer, for example, to ensure the growth of the neutrophilic heterotrophic microorganisms.

The removal of sulfur pollutants has been demonstrated in bioelectrochemical systems operated in neutral conditions with sulfate-reducing bacteria reducing sulfate to sulfide, which is electrochemically oxidized on the anode electrode (Rabaey et al., 2006; Zhao et al., 2009). Recent studies show that in highly acidic conditions RISCs can serve as the electron donor in bioelectrochemical (Sulonen et al., 2015; Ni et al., 2016; Sulonen et al., 2016) and electrochemical systems (Sulonen et al., 2017). RISCs could thus be used as the partial source of energy for the recovery of metals, while simultaneously removing both RISCs and metals from acidic mining waters. Even though the anodic (Sulonen et al., 2015; Ni et al., 2016) and cathodic (ter Heijne et al., 2010; Rodenas Motos et al., 2015) reactions have been individually demonstrated, simultaneous electrochemical removal of RISCs and metals has not been previously studied. The study of the electrochemical system as a whole is essential in order to determine the amount of external energy required to realize both the oxidation and reduction reactions, the effect of the applied cell voltage on the anode and cathode potentials and the effect of reaction products on the characteristics of the anodic and cathodic solutions (e.g. pH, conductivity). Several RISCs degrading microorganisms are acidophilic (Johnson and Hallberg, 2008) and, therefore in an electrochemical system with RISC degrading anode and metal reducing cathode, both anode and cathode could be operated in acidic conditions to avoid the formation of pH gradient over the membrane, which increases the internal resistance of the system (Sleutels et al., 2012). RISC degrading microorganisms also often have a high tolerance for heavy metals (Dopson et al., 2003), and the risk of microbial growth inhibition caused by the metal ions leaking from the cathode to anode is low.

The objective of this study was to simultaneously remove tetrathionate and recover copper from acidic simulated mining water in (bio)electrochemical systems by applying external voltage. Tetrathionate was used as the electron donor at the anode and copper as the electron acceptor at the cathode in bioelectrochemical and electrochemical systems. Current generation, tetrathionate degradation, and copper removal and recovery were studied at applied cell voltages ranging from 0.2 V to 1.5 V. The experiments were conducted with two-chamber flow-through reactors at ambient temperature (20 $\pm$ 2 °C) under highly acidic anodic and cathodic conditions (pH < 2).

2. Materials and methods

2.1. Experimental setups

External voltage was applied to tetrathionate-degrading copper reducing bioelectrochemical (MECs) and electrochemical systems (ECs). The cell voltage (ranging from 0.2 V to 1.5 V) was either gradually increased (MEC, EC$_I$) or constant cell voltage was applied (EC$_{II}$). The current generation was compared to two abiotic electrochemical control reactors, one with phosphate buffered (20 mM K$_2$HPO$_4$) water (Cont$_{H_2O}$) and the other with mineral salts medium (Cont$_{Media}$) as the anolyte, to study the contribution of water (Cont$_{H_2O}$) and media compounds (Cont$_{Media}$) to the current generation. Copper (initial concentration 1 g Cu^{2+} L^{-1}, added as CuCl$_2$) was used as the electron acceptor at the cathode, if not otherwise stated.

2.2. Cell construction

The electrochemical systems used have been previously described by ter Heijne et al. (2008). The anode and cathode chambers (33 cm^3 each) were separated with an anion exchange membrane (AMI-7001, Membrane International, USA). Graphite plates (MR Graphite, Germany) covered with carbon paper (Graphite foil, Coidan graphite products, USA) were used as the anode and cathode electrodes, the effective surface area being 22 cm^2. Anode and cathode potentials were measured against Ag/AgCl reference electrodes (Sentek, UK; estimated standard potential 205 mV vs. Normal Hydrogen Electrode (NHE)) placed in 3 M KCl and connected to the anolyte or catholyte with a glass capillary (QiS, the Netherlands). The potential values are presented against Ag/AgCl, if not otherwise stated. The reactors were operated at room temperature (20 °C $\pm$ 2 °C) in a fed-batch mode. The anolyte and catholyte solutions (volume of each 0.5 L) were continuously recirculated (166–170 mL min^{-1}) over a recirculation bottle.

2.3. Bioelectrochemical cells

In bioelectrochemical systems (MEC$_I$ and MEC$_{II}$), potassium buffered (20 mM K$_2$HPO$_4$) medium containing 10% (v/v) of mineral salts medium (MSM) and 1% of trace element solution (TES) was used as the anolyte (conductivity 11.5 mS cm^{-1}) (Sulonen et al., 2015). To remove oxygen, anolyte and catholyte solutions were purged with nitrogen (15 min) prior inoculating the anolyte with an enrichment culture that originated from hydrometallurgical mining process water and had been enriched in tetrathionate-fed MFC for over eight months (10% (v/v)). After inoculation and every four weeks, 1% (v/v) of 1 M sodium bicarbonate (NaHCO$_3$) was added to the anolyte to provide a carbon source for the anodic microorganisms. The initial tetrathionate concentration was 2 g L^{-1} and pH 2. MECs were fed by adding medium solution containing 125 g L^{-1} S$_4$O$_6^{2-}$ (final concentration 2–2.5 g L^{-1} S$_4$O$_6^{2-}$) to the anode chamber after the tetrathionate concentration of the anolyte decreased below 0.5 g L^{-1}.

MECs were started up as MFCs connected to an external resistor of 1000 Ω with 2 g L^{-1} Fe^{3+} (FeCl$_3$, pH 1.5) as the terminal electron acceptor at the cathode. In MEC$_I$, the catholyte was changed to 1 g L^{-1} Cu^{2+} (CuCl$_2$, pH 2) on day 48 and the cell was operated as an MFC up to day 104 to study the electricity production and copper recovery in tetrathionate-fed BES without applied cell voltage. After day 104, the applied cell voltage was gradually increased from 0.2 V to 1.5 V, the operation time at each voltage being 20–40 days to ensure the biofilm growth/acclimation. In MEC$_{II}$, the applied cell voltage was gradually increased starting from 0.2 V with steps of 0.2 V until the anode potential reached 1.0 V vs. Ag/AgCl (obtained at applied cell voltage of 0.6 V on day 46). Fe^{3+} was used as the cathodic electron acceptor during the increasing of the applied cell voltage for efficient current generation. MEC$_{II}$ was operated with each applied cell voltage for at least 7 days before increasing the voltage. The catholyte was replaced with 1 g L^{-1} Cu^{2+} (CuCl$_2$, pH 2) on day 46, after which voltage of 1.2 V was applied for 21 days. The applied cell voltage was then further increased to 1.5 V and the cell was operated at this voltage for 17 days. All catholyte solutions were prepared in MilliQ water and the pH was adjusted to the presented value with 37% HCl.

The tetrathionate degradation was additionally studied in a bioelectrochemical control reactor, which was operated in open circuit (OC) mode. The operation conditions were the same than in MECs, but the anode and cathode electrodes were not connected. The OC cell was inoculated with the anolyte of tetrathionate-degrading microbial fuel cell and the catholyte contained 1 g L^{-1} Cu^{2+} (CuCl$_2$, pH 2). Moreover, biological tetrathionate degradation in anaerobic conditions was tested by inoculating two bottles containing phosphate buffered media solution (total volume 0.5 L, pH 2.5) with the anolyte of a tetrathionate-degrading microbial fuel cell. The bottles were purged with nitrogen (15 min) and the tetrathionate degradation was followed for 90 days.