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Hydrogen as electron donor for copper removal in bioelectrochemical systems

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ABSTRACT

Hydrogen gas is an attractive alternative electron donor since it is produced in large quantities as a side product in the metallurgical industry. Aim of this study was to demonstrate that microbial anodic hydrogen oxidation on a non-catalyzed graphite electrode can be coupled with cathodic copper reduction in a BES to simultaneously recover copper and produce power. The strategy was to first grow an anodic biofilm on acetate, then replace the acetate with hydrogen as electron donor, and finally combine hydrogen oxidation with copper reduction in the cathode. The maximum current density was 1.8 A/m^2 at −250 mV anode potential vs Ag/AgCl. When coupled with Cu^{2+} reduction, the maximum power density was 0.25 W/m^2 at a current density of 0.48 A/m^2. Anode overpotentials were higher compared to acetate oxidation, probably a result of limited hydrogen solubility and transfer.

Introduction

Significant volumes of heavy metal containing wastewaters are produced continuously at metal producing or electroplating companies. Heavy metals have been proven highly toxic for human, microbial and plant life [1,2]. Because heavy metals, even at low concentrations have negative effects on the environment, there is a need to remediate metal containing waste streams. Moreover, metal resources are finite, making their recycling crucial, since their production and transportation results in high energy consumption and arises unwanted and highly pollutant gas, solid and liquid emissions [3,4].

Conventional heavy metal removal technologies include electrochemical, chemical precipitation and ion-exchange. Although these technologies are applied in practice and at large scale their economic and environmental impact could still be improved by reduction of the high operational costs due to chemicals and energy consumption and the reduction of excessive production of hazardous wastes. This

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improvement could possibly also be achieved by the removal of these heavy metals in bioelectrochemical systems (BES) [3,5]. In order to improve economic revenue and environmental impact of heavy metal treatment, we propose the removal of metals with BES. In BES the costs for chemicals and also for energy are minimized, and even power is produced in some cases; the biological oxidation of organic substrates provides part of required energy input. An anode, where substrate is oxidized and electrons are entering an electrical circuit, a cathode where a reduction reaction takes place and electrons are leaving the electrical circuit and, in most of the cases, an ion-exchange membrane that keeps the anolyte and catholyte separated and prevents substrate/product crossover [6].

Several metals have been demonstrated as electron acceptors in BES cathodes such as silver [7,8], iron [9–11], Nickel [12], zinc [13] and copper [13–19]. A common feature in all these studies is that the electron donor in the anodic compartment is an organic substrate. Electrochemically active bacteria are efficient oxidizers of organic substrates such as glucose, ethanol, glycerol, cellulose feedstocks, sewage sludge and aromatic compounds, but also inorganic such as hydrogen and sulfur compounds [20–22]. The use of organic substrates limits application of BESs to certain locations were organic wastewaters are available, but in reality organic waste streams are not ubiquitous. At the same time, mining and metal industries, being the ones most interested in metal recovery, produce large amounts of hydrogen as a side product of their electroplating activities [23,24]. Hydrogen is also produced in reduction furnace operations [25] and as a side product of electro-catalytic treatment for acidity in mine waters [26,27].

Hydrogen can be used as electron donor in chemical fuel cells where it reacts with oxygen to produce electric current. The drawbacks of fuel cells are that they utilize noble metal catalysts like platinum, which are expensive and rare materials, and often operate at extreme conditions [28,29]. Microorganisms could serve as an alternative catalyst for the hydrogen oxidation reaction. Production of current by hydrogenotrophic anodophilic bacteria in MECs has already been reported by a number of researchers [30–32]. Rozendal et al. (2008) [33] used hydrogen as electron donor in order to grow a bioanode, which was after start-up changed to a hydrogen producing biocathode by reversing the polarity of the electrode. Moreover, Wang et al. (2014) [34], succeeded in perchlorate reduction in a bioelectrochemical reactor utilizing autotrophic hydrogen oxidizing bacteria. Both studies did not analyze the performance of a hydrogen oxidizing biofilm on the anode.

The main objective of this study was to explore the feasibility to utilize hydrogen as electron donor in combination with electrochemically active microorganisms at the anode for the recovery of copper at the cathode of a bioelectrochemical system. The strategy was to first to grow an anodic biofilm on acetate, then replace the acetate with hydrogen as electron donor and finally couple the hydrogen oxidation to copper reduction in the cathode. The performance of this system was studied by analyzing current as a function of anode potential, and, when coupled to copper reduction, power production.

Materials and methods

Experimental set up

Two identical cells (biotic and abiotic control) with a surface area of 22 cm^2 were constructed, as described by ter Heijne et al. (2008) [35]. Each of them comprised of two graphite plates (Müller & Rössner GmbH & Co., Troisdorf, Germany) serving as anode current collector and cathode. The anode material was graphite foil (1.0 g/cm^3 density, 99% purity; Coidan Graphite Products Ltd., York, UK), which was pressed on the anode current collector.

Two plexiglass plates with a single flow channel as middle compartments contained anolyte and catholyte and were separated by a Ralex anion exchange membrane (MEGA a.s., Stráž pod Ralskem, Czech Republic). Two additional plexiglass plates served as temperature control (30 °C) on the outside of the cell.

Temperature and pH were continuously logged (Endress + Hauser, Liquiline data logger) through pH electrodes (Endress + Hauser, CPS41 D) that were placed in the recirculation of anolyte and catholyte. In the headspace of each of the recirculation bottles, a gas sampling point was placed. The outgoing gas flow was measured using a bubble counter (MilliGascounter, Type MGC-1, Ritter, Bochum, Germany).

Electron donor and electrolyte composition

The anode of both cells was first fed with an acetate containing solution (20 mM) at a rate of 2 mL/min. This solution furthermore contained the following buffer and nutrients: 0.68 g/L KH_2PO_4, 0.87 g/L K_2HPO_4, 0.74 g/L KCl, 0.58 g/L NaCl, 0.28 g/L NH_4Cl, 0.1 g/L $MgSO_4 \cdot 7H_2O$, 0.1 g/L $CaCl_2 \cdot 2H_2O$ and 0.1 mL/L of a trace element mixture [36].

The anolyte chamber was operated in a continuous mode and the catholyte in a batch mode. The anolyte was recirculated at 200 mL/min via two recirculation bottles of 0.5 L each. The catholyte was recirculated with the same rate in a 1 L bottle, which was shared by both the biotic and abiotic cell.

During stage 1, the bioanode tests on acetate and hydrogen, the catholyte consisted of 10 mM of phospha during stage 1, the bioanode tests on acetate and hydrogen, the catholyte consisted of 10 mM of phosphate buffer solution (pH 7). In stage 2, the bioanode coupled to copper reduction, the catholyte consisted of 1 g/L Cu^{2+} (prepared from $CuCl_2$ and deionized water; pH = 4).

The cathode was kept anaerobic by flushing with nitrogen gas.

In the second stage both cells were fed with hydrogen gas as electron donor. This hydrogen gas inflow was controlled with a mass flow controller (Bronkhorst HICH-TECH BV, Ruurlo, Nederland) at 3, 10 and 30 mL/min. Hydrogen was sparged in the recirculation bottles and continuously recirculated through the headspace of the recirculation bottles with a vacuum pump to achieve saturation of the anolyte with hydrogen. Buffer and nutrients remained the same when the hydrogen gas served as electron donor.