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# Combined wastewater treatment and recovery of copper from ash leachate

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**Abstract:** Ashes from incineration of municipal solid waste contain metals, such as copper and zinc, in high concentrations. The metals can be leached out from the ashes using acids and recovered by electrolysis. To lower the energy demand of the electrolysis step, we have investigated a bioelectrochemical system for combined wastewater treatment and copper recovery from simulated ash leachate. Bacteria at the anode oxidize wastewater organics and produce a current that flows through an external circuit to the cathode, where copper is reduced and recovered. We tested a bioelectrochemical system with carbon anode and titanium cathode. With a cathode potential poised at -0.3 V, the energy required for copper reduction was reduced from 1.46 kWh/kg Cu with an abiotic anode compared to 0.23 kWh/kg Cu with a biological anode oxidizing acetate. With a cathode potential of 0.1 V, electrical energy could be recovered from the system together with copper.

**Keywords:** ash leachate; bioelectrochemical system; copper; metals; wastewater

## Introduction

Valuable metals such as copper are extracted from the lithosphere at an increasing rate. Spatari et al. estimated that approximately 40% of the copper extracted during the 20<sup>th</sup> century remain in use today, while 60% has been lost or ended up in waste repositories such as landfills (Spatari et al. 2005). A continuing loss of metals to waste repositories is not sustainable.

Incineration is an increasingly popular treatment method for municipal solid waste. The resulting ashes contain high amounts of metals and some valuable metals (e.g. Cu, Zn and Mo) are present in amounts comparable to the content in workable ores. The ashes are an environmental problem because of the risk for uncontrolled metal leaching and therefore has to be deposited into technically advanced and expensive landfills. Instead, the metals can be extracted using e.g. acid and subsequently recovered using electrolysis. The electrolysis step, however, can be very energy consuming. A microbial bioelectrochemical system (BES) can be used to recover copper from solutions (Ter Heijne et al. 2010, Tao et al. 2011). The energy required for electrolysis is provided by organic compounds present in wastewater. A BES consists of an anode and cathode. Living microorganisms oxidize organic compounds and use the anode as electron acceptor. The electrons flow through an external circuit to the cathode where a reduction reaction takes place. The most common type of BES is the microbial fuel cell (MFC), which converts organic matter directly into electrical energy (Rabaey et al. 2003, Liu et al. 2004). In this study, we investigate bioelectrochemical copper recovery from simulated acid municipal solids waste leachates.

## Material and Methods

A cylindrical bioelectrochemical reactor containing a carbon felt anode in 17 ml anode chamber and a cathode (usually titanium) in a 10 ml cathode chamber, separated by a Nafion 117 proton exchange membrane was used in the experiments.

Two litres of synthetic wastewater containing acetate was circulated through the anode chamber whereas the cathode chamber was loaded with about 10 mL 2M H<sub>2</sub>SO<sub>4</sub> containing 1 g/L Cu<sup>2+</sup>.

## Results and Conclusions

Titanium, steel, graphite, and copper cathodes were compared using cyclic voltammetry (Fig. 1). The titanium electrode showed no reaction peaks with only 2M H<sub>2</sub>SO<sub>4</sub> as the catholyte. With the addition of 1 g/L Cu<sup>2+</sup>, distinct cathodic and anodic current peaks appeared, suggesting copper was reduced and subsequently oxidized. The graphite electrode showed similar behavior although some, possibly oxygen-dependent, current peaks also could be observed with 2M H<sub>2</sub>SO<sub>4</sub> as the catholyte. The copper electrodes displayed a cathodic current peak similar to the titanium and graphite electrodes; however, a very strong anodic current was observed above 0.3 V as a result of the electrode itself being oxidized. The steel electrode differed from the other three and did not exhibit any peaks obviously related to copper in the scanned range. Zinc (1 g/L) did not show any peak in the scanned range for any of the cathodes. The titanium cathode was chosen for electrolysis tests.

The anode was incubated at a set potential of initially 0.2 V and later -0.1 V until current production began. The current rose to a magnitude of about 3 mA (~0.1 mA/cm<sup>2</sup> anode surface area). The reactor was characterized using linear scan voltammetry and electrochemical impedance spectroscopy. The anode potential was around -0.2 to -0.1 V at currents from 0 to 2.5 mA (Figure 2). The cathode potential drops dramatically at a current of about 1 mA. This indicates that the current is limited by diffusion of copper ions to the cathode. At cathode potentials below -0.35 V, the current increases again as a result of hydrogen evolution. The internal ohmic resistance of the cell was about 4.4 Ω.

Copper recovery was examined in 2 hours tests with titanium cathode and constant cathode potentials of -0.3V, -0.1V, or 0.1V (Table 1). Copper recovery was calculated from the measured charge transfer in the system since the cyclic voltammogram (Figure 1) suggested that no other reactions contributed to Faradaic charge transfer in the range of cathode potentials used. The amount of copper deposited on the cathode was analysed in tests 3 and 4 by dissolving the copper in HNO<sub>3</sub>(conc). This was not possible in tests 1 and 2 as the deposited copper fell off from the cathode during handling. In test 3, the copper remained on the cathode although it was possible to wipe it off with paper. In test 4, with a cathode potential of 0.1 V, the copper remained firmly attached to the cathode and was difficult to wipe off. Thus, the higher the potential, the stronger the deposited copper was attached to the titanium cathode. The energy required for copper deposition was lower with a biological anode than under abiotic conditions. At a cathode potential of -0.3V copper was recovered with an electrical energy consumption of 1.46 kWh/kg Cu with an abiotic anode. The energy consumption was lowered to 0.23 kWh/kg Cu with a biologically active anode. At a cathode potential of 0.1 V, the tests confirmed the results of Ter Heijne et al. (2010) and Tao et al. (2011), i.e. showing that copper could be recovered with a net energy output from the system. This study has demonstrated a new concept for recovery of copper from simulated acid ash leachates using a bioelectrochemical system powered by wastewater organics.

## References

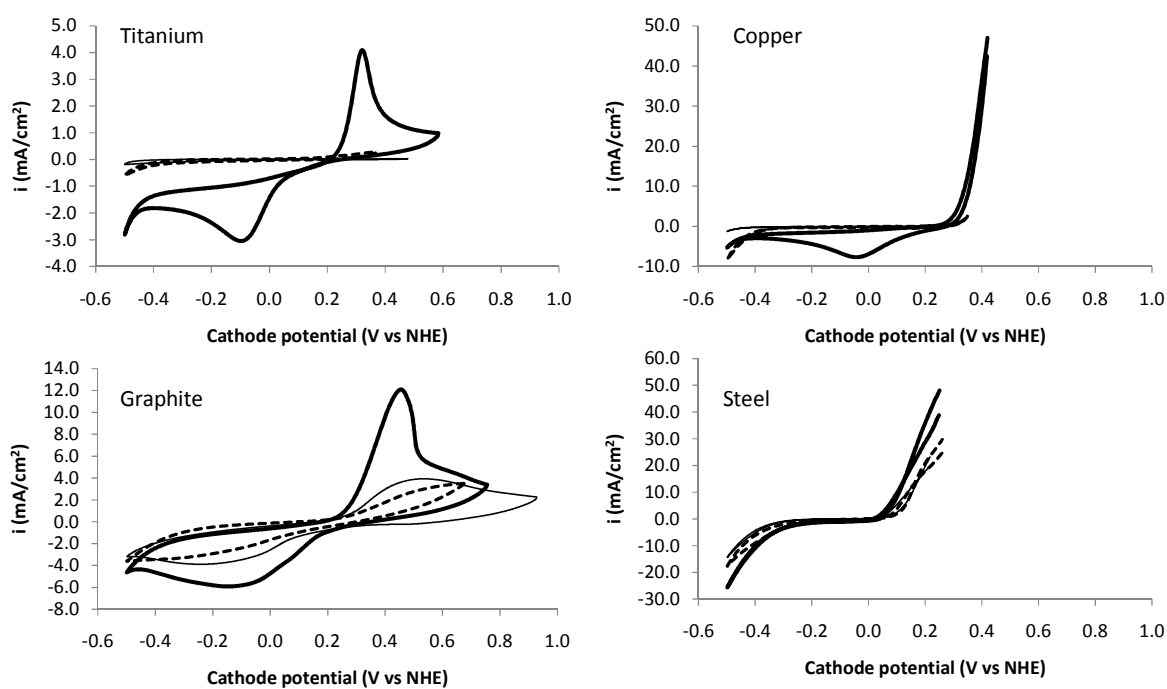
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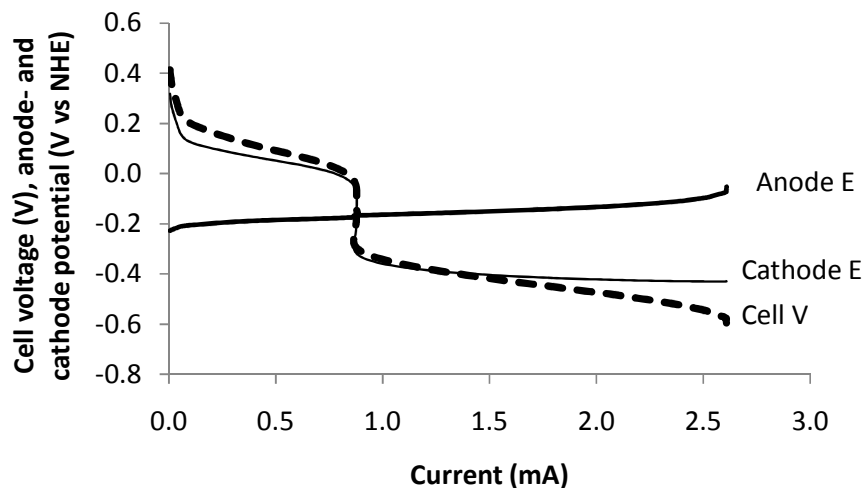
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**Figure 1.** Cyclic voltammety tests with various cathode materials. The catholyte was either 2M H<sub>2</sub>SO<sub>4</sub> (thin lines), 2M H<sub>2</sub>SO<sub>4</sub> amended with 1 g/L Cu<sup>2+</sup> (thick lines), or 2M H<sub>2</sub>SO<sub>4</sub> amended with 1 g/L Zn<sup>2+</sup> (dashed lines).



**Figure 2.** Linear scan voltammetry of bioelectrochemical cell. The cell voltage is measured as the cathode vs the anode, which means that a positive value suggests the system can be operated as a galvanic cell whereas at negative values the system requires electrical energy input.

**Table 1.** Experimental conditions and results under four 2-h copper electrodeposition tests.

Test	$E_{\text{cat}}$ (V vs NHE)	Cu rec. <sup>a</sup> (mg)	Cu rec. <sup>b</sup> (mg)	Energy cons. (kWh/kg Cu)
1 (abiotic)	-0.3	1.56	N.M.	1.46
2	-0.3	2.09	N.M.	0.23
3	-0.1	2.19	1.63±0.02	0.06
4	0.1	1.60	1.78±0.02	-0.08

<sup>a</sup>Cu recovery calculated based on measured charge transfer.

<sup>b</sup>Amount of copper recovered from cathode surface.

N.M. Not measured.