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Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions

Oskar Modin[1]*, Xiaofei Wang[1], Xue Wu[1], Sebastien Rauch[1], Karin Karlfeldt Fedje[1,2]

[1]Division of Water Environment Technology, Department of Civil & Environmental Engineering,
Chalmers University of Technology, 412 96 Gothenburg, Sweden
[2]Renova AB, Box 156, 401 22 Gothenburg, Sweden
*Corresponding author, Email: oskar.modin@chalmers.se, Telephone: +46 31 7722138

Abstract

In a microbial bioelectrochemical system (BES) living microorganisms catalyze the anodic oxidation of organic matter at a low anode potential. We used a BES with a biological anode to power the cathodic recovery of Cu, Pb, Cd, and Zn from a simulated municipal solid waste incineration ash leachate. By varying the control of the BES, the four metals could sequentially be recovered from a mixed solution by reduction on a titanium cathode. First, the cell voltage was controlled at zero, which allowed recovery of Cu from the solution without an electrical energy input. Second, the cathode potential was controlled at -0.51 V to recover Pb, which required an applied voltage of about 0.34 V. Third, the cathode potential was controlled at -0.66 V to recover Cd, which required an applied voltage of 0.51 V. Finally, Zn was the only metal remaining in solution and was recovered by controlling the anode at +0.2 V to maximize the generated current. The study is the first to demonstrate that a BES can be used for cathodic recovery of metals from a mixed solution, which potentially could be used not only for ash leachates but also for e.g. metallurgical wastewaters and landfill leachates.

Keywords: microbial electrolysis cell; metal recovery; ash leachate; electrowinning; municipal solid waste

1. Introduction

In microbial bioelectrochemical systems (BES) living microorganisms interact with solid electrodes. A wide range of bacteria are capable of oxidizing organic compounds and utilize an anode as electron acceptor at low redox potential [1]. This makes it possible to use the energy content of organics present in e.g. wastewater to drive electrochemical processes. The microbial fuel cell (MFC) is a type of BES that can be used to convert organics in wastewater to electrical energy. The biological anode is combined with an oxygen-reducing cathode. Since the overall reaction (oxidation of organics and reduction of oxygen) is thermodynamically favorable, electrical energy can be recovered from the MFC [2]. The microbial electrolysis cell (MEC) is another type of BES, which requires an input of electrical energy to drive product formation. For example, with a small voltage input, protons can be reduced to hydrogen gas at the cathode [3, 4]. BESs have also been investigated for a range of other applications including denitrification [5], production of hydrogen peroxide [6] and alkaline solutions [7], and redistribution of alkalinity between process streams in a wastewater treatment plant [8].

Regarding metal recovery, copper (Cu^{2+}) [9-11] and hexavalent chromium ($Cr_2O_7^{2-}$) [12, 13] have been used as electron acceptors in the cathode of MFCs. Both Cu^{2+} and $Cr_2O_7^{2-}$ have high reduction potentials (0.340 V and 0.365 V, respectively), which means that electrical energy production and metal recovery can be achieved simultaneously. However, a BES could potentially also be used to energy-efficiently recover other metals with lower reduction potentials.

Valuable metals are extracted from the lithosphere at an increasing rate [14]. The amount of easily extractable ore is a finite resource. It is therefore important to recycle the metals used in society. Spatari et al. estimated that 60% of the copper waste is not recycled but is lost or ends up in landfills [15]. Incineration of municipal solid waste (MSW) is an increasingly common waste treatment method that reduces the volume of the waste and generates some energy. The remaining ashes contain high concentrations of various metals which to a large extent can be leached out using e.g. acids [16]. From these leachates metals could be recovered using e.g. solvent extraction and electrolysis [17, 18], but the high energy consumption of electrolysis is an important factor for the profitability.

In a conventional electrolytic reactor, anodic water oxidation would generate the electrons needed for the cathodic reduction of metal ions. Water oxidation is a reaction with high redox potential and high overpotential on most electrode materials, which means that a high energy input is needed to drive the process. In a BES, the biological anode achieves oxidation of organics, such as acetate, at low potential. This means that with low or zero input of electrical energy, metal recovery at the cathode and wastewater treatment at the anode can be achieved simultaneously. In this study we demonstrate for the first time bioelectrochemical recovery of metals from a mixed solution containing Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}.

2. Materials and methods

2.1 Bioelectrochemical system

The bioelectrochemical reactor (Figure 1) consisted of two compartments with internal dimensions 3 x 3 x 10 cm^3. The compartments were separated by a 7.1 cm^2 anion exchange membrane (AMI-7001, Membranes International Inc., USA). The anode was made two pieces of carbon felt (TMIL, Japan) with dimensions 8 x 3.7 x 0.2 cm^3, each attached to a 9 cm long, 0.5 cm diameter graphite rod (Svenska Tanso). Titanium wire (Alfa Aesar) with a diameter of 0.81 mm was used as cathode. A 4-cm long piece of wire with a surface area of 1.02 cm^2 was used unless otherwise specified.

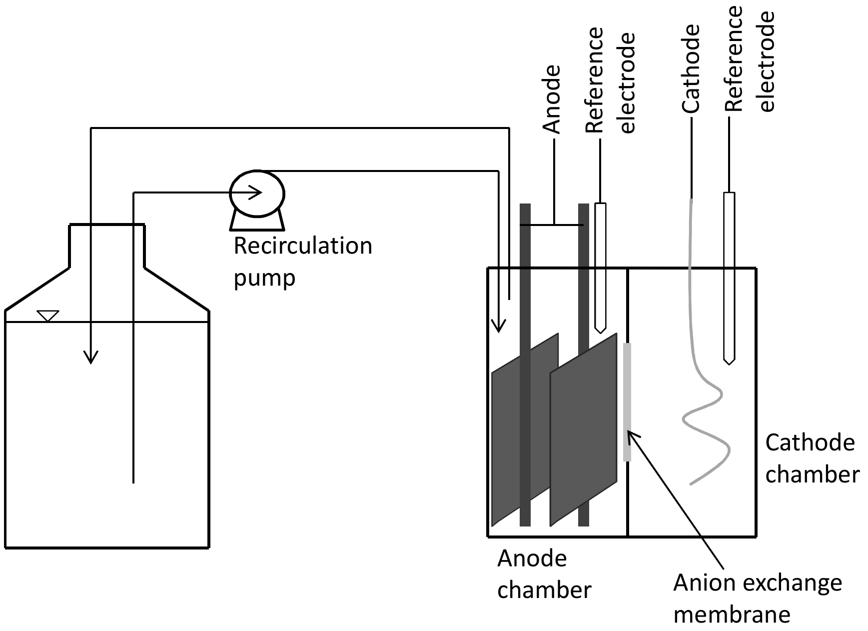

Figure 1. Schematic of the experimental setup.

A nutrient solution with acetate as the only source of carbon was circulated through the anode compartment from a 1-litre bottle at a flow rate of 55 mL/min. The nutrient solution had the following composition (mg/L): 2925 NaCl, 100 $MgSO_4{\bullet}7H_2O$, 100 $CaCl_2{\bullet}2H_2O$, 100 NH_4Cl, 2 $FeCl_2{\bullet}4H_2O$, 0.05 H_3BO_3, 0.05 $ZnCl_2$, 0.03 $CuSO_4$, 0.5 $MnCl_2{\bullet}4H_2O$, 0.05 $(NH_4)Mo_7O_{24}$, 0.05 $AlCl_3$, 0.05 $CoCl_2{\bullet}6H_2O$, 0.05 $NiCl_2$, 0.1 Na_2SeO_3, 0.05 $Na_2WO_4{\bullet}2H_2O$. It also contained a 100 mM phosphate buffer and 20 mM CH_3COONa. The pH was approximately 7.2.

The cathode compartment contained a simulated MSW fly ash leachate solution. The salts $CuCl_2{\bullet}2H_2O$, $Pb(NO_3)_2$, $2(CdCl_2){\bullet}5H_2O$, and $ZnCl_2$ were dissolved in the 2 M HCl solution either individually or in a mixture to concentrations of approximately 0.8 g/L Cu^{2+}, 0.4 g/L Pb^{2+}, 0.8 g/L Cd^{2+}, and 0.3 g/L Zn^{2+}. The solution (80 mL) was standing in the cathode chamber without recirculation. Cu, Pb, Cd, and Zn are four metals that are present in real MSW incineration fly ash in high concentrations and leachate concentration in the g/L range are possible [16].

2.2 Operation of the bioelectrochemical reactor

The anode of the bioelectrochemical reactor was inoculated with a mixture of aerobic and anaerobic sludge from a wastewater treatment plant, and subsequently incubated at a constant anode potential of +0.2 V using a KP07 potentiostat (Bank IC).

After inoculation of the anode, the reactor was operated for a total of 77 days. Electrolytic recovery of individual metals was investigated in the reactor between day 14 and 36. The cathode compartment was supplied with 80 mL of 2 M HCl containing either Cu^{2+}, Pb^{2+}, Cd^{2+}, or Zn^{2+}. The cathode was controlled at a certain potential for a time interval of 0.2 to 2.0 hours and the current was monitored. At the end of the test, the cathode was removed and placed in concentrated HNO_3 overnight to dissolve the deposited metals. Finally, the metal content of the HNO_3 solution was analyzed to study to which extent metals had been deposited on the cathode surface.

Bioelectrolytic recovery of metals from a mixed solution was investigated between day 56 and 74. The cathode compartment was supplied with 80 mL of 2 M HCl containing a mixture of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. The test was divided into four periods to sequentially recover metals with decreasing reduction potential, i.e. Cu (period 1), Pb (period 2), Cd (period 3), and Zn (period 4). Each period consisted of 2 to 4, 20-24 hour long intervals. At the start and end of each interval, samples were taken from the anolyte (10 mL) and the catholyte (0.5 mL) and the old cathode was replaced with a clean titanium wire. In the first two intervals of period 1, a 37-cm long wire cathode was used. In the third interval, a 20-cm long wire cathode was used. In all other intervals in periods 2-4, 4-cm long cathodes were used. Fresh anolyte solution was prepared for the start of each period. In the middle of period 3, the experiment was stopped for four days. When it was restarted, the anolyte was exchanged to prevent substrate limitation or low pH at the anode to limit the performance of the reactor.

2.3 Analytical methods

Concentrations of organic carbon were measured in filtered samples (0.7 µm glass fiber filters, VWR) using a total organic carbon analyzer (TOC-V, Shimadzu). Metal concentrations were measured using a quadropole ICP-MS system (Elan 6000, Perkin Elmer Sciex). Because catholyte samples were diluted 10^4 times before analysis, the detection limits for metal in the catholyte were 1.1 mg/L Cu^{2+}, 2.5 mg/L Pb^{2+}, 7.4 mg/L Cd^{2+}, and 19.8 mg/L Zn^{2+}. Voltages were recorded using a USB-2011 data logger (National Instruments). Electrode potentials are reported versus the standard hydrogen electrode (SHE), but were measured against Ag/AgCl reference electrodes (BAS Inc.) with an offset of +0.20 V vs SHE.

Polarization curves for the bioelectrochemical reactor were obtained using linear sweep voltammetry of the cell voltage at a scan rate of 1 mV/s starting from open-circuit voltage. The polarization analysis was carried out on day 77 of the experiment. Polarization curves were obtained under five conditions: (i) with the 2 M HCl catholyte in the absence of any metal ions, (ii) with Cu^{2+}, (iii) with Pb^{2+}, (iv) with Cd^{2+}, or (v) with Zn^{2+}. Cyclic voltammetry (CV) tests of the cathode electrodes were carried out using a Gamry series G750 potentiostat and a scan rate of 100 mV/s.

2.4 Calculations

The anodic coulombic efficiency (CE) represents the fraction of acetate charge equivalents that were converted into current in the anode compartment. The cathodic CE represents the fraction of current charge equivalents that were used to reduce metal ions in the cathode compartment. Equations 1 and 2 were used to calculate the anodic and cathodic CE, respectively.

$$CE_{anode} = \frac{\int_t^{t+\Delta t} Idt}{\Delta C_{Ac-} \times 8 \times V_{an} \times F}$$

(1)

$$CE_{cathode} = \frac{\int_t^{t+\Delta t} Idt}{\Delta C_{M2+} \times 2 \times V_{cat} \times F}$$

(2)

where *I* is the current (A), *t* is time and *Δt* is the duration of the experimental run (s), *ΔC* is the change in acetate (C_{Ac-}) or metal ion (C_{M2+}) concentration during *Δt* (M), *8* refers to the mol electrons liberated in the oxidation of one mol acetate, *2* refers to the mol electrons required to reduce one mol of metal ions, *V* is the volume of the anolyte or catholyte (L), and *F* is Faraday's constant (96485.3 C/mol electrons).

3. Results and discussion

3.1 Enrichment of the biological anode

During the first 55 days of the experiment, the anode was operated at a constant anode potential of 0.2 V and the current was monitored (Figure 2). The anode was operated in fed-batch mode and each feeding occasion resulted in a current peak. The current then decreased as acetate was consumed in the anode nutrient medium. On day 31, the anode medium was inadvertently acidified, which led to the current dropping to nearly 0 mA. The current again started to increase after day 36, suggesting that the electrochemically active microbial community on the anode had begun to recover. When the bioelectrolytic recovery of metals from a mixed solution was tested on day 56, the biological anode was capable of producing a current of over 40 mA at an anode potential of 0.2 V.

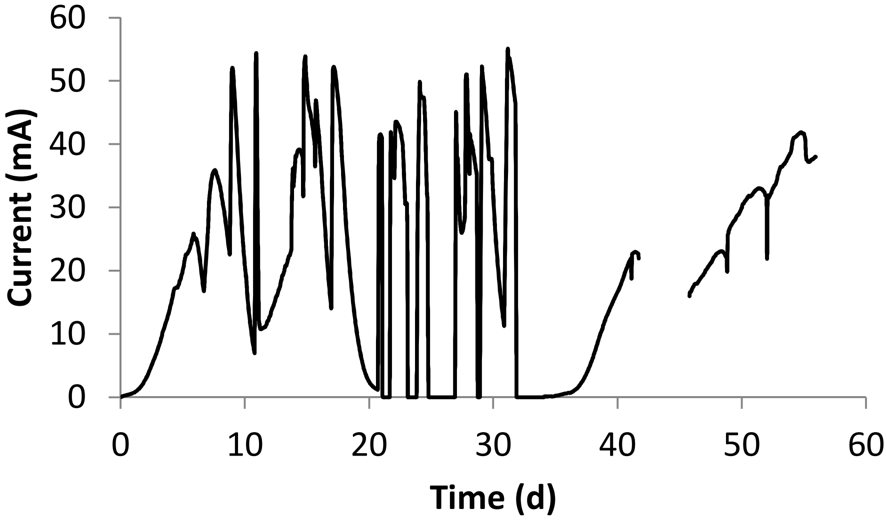

Figure 2. Current generated by the anode during the first 55 days of the experiment.

3.2 Recovery of individual metals on titanium cathodes

Under standard conditions the reduction potentials for Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} are 0.34 V, -0.13 V, -0.40 V, and -0.76 V, respectively. CV tests were carried out to test the actual cathode potentials needed for reduction of the four metal ions in the experimental system. The cyclic voltammograms are shown in

Figure 3. For pure 2 M HCl, no cathodic (negative) or anodic (positive) current peaks are observed until hydrogen generation starts at a potential of approximately -1.0 V, which is shown by the rapid rise in cathodic current at this point. For Cu, Pb, and Cd, cathodic currents caused by the reduction of the metal ions on the titanium electrode are followed by an anodic current caused by the re-oxidation of the reduced metals during the reverse scan. Zn reduction takes place at a potential of approximately -1.0 V, which is similar to the potential where hydrogen generation occurs. The deposition of metals on the titanium surface also seems to facilitate hydrogen generation. This is especially evident for copper, which has a cathodic current peak at about -0.2 V due to the reduction of Cu^{2+} ions, and then another continuous rise in cathodic current at a potential of -0.6 V caused by the reduction of H^+ to H_2 gas.

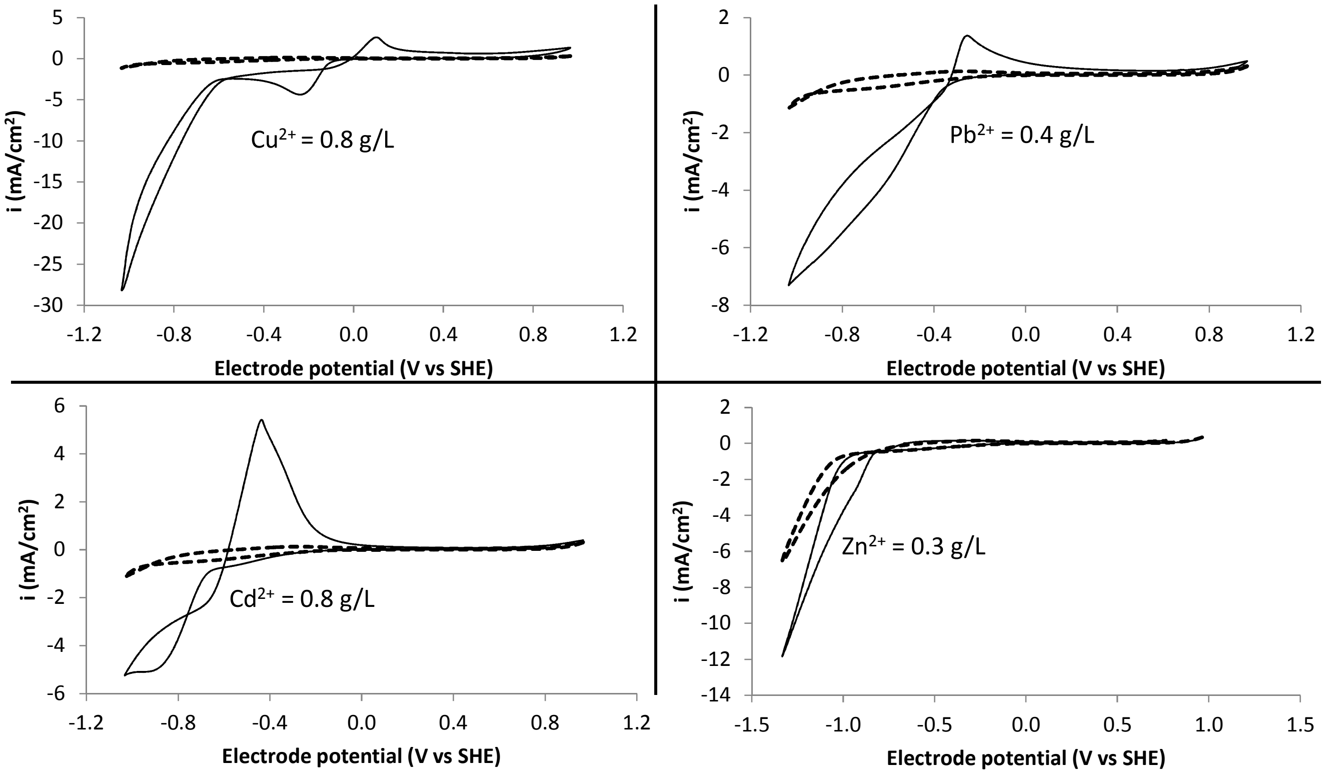

Figure 3. Cyclic voltammetry of titanium wire electrodes in solutions containing pure 2M HCl (dashed lines) and Cu^{2+}, Pb^{2+}, Cd^{2+}, or Zn^{2+} in 2M HCl (solid lines).

Based on the cyclic voltammetry scans, some cathode potentials were chosen for constant-potential electrolysis of the metal ions (Table 1). Cu could be reduced by controlling the cell voltage at 0 V, which is equivalent to short-circuiting the cathode with the biological anode, and means that Cu could be recovered without an energy input. This is not surprising since Cu^{2+} has a high reduction potential and has previously been used in the catholyte of MFCs [9-11]. Pb^{2+} could not be recovered under short-circuit conditions. However, at cathode potentials of -0.51 and -0.61 V, Pb was deposited on the cathode surface, with the lower potential leading to higher current. Cd was recovered at potentials of -0.66 and -0.81 V. Although current could also be observed at -0.61 V, Cd deposition could not be confirmed by redissolution of deposits in HNO_3. At -0.81 V, hydrogen generation was clearly observed on the cathode surface, especially in the end of the run. Zn was recovered at -1.0 V but not at -0.66 V.

Table 1. Electrolysis of individual metals on 4-cm long titanium wire cathodes.

Metal	**Duration (h)**	**$E_{cathode}$ (V vs SHE)**	**I^a (mA)**	**Metal deposit**
Cu	2	-0.12~ -0.09[b]	1.0~1.3	Yes
Cu	2	-0.23	1.0~2.4	Yes
Cu	2	-0.33	1.0~2.4	Yes
Pb	2	-0.24~ -0.22[b]	0.0	No
Pb	2	-0.51	0.6~2.1	Yes
Pb	2	-0.61	2.6~4.6	Yes
Cd	0.2	-0.51	0.1	No
Cd	0.5	-0.61	0.9~0.7	No
Cd	1	-0.66	0.7~6.0	Yes
Cd	1	-0.81	1.5~21.9	Yes
Zn	1	-0.66	0.3~0.4	No
Zn	2	-1.00	20.5-13.3	Yes

[a] Shows current in the beginning and end of experimental run

[b] Test was run with anode and cathode short-circuited

3.3 Bioelectrochemical recovery of metals from mixed solution

The bioelectrochemical recovery of Cu, Pb, Cd, and Zn from a mixed solution in 2 M HCl was carried out in four experimental periods to recover the metals in order of decreasing reduction potential.

- Period 1: The cell voltage of the bioelectrochemical reactor was controlled at 0 V to recover Cu.
- Period 2: The cathode potential was controlled at -0.51 V to recover Pb.
- Period 3: The cathode potential was controlled at -0.66 V to recover Cd.
- Period 4: The anode potential was controlled at +0.2 V to maximize current generation and recover Zn. Since Zn reduction coincides with hydrogen generation, this can lead to high currents. By controlling the anode potential we ensured that the biological anode was not damaged by currents exceeding its capacity.

Changes in parameters both in the anode medium and catholyte are shown in Figure 4. On the anode side, the nutrient medium TOC concentration and pH dropped as a result of acetate oxidation and charge migration (Figure 4C). Since an anion exchange membrane was used to separate the anode and cathode compartment, migration of chloride ions from the cathode compartment probably accounted for most of the ionic charge transfer, causing the drop in pH observed at the anode. In period 3 at 230 h, the experiment was stopped for four days. When it was restarted, fresh nutrient medium was fed to the anode, which explains the jump in TOC concentration and pH observed. During periods 1-3, the anode potential was stable between -0.25 and -0.17 V (Figure 4D). This low anode potential is close to the theoretical redox potential of acetate (-0.28 V), which means that the energy content of acetate could efficiently be used to power metal reduction in the bioelectrochemical reactor.

On the cathode side, the metal ion concentrations are shown in Figure 4A. During period 1, Cu^{2+} was rapidly removed from the catholyte whereas little change could be seen in the concentration of the other three metal ions. In period 2, Pb^{2+} was removed rapidly and there was also a reduction in the concentration of Cd^{2+}. In period 3, Cd^{2+} was removed rapidly and in period 4 rapid Zn^{2+} removal was observed. The small jump in Cd^{2+} concentration observed at 230 h in period 3 may have been caused by redissolution of Cd precipitates in the liquid during the four day storage period when the experiment was stopped. At the end of the experimental run, the concentrations of all metal ions were below the detection limit.

The input voltage required to recover the metals in the bioelectrochemical reactor increased with decreasing cathode potential (note that a negative cell voltage means input of electrical energy in Figure 4B). Cu was the only metal that could be recovered without an input voltage. In period 1, the current was highest in the beginning (6.6 mA) when the Cu^{2+} concentration was high, but decreased to 0.1 mA in the end when Cu^{2+} was nearly depleted. It has previously been shown that Cu^{2+} concentration has an effect on the current density in MFCs. With a graphite foil cathode, the current density was as high as 6 A m^{-2} under aerobic conditions and a Cu^{2+} concentration of 0.6 g/L and as low as 0.1 A/m^2 under anaerobic conditions and the Cu^{2+} being depleted [11]. On the titanium wire cathode used in this experiment, the current density was 7.0 A/m^2 (6.6 mA) in the beginning, which decreased to about 0.2 A/m^2 (0.1 mA) in the end of period 1. In period 2, the average input voltage was 0.34±0.03 V. The current ranged from 0.1 to 5.2 mA. In period 3, the average input voltage was 0.51±0.05 V. The current increased from about 0.1 mA when a clean titanium wire cathode was placed in the catholyte to as high as 6.1 mA when the titanium cathode was harvested after 20-24 hours. The increasing current was probably caused by proton reduction to hydrogen catalyzed by the Cd deposited on the cathode surface. This was observed visually as more bubbles appeared to evolve on the cathode when more cadmium deposits were present. In period 4, the anode potential was controlled and the generated current ranged from 17.1 to 25.2 mA. The cathode potential was around -1.10 V; however, it dropped rapidly to -1.66 in the end of the period, probably as a result of Zn^{2+} depletion in the catholyte. The cell voltage was around -1.7 V, but dropped in the end as a result of lower cathode potential.

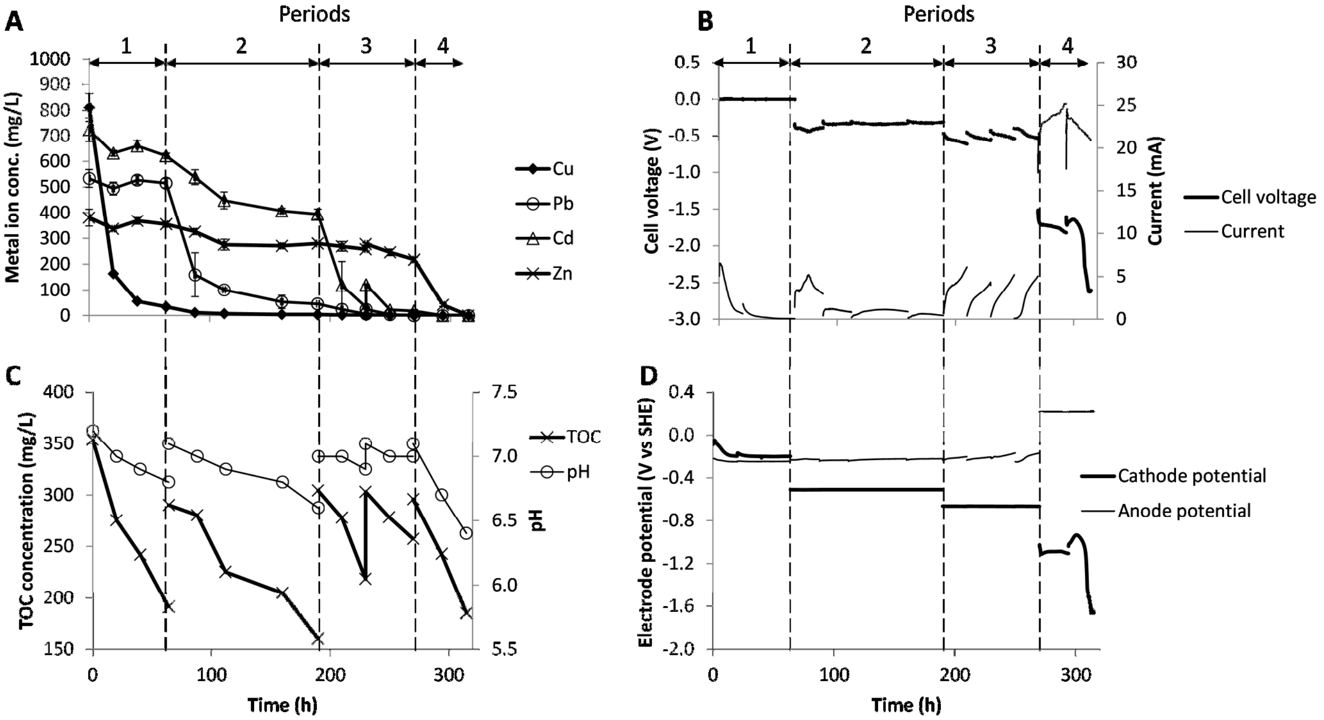

Figure 4. (A) Concentrations of metal ions in the catholyte, (B) cell voltage (negative value means voltage input) and current, (C) TOC concentration and pH in the anolyte, and (D) cathode and anode potential during the test for recovery of metals from a mixed solution catholyte. Metal ion concentrations are average of two or three measurements. Error bars show maximum and minimum concentrations.

The CE and energy consumption for metal recovery were calculated for each period and are shown in Table 2. The anodic CE ranged from 4.2 to 19.3% in periods 1-3. In period 4, which had the highest current, the anodic CE was 95.4%. Other processes such as sulfate reduction and methanogenesis could have contributed to lowering the anodic CE. Intrusion of air into the anolyte recirculation vessel may also have led to lowering the CE.

Table 2. Coulombic efficiencies (CE), metal capture efficiency, and electrical energy consumption for metal reduction in periods 1 (Cu), 2 (Pb), 3 (Cd), and 4 (Zn).

Period	**Anodic CE**[a] (%)	**Cathodic CE**[b] (%)	**Captured metal**[c] (%)	**Energy cons.**[d] **(kWh/kg metal)**
1	4.2	77.2	84.3	0.0
2	13.9	5.3	47.5	3.8
3	19.3	5.3	62.0	7.7
4	95.4	1.2	44.2	283.9

[a] Fraction of acetate charge equivalent converted into electrical current

[b] Fraction current charge equivalents used to reduce metal ions in the catholyte

[c] Fraction of metals ion removed from the catholyte proven to have been deposited on the cathode surface by redissolution in concentrated HNO_3 or aqua regia

[d] Electrical energy used to drive the electrochemical cell per kg of metal proven to have been deposited on the cathode surface

The cathodic CE was 77.2% in period 1. In a previous study, Ter Heijne et al. obtained a cathodic CE of 43% under aerobic conditions and 84% under anaerobic conditions [11]. In the present study, the dissolved oxygen concentration was not controlled; however, the catholyte was exposed to air (though it was not actively aerated) and dissolved oxygen was likely present at least in the beginning of the run. In periods 2-4, the cathodic CE was only 1.2-5.3%. Hydrogen generation and to a lesser extent oxygen reduction were most likely responsible for the very low cathodic CE in terms of metal recovery in these periods. Since the catholyte was a rather strong acid (2 M HCl), redissolution of deposited metals in solution could also have been partly responsible for lowering the cathodic CE in all periods.

To prove that the metals removed from solution were indeed deposited on the cathode, the cathode deposits were redissolved in concentrated HNO_3 (Cu) or aqua regia (Pb, Cd, Zn). Between 44.2% and 84.3% of the metals removed from the catholyte were redissolved in the concentrated acids (Table 2). The remaining metals may have been lost during handling of the samples. For example, small amounts of metals could have fallen off the titanium wire during sampling and not all of the deposited metal may have been completely redissolved in the concentrated acids. A small amount of metal ions may also have diffused from the catholyte into the anolyte. In period 1, Cu represented 99.9% of the metals redissolved from the cathode surface. Pb was also detected in trace amounts. In period 2, Pb represented 92.7% of the metals redissolved from the cathode. Cu accounted for the other 7.3%. No Cd and Zn were observed. However, a decrease in Cd^{2+} concentration in the liquid suggested that Cd may also have been present on the cathode surface in small amounts that were not detected after redissolution in acid. Cd precipitation on the bottom of the reactor chamber or diffusion into the anode chamber may be other reasons for the drop in concentration. The jump in Cd^{2+} concentration seen in period 3 (at 230 h) when the experiment was stopped for four days indicates that Cd precipitates could form and redissolve in the liquid. In period 3, Cd represented 82.3% of the metals redissolved from the cathode, Pb 16%, and Cu 1.7%. No Zn was observed. In period 4, in the first interval Zn accounted for 89.1% of redissolved metals while Cd accounted for the other 10.8%. In the second interval, Zn represented 100% of the redissolved metals from the cathode. This shows that at least Cu and Zn can be recovered as valuable high purity metals from a mixed solution, whereas Pb and Cd would need further purification.

The electrical energy consumption for metal recovery was calculated from the amount of metal proven to have been deposited on the cathode surface (Table 2). For Cu, the energy consumption was zero since the system was operated with a cell voltage of zero. The high energy consumption for Zn recovery was caused by hydrogen generation and low cathodic CE. If the hydrogen gas could be captured and utilized, the energy efficiency of the overall process would improve.

3.4 Polarization analysis

Polarization curves for various catholyte conditions are shown in Figure 5. The anode potential exhibits similar behavior irrespective of the catholyte used. The average internal resistance associated with the anode from the five polarization curves was calculated to 65±11 mΩ•m^2, based on the projected surface area of the carbon felt anode (128 cm^2).

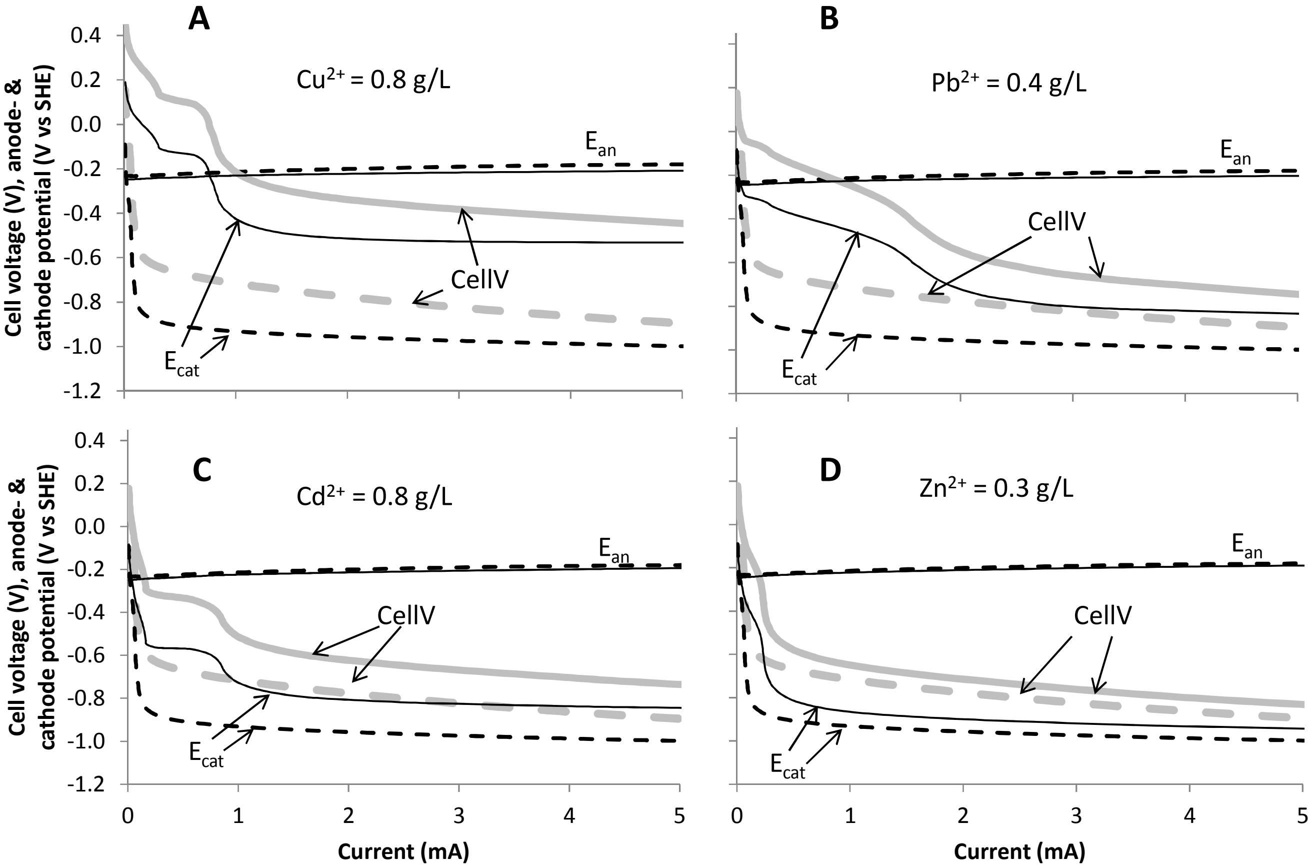

Figure 5. Polarization curves for the bioelectrochemical reactor. The dashed lines show results for 2 M HCl catholyte without metals and are used as a reference in all four graphs. The solid lines show results for catholytes containing 2 M HCl and either Cu^{2+}, Pb^{2+}, Cd^{2+}, or Zn^{2+}. Grey lines show cell voltage (CellV) whereas black lines show anode (E_{an}) and cathode (E_{cat}) potentials as indicated in the figure.

With only 2 M HCl as catholyte, the cathode potential and cell voltage drop very rapidly as the current increases from 0 to 0.1 mA (0.1 mA/cm^2, cathode surface area). The cathode potential approaches the potential needed for hydrogen generation.

With Cu^{2+} ions in the catholyte, the cathode potential drops more slowly, as Cu^{2+} can be reduced to Cu(s) at higher potential. Cathode potentials down to -0.14 V improves Cu^{2+} reduction. Reducing the potential further does not significantly improve Cu^{2+} reduction. When the current reaches about 0.8 mA (0.8 mA/cm^2), the cathode potential drops rapidly as hydrogen generation commences. However, the cathode potential reaches about -0.53 V at 5 mA, which high compared to -1.00 V for titanium wire without Cu deposits. We can also see that up to a current of 1 mA, the cell voltage is positive, which means that electrical energy and copper recovery are achieved simultaneously.

With Pb^{2+} ions in the catholyte, reducing the cathode potential to -0.51 V appears to improve the rate of Pb^{2+} reduction. The rapid drop in cathode potential occurs at a current of about 1.5 mA (1.5 mA/cm^2). Pb deposits on the titanium wire also seem to facility the hydrogen generation reaction as the cathode potential reaches -0.84 V at 5 mA, which is higher than for titanium wire alone.

The results are similar with Cd^{2+} ions in the catholyte. Reducing the cathode potential to -0.60 V improves rate of Cd^{2+} reduction. The rapid drop in cathode potential occurs at a current of about 0.8 mA (0.8 mA/cm^2) and the cathode potential reaches -0.85 V at 5 mA.

With Zn^{2+} ions in the catholyte, the cathode potential drops rapidly at a current of 0.2 mA (0.2 mA/cm^2). Although a small shoulder in the cathode potential curve can be seen around -0.5 V, it is unlikely that Zn^{2+} reduction occurs at this potential since the standard reduction potential of Zn^{2+}/Zn is -0.76 V. Low concentrations of other metals contaminating the catholyte may have contributed to the observed shoulder. Zn^{2+} is likely reduced simultaneously with hydrogen generation at a potential of about -0.9 to -1.0 V, which also can be seen in Figure 3.

The total internal resistance of the cell could be calculated based on the slope of the cell voltage curves. By substracting the anode resistance and cathode resistance from the total internal resistance for the part of the graph between 3 and 5 mA (which was nearly linear for all curves), the resistance associated with ion migration in the anolyte, catholyte, and through the membrane could be calculated to 20.1±3.5 Ω (or 14.2±2.5 mΩ•m^2 normalized to the surface area of the membrane). The internal resistance of the electrochemical cell is very important for its performance and could be minimized by placing the anode and cathode close to each other and increasing the surface area of the membrane.

3.5 Implications

The biological anode in the bioelectrochemical reactor has two important features: (1) it lowers the overall electrical energy consumption for metal electrolysis by oxidizing organics, and (2) it allows simple and selective extraction of Cu from a mixed metal catholyte.

The electrical energy consumption by an electrochemical reactor depends on the cell voltage and the current (Equation 3). The cell voltage depends on several factors including the anode- and cathode potential, ohmic resistance, and salinity gradient across the ion exchange membrane (Equation 4).

$$P = I \times U_{cell} \tag{3}$$

where P is power (W), I is the current (A), and U_{cell} is the cell voltage.

$$U_{cell} = E_{cathode} - E_{anode} - I \times R_{ohmic} + U_{salinity} \tag{4}$$

where E is the electrode potential for the anode or cathode (V vs SHE), R_{ohmic} is the internal resistance associated with ion migration through the liquid and membrane and current flow through the circuitry (Ω), $U_{salinity}$ is the voltage drop over the cation exchange membrane caused by salinity gradients between anolyte and catholyte.

As shown in Equation 4, a high anode potential (E_{anode}) contributes to a more negative cell voltage (U_{cell}), which means that a larger energy input is needed to drive the electrochemical reactions. The biological acetate-oxidizing anode in the experiment typically operated at a potential of -0.25 to -0.17 V whereas an abiotic water-oxidizing anode would operate at a potential over 1.23 V, which is the standard reduction potential of O_2/H_2O. Thus, the voltage input to the system can be lowered by at least 1.40 V by using a biological anode instead of an abiotic water-oxidizing anode. For Cu, 1.40 V represents an energy saving of 1.18 kWh/kg Cu recovered.

The bioelectrochemical reactor could recover Cu without an electrical energy input. Thus, by simply short-circuiting the cathode with the biological anode, Cu was reduced on the cathode surface. This was not possible for any of the other metal ions in solution, which means that Cu could selectively be extracted from the mixed metal catholyte. The use of a biological anode allowed recovery of Cu from a mixture of Cu, Pb, Cd, and Zn without the need to control the cathode potential against a reference electrode, which greatly simplified operation. The effect of other metal ions on the possibility to selectively extract Cu should be investigated in further studies.

4. Conclusions

A bioelectrochemical reactor could be used for selective recovery of Cu, Pb, Cd, and Zn from a simulated MSW incineration ash leachate. The reactor was especially useful for extraction of Cu from the metal ion mixture, as it allowed selective reduction of Cu^{2+} by simply short-circuiting the cathode with the biological anode. The other three metals required an input of electrical energy for electrolysis. An applied voltage of about 0.34 V, 0.51 V, and 1.7 V were needed for Pb, Cd, and Zn, respectively. Cu and Zn could be deposited on the cathode surface as pure metals without detectable contamination of the other metals. However, when Pb was recovered, small amounts of Cu could also be detected in the deposits and when Cd was recovered, small amounts of Cu and Pb were also detected. Cu was recovered on the cathode with high efficiency (cathodic CE = 77.2%). The other metals were recovered with much lower cathodic CE (1.2-5.3%) as a result of simultaneous hydrogen generation or reduction of dissolved oxygen.

Metals which are present in waste should be recovered and reused in order to limit the extraction of finite resources. BES technology offers the possibility to extract metals from contaminated solutions, e.g. wastewater and leachates, with limited energy requirements while simultaneously treating wastewater. BES can therefore be considered a sustainable technology for the treatment of metal contaminated wastes.

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References

[1] K. Rabaey, N. Boon, S.D. Siciliano, M. Verhaege, W. Verstraete, Biofuel cells select for microbial consortia that self-mediate electron transfer, Applied and Environmental Microbiology, 70 (2004) 5373-5382.
[2] H.-J. Kim, H.-S. Park, M.-S. Hyun, I.-S. Chang, M. Kim, B.-H. Kim, A mediator-less microbial fuel cell using a metal reducing bacterium, Shewanella putrefaciens, Enzyme and Microbial Technology, 30 (2002) 145-152.
[3] H. Liu, S. Grot, B.E. Logan, Electrochemically assisted microbial production of hydrogen from acetate, Environmental Science & Technology, 39 (2005) 4317-4320.
[4] R. Rozendal, H. Hamelers, G. Euverink, S. Metz, C. Buisman, Principle and perspectives of hydrogen production through biocatalyzed electrolysis, International Journal of Hydrogen Energy, 31 (2006) 1632-1640.
[5] P. Clauwaert, K. Rabaey, P. Aelterman, L. de Schamphelaire, T.H. Pham, P. Boeckx, N. Boon, W. Verstraete, Biological denitrification in microbial fuel cells, Environmental Science & Technology, 41 (2007) 3354-3360.
[6] R.A. Rozendal, E. Leone, J. Keller, K. Rabaey, Efficient hydrogen peroxide generation from organic matter in a bioelectrochemical system, Electrochemistry Communications, 11 (2009) 1752-1755.
[7] K. Rabaey, S. Bützer, S. Brown, J. Keller, R.A. Rozendal, High current generation coupled to caustic production using a lamellar bioelectrochemical system, Environmental Science & Technology, 44 (2010) 4315-4321.
[8] O. Modin, K. Fukushi, K. Rabaey, R.A. Rozendal, K. Yamamoto, Redistribution of wastewater alkalinity with a microbial fuel cell to support nitrification of reject water, Water Research, 45 (2011) 2691-2699.
[9] H.-C. Tao, W. Li, M. Liang, N. Xu, J.-R. Ni, W.-M. Wu, A membrane-free baffled microbial fuel cell for cathodic reduction of Cu(II) with electricity generation, Bioresource Technology, 102 (2011) 4774-4778.

[10] H.-C. Tao, M. Liang, W. Li, L.-J. Zhang, J.-R. Ni, W.-M. Wu, Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell, Journal of Hazardous Materials, 189 (2011) 186-192.
[11] A. Ter Heijne, F. Liu, R. van der Weijden, J. Weijma, C.J.N. Buisman, H.V.M. Hamelers, Copper recovery combined with electricity production in a microbial fuel cell, Environmental Science & Technology, 44 (2010) 4376-4381.
[12] L. Huang, X. Chai, S. Cheng, G. Chen, Evaluation of carbon-based materials in tubular biocathode microbial fuel cells in terms of hexavalent chromium reduction and electricity generation, Chemical Engineering Journal, 166 (2011) 652-661.
[13] M. Tandukar, S.J. Huber, T. Onodera, S.G. Pavlostathis, Biological chromium(VI) reduction in the cathode of a microbial fuel cell, Environmental Science & Technology, 43 (2009) 8159-8165.
[14] R.B. Gordon, M. Bertram, T.E. Graedel, Metal stocks and sustainability, Proceedings of the National Academy of Sciences, 103 (2006) 1209-1214.
[15] S. Spatari, M. Bertram, R. Gordon, K. Henderson, T. Graedel, Twentieth century copper stocks and flows in North America: A dynamic analysis, Ecological Economics, 54 (2005) 37-51.
[16] K. Karlfeldt Fedje, C. Ekberg, G. Skarnemark, B.-M. Steenari, Removal of hazardous metals from MSW fly ash-An evaluation of ash leaching methods, Journal of Hazardous Materials, 173 (2010) 310-317.
[17] S. Schlumberger, M. Schuster, S. Ringmann, R. Koralewska, Recovery of high purity zinc from filter ash produced during the thermal treatment of waste and inerting of residual materials, Waste Management & Research, 25 (2007) 547-555.
[18] K. Karlfeldt Fedje, C. Ekberg, G. Skarnemark, B.-M. Steenari, Initial studies on the recovery of Cu from MSWI fly ash leachates using solvent extraction, Waste Management & Research, (in press).