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Introduction

Circular economy and resource recovery must ensure the return of materials and elements from anthropogenic use to natural reserves [1]. Fly ash (FA) and bottom ash (BA) of municipal solid waste incineration (MSWI) are low concentration streams of high-tech metals, with estimated annual flows of tens of kilograms and a total metal content comparable to low-grade active mines [2]. As a result, there is a pressing need for these critical and scarce metals remaining in FA and BA to be extracted and recovered using sustainable technologies [3]. Electrochemical removal of metals was tested on MSWI residues at bench scale [4], but further research is needed to reach higher TRL. Bioleaching and electrochemical remediation were recently used e.g., on tungsten mine wastes [5], zinc remediation of contaminated soil, and phosphorus recovery from sewage sludge, but never to recover metals from MSWI FA.



This work aims to investigate if bioleaching using acidophilic bacteria (BAB) coupled with electrochemical remediation (ED) enhances metal recovery from MSWI FA as a proof of concept of microbial recovery cell (MRC).

MSWI FA

The studied FA comes from an Italian WTE plant (grate-furnace system) with waste processing capacity of 1.4×10^5 t/a, while the total FA produced is around 3×10^3 t/a. The collected sample is a fine-grained and dusty material, high metal loaded, with colour and grain-size rather homogeneous upon visual inspection; material pre-treatment included drying at 50 °C for 48 h and thorough milling in an agate vibratory disk mill. The bulk chemical composition by ICP-MS of the starting material after total digestion is given in Table 1. The pH of the starting material in normal conditions equals to 12.

Table 1

Major elements (g/kg)					
Ca	Si	Fe	Ti	Alkali+Cl	S
336	115	16	18	37	280
Ore metals (g/kg)					
Al	Zn	Cu	Sb	Cr	Mg
61	20	1	2	3	32

EXPERIMENTAL

We performed three experiments in a 2-compartment electrochemical cell with a total volume of 120 mL using a cation exchange membrane (CMI-7000 S; Membranes International, Inc.) as a separator (Fig. 1). The experiments were conducted at room temperature for 96 h, with constant stirring (150 rpm) in an orbital shaker, using 10 g/L MSWI FA in the anode compartment. To test the effect of low-level direct current in abiotic and biotic conditions one ED experiment was supplied with 1 V current voltage, the BAB experiment was in absence of current with a mixed microorganisms' culture containing sulphur and iron oxidising bacteria [6], and experiment #3 was a combination of both ED+BAB with 1 V cell voltage applied. The anode compartment contained MSWI FA and the nutrient medium [6]; the catholyte used was 0.01 M NaCl. The electrodes were graphite rods (Alfa Aesar), with 10 cm length and 6 mm diameter. Samples for analysis were collected at 2, 4, 6, 24, 48, 72, and 96 h while the pH in the anolyte and the catholyte was measured at each sampling using a pH meter Eutech Instruments.

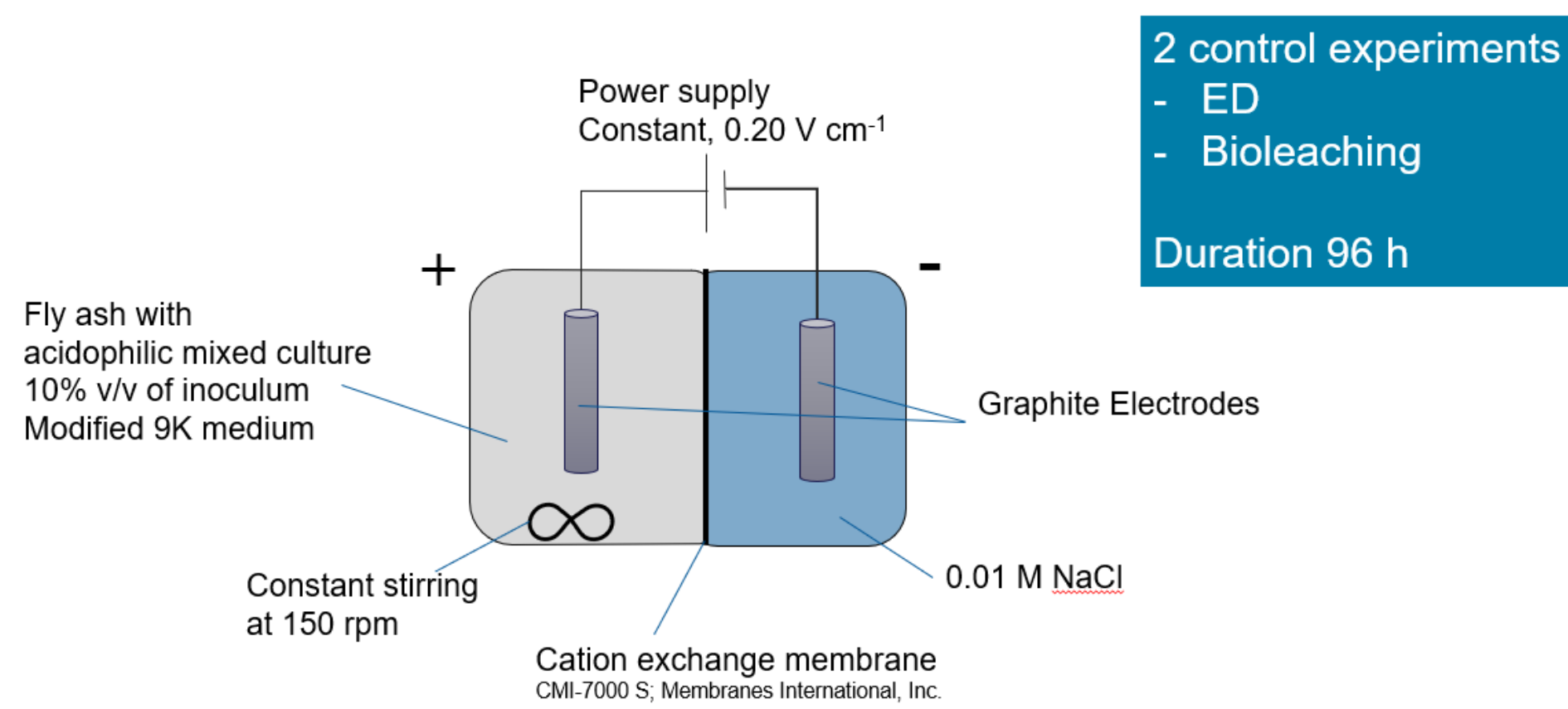


Figure 1 – Schematic picture of experiment setup

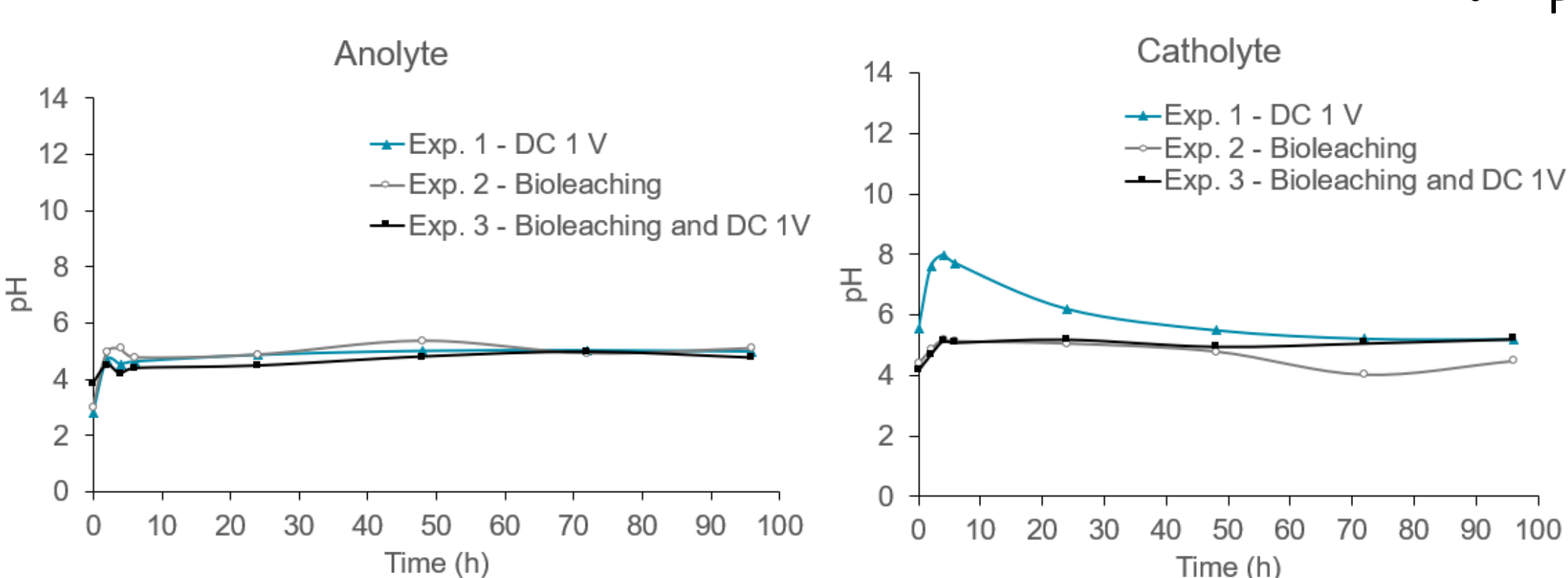


Figure 2 – Variation of pH as a function of time in catholyte and anolyte

The pH values measured (Fig. 2) show that the production of H⁺ in the anode due to the oxidation of water (eq. 1) is buffered by the alkalinity of MSWI FA. The values tend to level out in both anolyte and catholyte in all the experimental conditions (pH ~ 5). Only the catholyte in the control ED showed values up to 8 in the first ten hours, and then decrease until stabilising at pH 5 (exp. 1 in Fig. 2). The pH values show that the low voltage applied in the experiments does not generate enough H⁺ to provide optimal conditions to the acidophilic bacteria.



Further optimisation of the combination of the two techniques either will demand acid addition to ensure optimal pH values or higher applied voltages.

The pH level of the BAB experiment without energy supply (exp. 2 in Fig 1) decreased after fifty hours in the catholyte. This phenomenon might relate to bioproduction of H₂SO₄ by S-oxidizers that spontaneously, i.e., without external supply of energy, forced reduction at the catholyte. Metals such as Co, Zn, Li, Pb, and Ni slowly decreased over time in the anolyte. Cadmium (Cd) is the exception and tends to increase over time. Metal concentrations in the cathode compartment are higher when combining the ED with BAB (exp. 3 in Fig. 3), with a sharp increase in the last 24 h (Fig. 3). The highest concentrations measured in the catholyte correspond to Zn (28.4 mg L⁻¹), Cd (22.6 mg L⁻¹), Al (21 mg L⁻¹), Pb and Sr (10.2 mg L⁻¹) when combining ED with BAB (exp. 3). This soluble fraction mainly came from the exchangeable and carbonate bound metals in the MSWI FA. The metals solubilised by bioleaching are likely transported to the cathode compartment by electromigration, which explains the higher concentrations, when compared with the control experiments (exp. 1 and 2 in Fig. 3). Other studies reported an increase in activity and growth rate of iron oxidizing bacteria, which rapidly oxidized more Fe²⁺ to Fe³⁺, resulting in this synergistic effect [7].

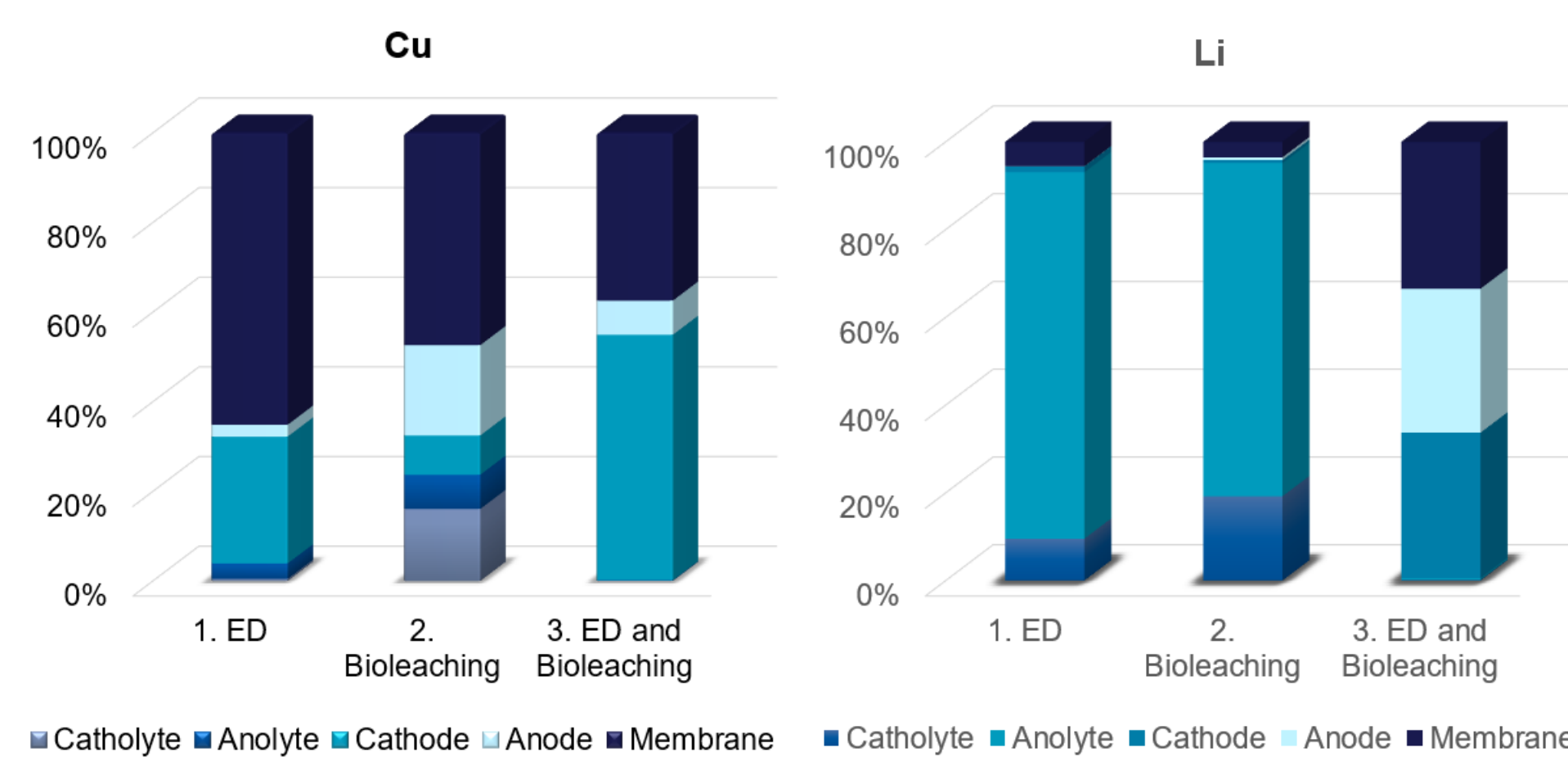


Figure 4 – Metal extraction percentages in the catholyte, anolyte, cathode, anode, and cation exchange membrane in each experiment based on ICP-MS analysis of leachate solutions and digested solid MSWI FA.

Also, we conducted a chronoamperometric testing of MRC system (Fig. 5). Chronoamperometry is used to measure the current flowing in the electrochemical systems during the application of external electric potential.

In these experiments the MRC has a starting setpoint pH of 3 (using H₂SO₄ and HCl in the anode and cathode compartments, respectively) to provide conditions favourable to the development of acidophilic bacteria. The pH values slightly decreased from setpoint, in both anode (average pH 2.6) and cathode (average pH 2.7), likely due to the activity of bacteria, and stabilized at the end of the experiment providing clues of electrochemical reversibility.

Two different cell voltages were applied between anolyte and catholyte, forcing oxidative processes at anolyte and reduction at catholyte. Under the application of 0.5 V over 86400 seconds only 3.566 Coulombs were measured. By applying a cell voltage of 1.0 V over 345600 seconds, the charge is 110.529 Coulomb. According to the Faraday law, this charge corresponds to 1.145×10^{-3} mol of electrons.

Moving forward...

- Optimise L/S ratio, mixing, duration of the experiments, and pH
- Different membranes may allow a better separation of elements
- Test other ashes and bacterial consortia
- Assess recovery of high-tech/valued metals like REE and PGE
- Potential for metal recovery – market can be a barrier

→ fine-tuned electromigration of metals

References

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Results

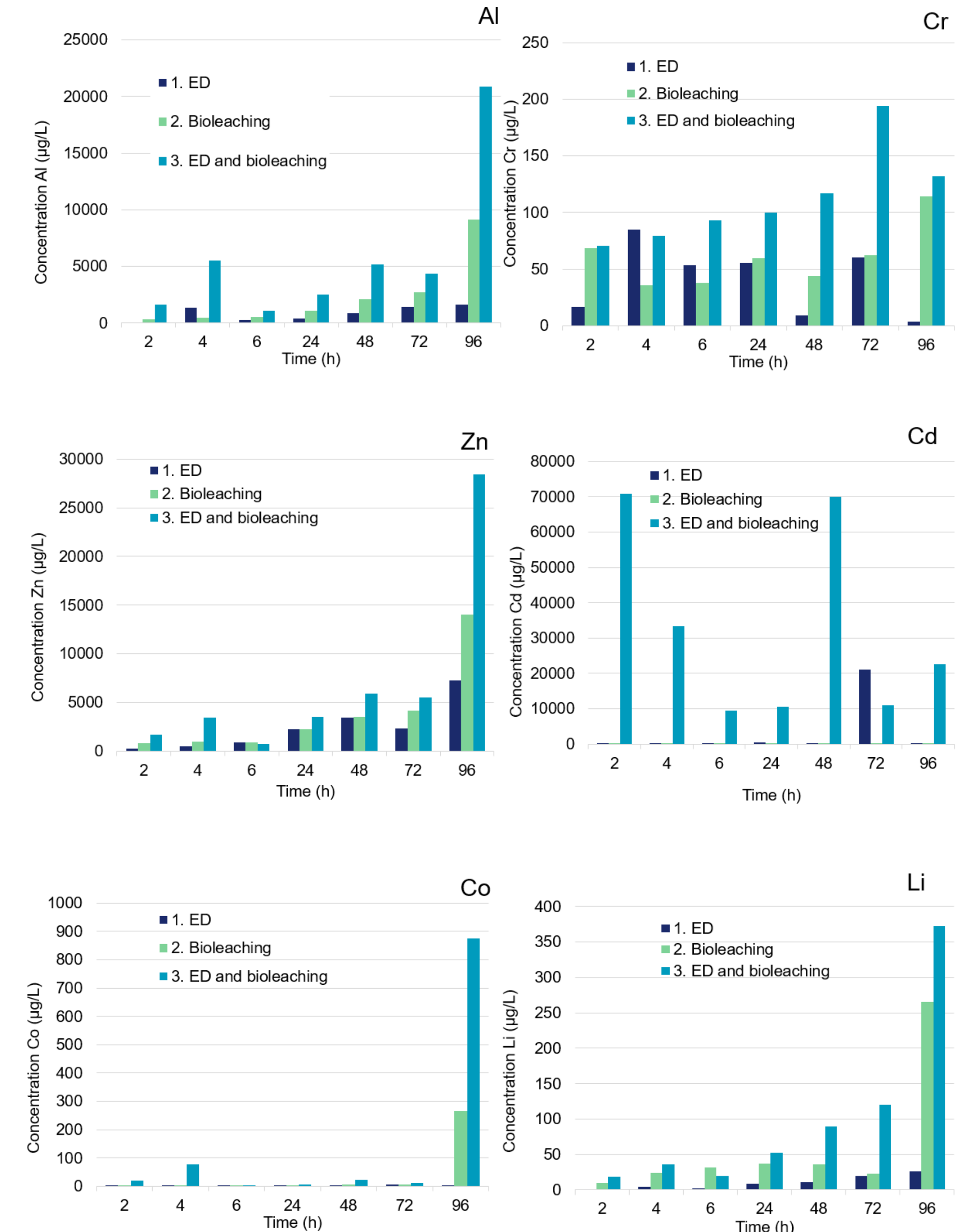


Figure 3 – Concentrations of selected metals by ICP-MS in the catholyte as a function of time

A relevant fraction of the metals is accumulating in the cation exchange membrane (Fig. 4). In the ED (exp. 1), between 6-65% of the metals are concentrated here: 6% Li, 9% Cd, Co and Zn, 13% Sr, 15% Cu, 17% Ni, 18% Al, 46% Pb and 65% Cr. The BAB (exp. 2 in Fig. 4) showed lower metal amounts in the membrane (4-24%), as the absence of the low-level direct current did not compel electromigration of metals to the cathode. While combining both technologies, the percentages of metals retained in the membrane are similar, varying between 31 % and 40 %.

According to Fig. 4, more metals are also deposited in the cathode when using both ED and BAB (31-55%), compared to ED (average of 13%) and BAB (average of 6%). The combination of both technologies appears to favour electrodeposition in the cathode when comparing them individually. It is also evident that lower amounts of metals (0.4-40%) can be found in the anolyte when using electrochemical (13-87%) and bioleaching (5-67%). This is consistent with other studies, which concluded that dissolved ions are continuously being removed during the electrochemical treatments, so no equilibrium is obtained between ash and solution, with the continuous removal enhancing dissolution processes [8].

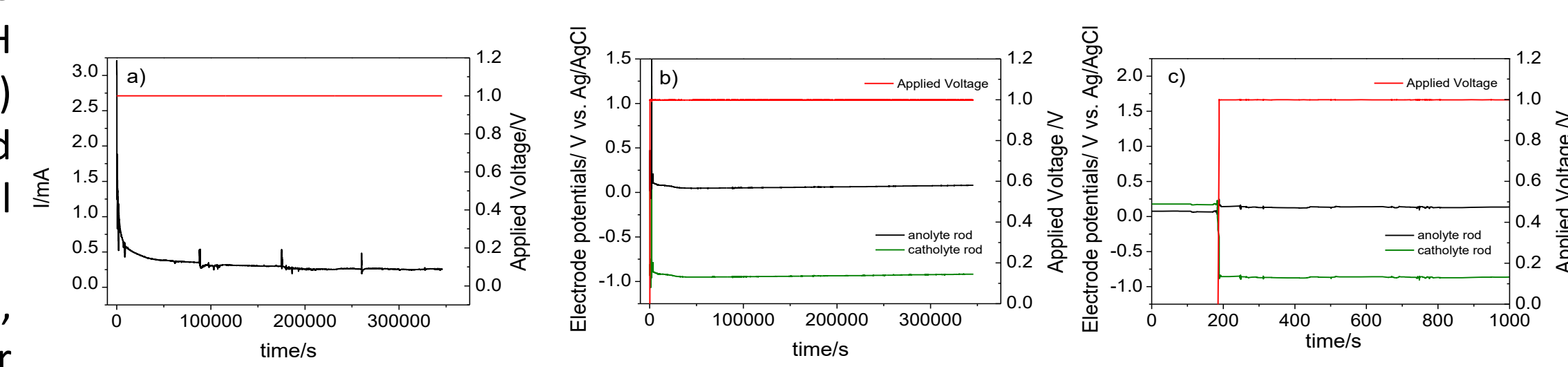


Figure 5 – Chronoamperometry of the experiment combining ED + BAB. Potential step (a) obtained by setting 1 V cell voltage between anolyte and catholyte and simultaneous reads of electrochemical potentials (b). Zooming of the first 2000 s window (c) reveals how the circuit is forced in the opposite direction to the current flow that is spontaneously generated by the cell.

Take home messages

MSWI FA are complex matrices and can be sources of critical raw materials in the circular economy if most suitable technologies are tested.

This study is a first proof of concept that bioleaching and electrochemical remediation can be combined for metal recovery from MSWI FA.

Data is preliminary and highlights, in particular, the need to ensure better conditions for bacteria survival.

The proposed MRC showed higher mobilisation of metals, both in anode and cathode compartments, compared to single techniques.

Reversible and irreversible redox processes must be recognized to exploit effectively electrical conduction in MRC. A good understanding of MRC properties, such as, charge transport, under different scenarios holds the potential to reveal bioelectronic applications of bioleaching bacteria.