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Biotechnological Recycling and Recovery of Metals from Waste Printed Circuit Boards and Spent Li-Ion Batteries—Selected Results from the ERAMIN EU BaCLEM Project †

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Abstract: This project investigated metal recovery from waste printed circuit boards (WPCBs) and spent lithium-ion batteries (LiBs) using pure and mixed-culture acidophilic microorganisms. It was shown that the mixed culture could recover 80% of Li and 98% of Co from a representative LiB sample under shaken flask conditions while using a single acidophilic microorganism in a two-step bioleaching step, 82% of Cu and 100% of Ni could be recovered from PCBs. The removal of iron from the bioleaching solution reached 100% using NaOH.

Keywords: PCBs; LiBs; mixed culture; bioleaching; precipitation

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1. Introduction

Approximately 20–50 million tons of electronic waste (e-waste) is generated worldwide each year. This represents 1–3% of municipal waste. The recycling of targeted metals from e-wastes supports the sustainability of resources and is a priority among the circular economy principles [1]. Lithium-ion batteries (LiBs), whose main component is lithium cobalt oxide ($LiCoO_2$)—a cathodic active material that constitutes 20–50% of the mass of a battery—can be recycled in the same way [2,3].

The demand for key e-mobility metals such as Cu, Co, Li and Ni is steadily increasing. Copper is particularly important due to its extensive use in batteries, electric motors, wiring and charging infrastructure [4]. Cobalt and lithium have been identified by the EU as primary critical raw materials (CRMs) due to their high supply risk and economic importance, which is essential for battery-based electric vehicles (EVs). Copper (Cu) and nickel (Ni) have also been identified as strategic raw materials in the latest EU CRM classification [5].

Biologically assisted leaching, or bioleaching, has the potential to be a viable alternative to established pyrometallurgical routes for e-waste recycling. A major drawback is the low leaching kinetics of native microbes (Fe^{2+} and S oxidizers) when the process is carried out at high pulp densities (PDs). Therefore, the development of a robust microbial community specifically tailored for metal recovery at higher pulp densities is expected to provide a breakthrough and competitive position for bioleaching against other more energy-intensive technologies used in e-waste recycling [6,7]. Developments include metal bioprecipitation, which is now being integrated into novel hydro-, bio- and hybrid metallurgical systems [8].

However, this study aims to investigate different bioleaching processes using single and mixed acidophilic microorganisms for metal recovery from representative samples of spent LiBs and PCBs. The pregnant leach solutions (PLS) from the bioleaching process are subjected to a pre-purification process to remove iron, which is considered as an impurity when it comes for recovery of the value-added metals downstream.

2. Materials and Methods

Spent lithium-ion batteries (LIBs) and waste printed circuit boards (WPCBs) were collected from the EXITCOM recycling plant in Turkey. An initial shredding aiming size reduction and discharging (for the LiBs) was carried out at the company premises. Prior to bioleaching studies, analytical characterization of both the representative samples was carried out to understand the elemental and chemical composition.

For the LiB bioleaching experiments, a mixed acidophilic consortium consisting of *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Leptospirillum ferriphilum* and *Acidithiobacillus thiooxidans* was used for microbial adaptation to the sample in modified 9K growth media [9]. The mixed culture was adapted at 0.5% pulp density prior to bio leaching experiments. The bioleaching experiments were carried out in a laboratory (the applied conditions are displayed in Table 1) in 250 mL Erlenmeyer flask at 100 mL working volume.

Table 1. Conditions for Mixed-culture bioleaching of LiBs.

Parameters	Value
Particle size (µm)	500
Pulp density (%)	0.5
Initial Fe (II) (g/L)	3–9
Initial pH	1.5–2
Bioleaching time	1–10 days
Temperature (°C)	30
Stirring (rpm)	150

The second group of experiments was related to a two-step bioleaching of PCBs. The experiments were conducted with pure culture of acidophilic bacteria *Acidithiobacillus ferrooxidans 61* in a 2 L stirred tank reactor. The culturing of the microorganism was realized in a modified 9K growth media to produce biogenic Fe^{3+} from initial Fe^{2+} without a sample (applied conditions displayed in Table 2). The PCB sample was then added to the biogenic ferric solution. The investigation was conducted on 1% pulp densities at 40 °C, 600 rpm and with 1 liter per minute of air supply. All tests were conducted in the same reactor.

Table 2. Conditions for single-culture bioleaching of PCBs.

Parameters	Value
Size (mm)	22
$FeSO_4 \times 7H_2O$ (g/L)	44.2–124
Time (days)	5–10
Stirring (rpm)	80
pH	1.8–1.9
Temperature (°C)	30

Quantitative and qualitative characterization of the PLS was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography. Fe^{2+}/Fe^{3+}

ratio and total organic carbon (TOC) were also followed. Prior to the bioprecipitation of the main metals (which was the preferred approach envisaged in this study fro down-stream processing), the PLS was pre-treated via Fe precipitation with sodium hydroxide.

3. Results and Discussion

3.1. Characterization Result

It was found that a granulometric cut of approximately 500 µm could effectively concentrate metals such as cobalt (Co), nickel (Ni), lithium (Li) and manganese (Mn) in the undersize fraction. In such a way the main metal concentrations in the LiBs were Li (2.86%), Co (19.75%), Ni (2.04%) and Mn (6.14). In the case of PCBs prior to bioleaching, the input samples were pre-treated by boiling with NaOH to remove the organic coating. The chemical assay for the PCBs reported the following main metals content for a representative sample: Cu (21.53%), Al (6.95%), Ni (5.12%), Pb (3.2%) and Fe (3.86%) [10].

3.2. Bioleaching of Li and Co from LiBs with a Mixed Culture

The effect of bioleaching duration was studied to fix the optimum time for Li and Co recoveries from LiBs. Figure 1 shows that both metal leaching efficiencies increase up to day 4. Afterwards, it starts decreasing; however, for such a duration, recovery of Li (65%) and Co (75%) was obtained.

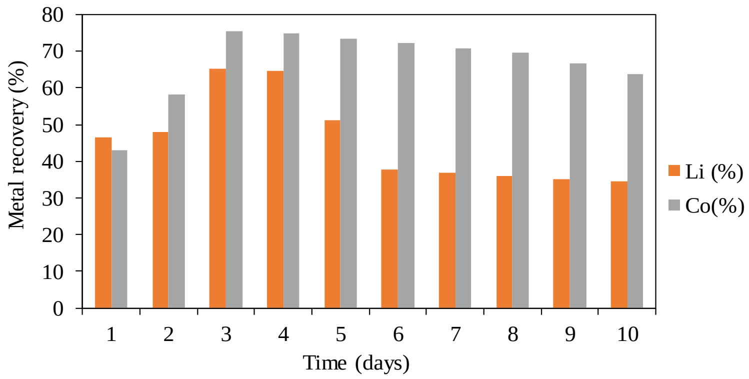

Figure 1. Effect of bioleaching time on Li and Co recovery from LiBs under preliminary shaken flask conditions.

The pH and ferrous iron concentration are important parameters in bioleaching with acidophilic microorganisms. The subsequent tests were therefore undertaken to optimize these two parameters for 4 days. The results are presented in Figure 2. From Figure 2a, Li recovery was 68%, 64% and 62% at pH 1.5, 1.8 and 2, respectively, whereas Co recovery reached 98%, 89% and 91% at the same pHs, respectively. Similarly, Li recovery was 80%, 53% and 61% at varying Fe^{2+} concentrations of 3 g/L, 5 g/L and 9 g/L, respectively, and for Co it was 98%, 78% and 89% for the same concentrations, respectively (Figure 2b).

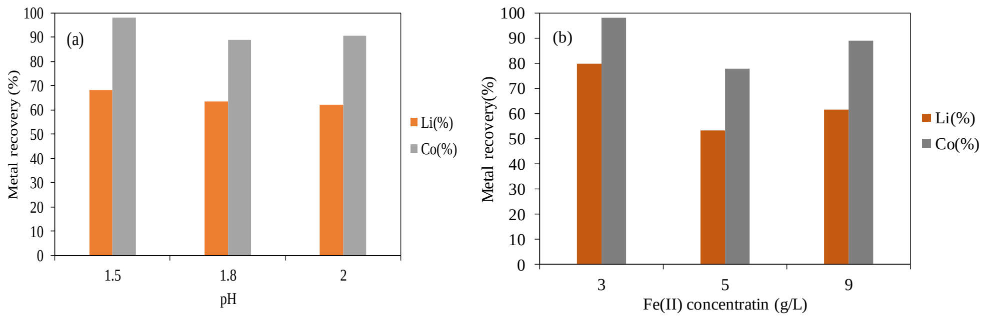

Figure 2. Effect of (**a**) pH and (**b**) Fe^{2+} concentration on bioleaching of Li and Co from LiBs under preliminary shaken flask conditions.

3.3. Bioleaching of Cu and Ni from PCBs with Non-adapted Acidophilic Culture

In this study, leaching with Fe^{3+} derived from *Acidithiobacillus ferrooxidans* 61 biogenic solution at different pH was investigated at 1% pulp density [10]. Figure 3a,b shows the results of Cu and Ni recoveries at 1% pulp density under different pH and Fe^{3+} concentrations for 24 h. The optimum recovery of Cu (87%) was reached at 15.5 g/L Fe^{3+}, whereas, the maximum Ni (100%) recovery was reached at 13.5 g/L Fe^{3+} (Figure 3a). In Figure 3b, pH 1 maintained high recoveries for both metals: 82% for Cu and 100% for Ni.

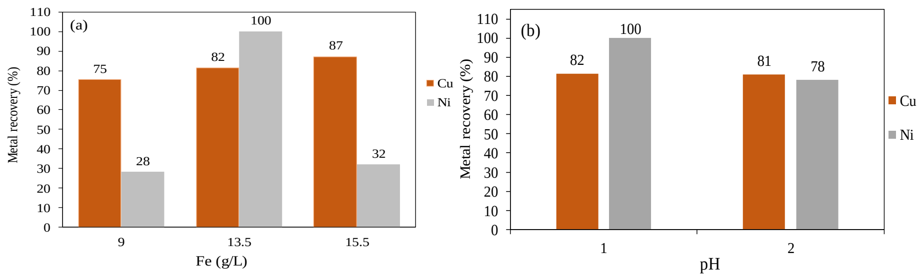

Figure 3. Biogenic Fe^{3+} leaching of metals from PCBs for (**a**) Fe^{3+} variation and (**b**) pH variation.

3.4. Iron Removal from the PLS

In order to facilitate metals extraction procedure from the PLS, Fe was purged out from the productive solution through precipitation and filtration. Hydroxides were thus obtained enabling about 70% of iron to be recovered by this method at pH 2.5 without major losses of any other divalent metals. The iron removal yield could be increased up to 99% at pH 2.5 by adding ferrihydrite particles as precipitation seeds in the PLS while minimizing the metal loss due to co-precipitation and adsorption.

4. Conclusions

A one-step bioleaching process of spent LiB samples for Li and Co recovery at laboratory scale was demonstrated in this research. As the process operated at a low pulp density (0.5%), Li recovery was 80% and Co recovery reached 98%. In the case of PCB bioleaching, indirect leaching with biogenic Fe^{3+} was demonstrated. Cu and Ni extraction was dependent on Fe^{3+} concentration and pH variation. At a feed particle size below 22 mm, Cu and Ni were recovered up to 82 and 100 %, respectively at pH 1 and Fe^{3+} concentration of 13.5 g/L. In the downstream process, 100% of the iron could be removed from the PLS using NaOH. Further optimization and scale-up tests are needed to validate the approach and provide added information on the metal dissolution mechanisms for the materials under study. Studies on the bioprecipitation of the valuable metals from the iron-depleted PLS reported here are underway.

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