Advancing biohydrometallurgy: metal extraction from mobile phone PCBs using spent microbial effluent

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Introduction

With the technological revolution and digitalization, the Electrical and Electronic Equipment sector is undergoing increasingly strong growth. When electronic equipment reaches its end-of-life (EoL) it becomes special waste (e-waste), that requires specific disposal treatments due to its composition in critical and hazardous elements. Among electronic equipment, mobile phones represent the most iconic example of how a device still functioning, easily becomes waste due to consumerism. End-of-life mobile phone represent a valuable reservoir of rare earth elements (REEs), platinum group metals (PGMs), and other critical raw materials (CRMs) at higher concentrations compared to primary ores. As the cost of extracting raw materials from minerals increases, recovering them from e-waste through urban mining practices becomes cost-effective. Despite numerous recycling technologies, in the framework of the circular economy, there is an emerging need for sustainable techniques with reduced energy consumption and pollutant emissions. In this regard, biohydrometallurgy is attracting interest among green technologies because it involves more sustainable process than the classic techniques employed by pyrometallurgy and hydrometallurgy (high extraction temperature and toxic compounds production respectively). Contrarily biological extraction of metals (bioleaching) uses milder conditions involving directly microorganisms or indirectly their biogenic products (lixiviants). Pure culture of microorganisms that are commonly involved in the bioleaching of metals from e-waste include iron and sulfur-oxidizing bacteria, cyanogenic bacteria, and fungi [1]. Though less studied, archaea are also attracting interest in the field of biohydrometallurgy due to their ancestral ability to withstand hostile environments and their interesting metabolic properties [2]. Within this context our work aims to apply microbial consortia belonging to organic municipal solid waste sludge for developing a biotechnological process for metal extraction from printed circuit boards (PCBs) of EoL-mobile phones. PCBs in fact, are made of a variety of valuable elements including PGMs (gold, silver, palladium and platinum), REEs (neodymium and erbium), and numerous CRMs (copper, lead, tin, aluminum, barium, nickel, iron, gallium, germanium, hafnium, beryllium, antimony, magnesium, niobium, tungsten, tantalum and vanadium), [3]. In detail, we are performing an indirect bioleaching approach testing the extractive power of spent effluent derived from anaerobic microbial digestion of dairy wastewaters on PCB powders. The diary wastewater itself was also used as control test to be compared with spent effluent. Metals extraction from PCBs reported in the present work is due to the presence of organic acids, including lactate, acetate, propionate, butyrate and valerate in both effluents [4].

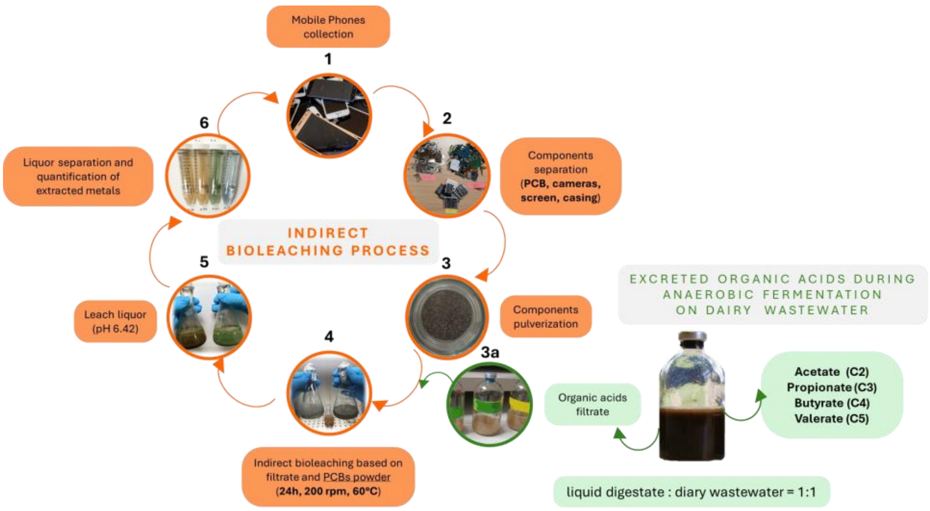

Figure 1 Overview of our indirect bioleaching process on PCBs from EoL mobile phones, step by step.

Materials and Methodology

After collecting 2 kg of EoL-mobile phones, these were manually dismantled to separate the different components including PCBs (*Figure 1*, **1**). Components were dismantled (**2**), shredded and pulverized by means of blade miller to homogeneous samples with particle sizes below 1 mm (**3**). The elemental composition of PCBs was done using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), while the organic component was analyzed by Thermogravimetric Analysis coupled with IR Detector (TGA-IR). The spent effluent used for the indirect bioleaching step was obtained after five days of anaerobic fermentation on a culture broth composed by digestate from anaerobic digestion process, mixed with diary spent water (1:1). The inoculum itself is derived from the anaerobic digestion process (**3a**). CO_2 and H_2 (20:80) were used as gas feeding to boost bio-methanation metabolism. At the end of the bio-methanation process, microorganisms were separated by filtering the liquid culture with a 0.2 μm filter, and the effluent was analyzed to determine the organic acid composition by High Performance Liquid Chromatography (HPLC). The bioleaching experiments (**4**) were conducted at laboratory scale in Erlenmeyer flasks with a total volume of 30 mL of liquid and a PCBs powder concentration of 10% w/v, using microbial effluent and the diary wastewater as control experiment. A part microbial cells filtration, the effluent was not further treated maintaining native organic acids composition. The leaching test lasted 24 h under stirring conditions (200 rpm) and 60°C. The supernatants were sampled at time zero and after 1h, 5h and 24h of contact with the powders (**5,6**), filtered and analyzed by ICP-OES to quantify the concentration of metals (in ppm) mobilized into solution over time.

Results and Discussion

HPLC analysis returned profiles of organic acids in the effluent and dairy wastewater (**Table 1**), highlighting how the diary wastewater is mainly rich in lactate (1173 mM), while the effluent is more heterogeneous with lactate, butyrate and acetate (68 mM, 59 mM and 42 mM respectively) because of the anaerobic fermentation on dairy wastewater. Metals mobilization from PCBs to liquid changed depending on the different organic acids content in the diary effluents and microbial effluent respectively. The results of our indirect bioleaching process are shown in **Figure 2**, representing dissolved metals concentration (ppm) at different sampling times

Table 1. Comparison between Diary wastewater (left) and Microbial Effluent (right) composition detected by HPLC analysis. n.d. stays for not detectable.

Organic acids (mM)	Dairy wastewater	Microbial effluent
Lactate	1172.7	68.1
Acetate	n.d.	42.3
i-Butyrate	20.5	n.d.
Butyrate	n.d.	59.2
i-Valerate	1.2	1.2
Valerate	n.d.	2.1

Considering copper (Cu) and iron (Fe), two of the most abundant elements in PCBs, we observed that the microbial effluent, rich in butyrate and acetate, is more efficient for Cu extraction (804 ± 5.5 ppm) after 5 h and a pH of 6.4, while the diary wastewater, dominated by lactate, is more effective on Fe (651 ± 38) after 5 h and a pH of 3.5 (*Figure 2*, A). Concerning the microbial effluent, after 24 h Cu decreased to 110 ± 3.5 ppm indicating that precipitation occurred presumably in the form of copper acetate (as denoted by supernatant color change from brown yellow to blue-green, *Figure 1*, **6**). The same occurs for Fe in diary wastewater, which dropped to 3.4 ± 0.9 ppm. Beyond Cu and Fe, other elements such as nickel (Ni), tin (Sn) and zinc (Zn) were mobilized with different yield according to the case, *Figure 3*, B and C. Ni and

Sn were higher extracted in the case of diary wastewater, after 24 h and 5 h with values of 130 ± 0.2 ppm and 343 ± 91.4 ppm respectively.

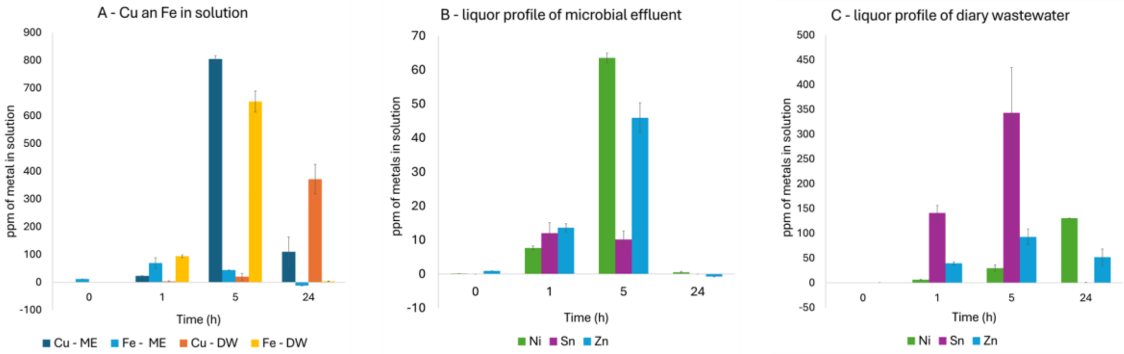

Figure 2: A) Copper and Iron solubilization in microbial effluent (ME) and diary wastewater (DW) in comparison; at five hours from the start of the experiment the maximum values of Cu and Fe in solution in the ME and DW respectively. B) and C): Liquors profile with highlighted metals gone in solution over time during bioleaching experiment using ME and DW respectively.

Concluding remarks

Our study aims to investigate the use of a microbial effluent obtained from anaerobic fermentation on diary wastewater to be applied for sustainable bioleaching process on e-waste. Both microbial effluent and diary wastewater were demonstrated to be valid lixiviant candidates for bioleaching experiments thanks to their peculiar composition in organic acids. The values of metals in solution were close to 100, 300, 600 and 800 ppm for Ni, Sn, Fe and Cu respectively. To calculate the metals extraction efficiency, we are performing ICP-OES and XPS analyses on PCB powder before and after bioleaching process as well as a morphologic analysis through SEM-EDX. A further achievement will be the identification of maximum dissolution values and precipitation points for each element. All these data together will support a deep knowledge of our bioleaching process based on raw microbial effluents by clarifying how to perform the subsequent metals recovery in a cost-effective and sustainable manner. Although still in a preliminary stage, our study already stands out for exploiting mixed microbial consortia rather than pure microbial cultures. Moreover, instead of synthetic growth media, we used mixtures of industrial effluents as nutrients and microbial diversity source. Eventually, our research provides a new perspective in the biohydrometallurgy field managing waste with waste strategy.

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