

A high productivity bioprocess for obtaining metallic copper from printed circuit boards (PCBs)

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HIGHLIGHTS

- An efficient biohydrometallurgical process with separation of effect has been carried out.
- High-purity copper cathodes were obtained from PCB waste.
- No inhibition in the biooxidation stage has been observed.
- High copper productivity has been achieved in the ferric leaching stage.

ABSTRACT

PCBs constitute a residue rich in metals, among which copper stands out due to its majority content, much higher than that found in natural deposits, so that it is a potential secondary resource. Many attempts have been made to recover copper via biohydrometallurgy because it is an environmentally friendly route, however, one of its main drawbacks is the low productivity achieved.

A global process based on circularity for obtaining copper cathodes from PCBs is proposed. First, PCBs from end-of-life mobile phones are shred to sizes between 800-2000 microns. Copper is leached from these pieces in a continuous stirred tank reactor (CSTR) at high ferric concentration, at a moderate temperature of 60°C. The solution that leaves the STR passes through a high-performance bioreactor for the regeneration of Fe(III). Concurrently, copper is

recovered in metallic state by solvent extraction and electrowinning with recirculation streams becoming a more profitable and sustainable complete global process.

1. INTRODUCTION

The rapid advancement of technology in recent decades has led to an alarming consumption of natural resources, ultimately resulting in a reduction of high-grade ore reserves. The supply of many essential materials in modern society is now at risk. In this context, recycling is a necessary solution, as it allows for the return of many of these materials to their supply chains while preventing further environmental and social implications. For this reason, more attention has been paid to industrial and urban waste, as they contain higher amounts of valuable metals than some natural ore resources. The process of reclaiming raw materials from spent products, commonly referred to as "urban mining," is an increasingly important activity. Each year, more than 40 million tons of Waste Electrical and Electronic Equipment (WEEE) are generated, and the United Nations Environmental Program estimates that this volume increases by a minimum of 3-5% per year, which is nearly three times faster than the growth of municipal waste (Baldé et al., 2017).

Printed circuit boards (PCBs) can be a potential alternative source of metals. PCBs are widely used in electronic devices, such as computers, smartphones, and televisions, and contain valuable metals such as copper, gold, silver, and palladium. These metals can be recovered through the recycling of PCBs, which can help reduce the demand for virgin metals and conserve natural resources. PCB recycling typically involves shredding and separating the different components of the board, including the metals and the non-metallic materials, such as plastics and ceramics. The metals can then be extracted through various processes, such as smelting, electroplating, or chemical leaching (Liu et al., 2021). Recycling PCBs not only helps recover valuable metals but also reduces the environmental impact of electronic waste. When PCBs are not properly disposed of, they can release toxic chemicals into the environment, including heavy metals and flame retardants, which can harm human health and the environment (Wang et al., 2020).

There are several challenges associated with the recovery of metals from printed circuit boards (PCBs). PCBs are complex and heterogeneous materials, and the recovery of metals requires the separation of different components, such as metals, plastics, and ceramics. This separation

process can be difficult, costly, and pose health and environmental risks due to the presence of hazardous substances. Additionally, the equipment and technologies required for the recovery of metals from PCBs can be expensive to acquire and operate, making the process economically unfeasible in some cases. Moreover, heterogeneity and variety of composition in PCBs have important implications for their recycling and disposal. The heterogeneity arises from the different materials used in their construction, as well as the different manufacturing processes involved. For instance, PCBs can vary in terms of their number of layers, and the types of materials used in each layer, apart from the different types of electronic components used, such as resistors, capacitors, and diodes (Cui and Forssberg, 2003). Traditionally, pyrometallurgy and hydrometallurgy have been used for the recovery of metals from e-waste.

Biohydrometallurgy offers a promising alternative to conventional processes for the recovery of metals from e-waste, as it is more environmentally friendly, cost-effective, and can potentially provide additional benefits such as promoting local employment since it can be implemented at low volumes. Biohydrometallurgy has several advantages over conventional processes for the recovery of metals from e-waste. Biohydrometallurgical processes typically generate lower emissions and waste compared to conventional processes, which can reduce the environmental impact. Biohydrometallurgical processes generally require less energy compared to conventional processes and enable circularity, which can lead to cost savings and reduced environmental impact. Biohydrometallurgical processes can be more cost-effective compared to conventional processes, as they require less equipment and space, and can operate at lower temperatures and pressures (Magoda and Mekuto, 2022). On the contrary, bioprocesses require more time to achieve the same efficiencies. This technology is still under development for industrial use due to the long operational period and time-consuming.

Several authors have reported multistep processes treating e-waste to metal recovery. In a study conducted by Shah et al., 2015, a two-step bioleaching process was utilized to extract Cu, Ni, and Zn from computer e-waste, using ferrous sulfate as a leaching agent. The study also examined the effect of particle size on metals extraction percentage. The authors observed that as the particle size decreased from 3360 to 74 μm , the metals extraction percentage increased. At 3360 μm particle size, the metal extraction percentage achieved by Cu and Zn were 71.25% and 79.56%, respectively, while at 74 μm particle size, the percentages increased to 97.35% and 99.80%, respectively. Further reduction of particle size resulted in a decrease in extraction percentage, according to authors, due to the particle collision and decrease in air diffusion at

the resulting higher apparent viscosity. Harikrushnan et al., 2016 conducted a study on the integrated biohydrometallurgical and hydrometallurgical processes for copper (Cu), nickel (Ni), and zinc (Zn) bioleaching from computer e-waste. The study employed the combination of the use of microorganisms and chemical leaching using *Acidithiobacillus ferrooxidans* microorganisms and 2 M HNO₃. The authors obtained metal recovery efficiencies of 85% for Cu, 98% for Ni and Zn at pulp density of 50 g/L, and approximately 60% of Cu and 97-98% for Ni and Zn at 100 g/L. However, none of these previous studies deal with the integral solution from the raw material up to the recovery of metallic elements in metallic state. Benzal et al. 2020 investigated a two-step bioleaching process for copper recovery from waste mobile phone PCBs, achieving high copper recovery rates of 95-100% in 48 hours using both filtration and sedimentation methods for biomass separation and including cementation as an additional step to recover copper powder. Otherwise, the patent WO2019206755A1 (2018) describes a process for the recovery of metals from electronic waste. The process includes a minimal preliminary mechanical treatment, followed by an acid and ferric leaching biogenerated to extract targeted metals, such as copper, nickel, and cobalt with an efficiency of 80% in less than 6 hours and 88% in 12 hours. The process includes the separation operations for the circularity of the process with the minimal secondary effluents. Iglesias-González et al. 2021 presents a two-stage biohydrometallurgical process involving the separation of chemical leaching of copper with ferric iron and bacterial oxidation of the ferrous iron adapting the BRISA process (Carranza et al, 1997). Large waste PCBs pieces were retained in a stirred tank reactor and a bioreactor in contact with circulating leaching liquor. The process separation configuration achieved 90% of copper extraction in 48 hours for large waste PCBs with a theoretically zero consumption of leaching agent and no emission of liquid effluents.

Table 1 shows a selection of works in which the recovery of copper from electronic waste by bioleaching was studied. Most of them have been carried out in batch reactors. In order to make a comparison between the performance of batch and continuous operations it is shown in Table 1, for the best conditions of each batch process, the total percentage of copper extracted (%Cu_{ex}), percentage of copper in the PCB (%Cu_{PCB}), pulp density of PCB (p.d.), reaction time (t_R) and volumetric copper productivity (Q_{Cu}). The latter calculated as:

$$Q_{Cu} = \frac{\%Cu_{ex} \cdot p.d. \cdot \%Cu_{PCB}}{t_R} \quad (\text{eq. 1})$$

As shown in Table 1, the highest productivity of copper bioleaching was obtained by Wu et al. (2018) with a value of 281 mg/L·h. Nevertheless, Yacizi and Devici (2014) reached productivities as high as 1850 mg/L·h with ferric sulphate leaching. They obtained this result in a 750 ml jacketed reactor with pitched blade impeller at 650 r.p.m. with 1% pulp density PCBs (18.5% Cu content) under 250 μm size leached with ferric iron concentration of 0.5 M and sulfuric acid of 0.53M at 50 °C. Therefore, it seems to indicate that maximum values of productivities of copper bioleaching from PCBs can be overcome if working with high ferric iron concentrations and at higher temperatures. This can be achieved by working with a process setup in which chemical and biological reactions are separated as done in our previous work (Iglesias-González et al., 2021). Furthermore, PCBs size is a key factor since the ferric leaching of copper from PCB is a process limited by mass transfer (Iglesias-González et al., 2021). Therefore, in the present work the chemical ferric leaching of the copper from the PCBs have been carried out using smaller PCBs pieces than in our previous work (PCB size between 0.8-2 mm instead of 10 mm); higher ferric iron concentration (40 g/L instead of 20 g/L) and higher temperature (60°C instead of 30°C).

Table 1. Comparison of efficiency and productivity in the bioleaching of copper from PCBs. *Refers to the hydraulic residence time (HRT). All the studies were carried out at temperature in the range 30-36°C.

Reference	Reactor mode	Particle size (mm)	%Cu _{ex}	Pulp density (g/L)	%CuPCB	t _R (h)	Q _{Cu} (mg/L·h)
Zhu et al. (2011)	Batch	0.178-0.250	96.8	12	83.8	45	216
Yang et al. (2014)	Batch	0.841-0.4	96.8	15	25.5	72	51
Yang et al. (2017)	Batch	0.178-0.250	92.57	12	83.8	78	119
Wu et al. (2018)	Batch	<0.4	93.4	100	65	216	281
Becci et al. (2020)	Batch	<0.5	94	50	25	216	58
Hubau et al. (2020)	Continuous	<1	>100	18	14.58	48*	65
Van Yken et al. (2020)	Batch	<0.75	86.2	10	58.7	48	105
Iglesias-González et al. (2021)	Batch	10	90	25	26.9	48	126

Therefore, in a process with separation of effects it would be possible to optimize the biooxidation process. Continuous ferrous iron biooxidation can be carried out in several kinds of bioreactor designs, such as stirred tank (Ojumu et al., 2008; Candy et al., 2009), rotating biological contactor, packed bed (Mazuelos et al., 2000; Chowdhury & Ojumu, 2014; Abbasi et al., 2021), fluidised bed and airlifts (Kaksonen et al., 2014; He et al., 2022). The highest biooxidation rate (5.8 g/Lh) is achieved in flooded packed bed bioreactors (Mazuelos et al., 2000).

Solvent extraction is commonly applied in downstream processing in (bio) hydrometallurgical processes. Because of aqueous raffinate from solvent extraction operations is recycled to extractive stages, organic reagents (solvents such as kerosene or extractant reagents of LIX series) can be present in (bio) reactors, both entrained in a form of tiny emulsion droplets and chemically dissolve in the aqueous raffinate by simple dissolution. These organics compounds can severely inhibit chemolithotrophic iron oxidizing bacteria such as *Leptospirillum ferriphilum*, *Leptospirillum ferrooxidans* and *Acidithiobacillus ferrooxidans* (Mazuelos et al., 2000, Dopson et al., 2006, Watling et al., 2009, Davis-Belmar et al., 2012, Liu et al, 2015, Vyrides, et al, 2015, Vardanyan and Vyrides, 2019). The inhibitory effects can slow irreversibly down microbial growth and iron oxidising metabolism up to 75%. To overcome this technical issue several solutions have been proposed:

- Avoiding organics leak from solvent extraction circuits (Davis-Belmar, et al, 2012).
- A pre-treatment of aqueous raffinate based on adsorption by activated carbon (Mazuelos et al, 2000).
- To detoxify the growth environment by co-inoculation of autotrophic acidophilic with heterotrophic acidophiles, such as *Acidiphilium acidophilum* (Watling et al, 2009), *Candida* spp (Vyrides et al, 2015) or other acidophilic yeast (Vardanyan and Vyrides, 2019).

It is well known, heavy metals-resistance (Cu, Cd, Ni) in acidophilic biomining microorganisms (Li and Ke, 2001, Pourhossein and Mousavi, 2018, Ramos-Zúñiga, et al, 2019). This tolerance ability to heavy metals commonly present at leachates from PCB ferric leaching depends on the kind of inoculum, protocols for adaptation process and growth medium composition, hence the dispersion of results in literature (Orrel et al, 2010). For instance, in continuous flooded packed bed bioreactors for ferrous iron concentration inoculated with

Acidithiobacillus ferrooxidans and *Leptospirillum ferrooxidans*, when Cu concentration is progressively increased, iron oxidising microorganisms allows to operate at Cu concentrations up to 20 g/L with drops of iron biooxidation rates lower than 15 % (Mazuelos et al, 2019). This inhibition on microbial activity is reversible when Cu in fed is removed.

With all this background, this paper aims to validate the feasibility and interest of applying a biohydrometallurgical process to obtain high-purity copper from printed circuit boards residues. It is based on the process previously proposed by the group for obtaining copper from secondary copper sulphides (BRISA process, Palencia et al., 2002).

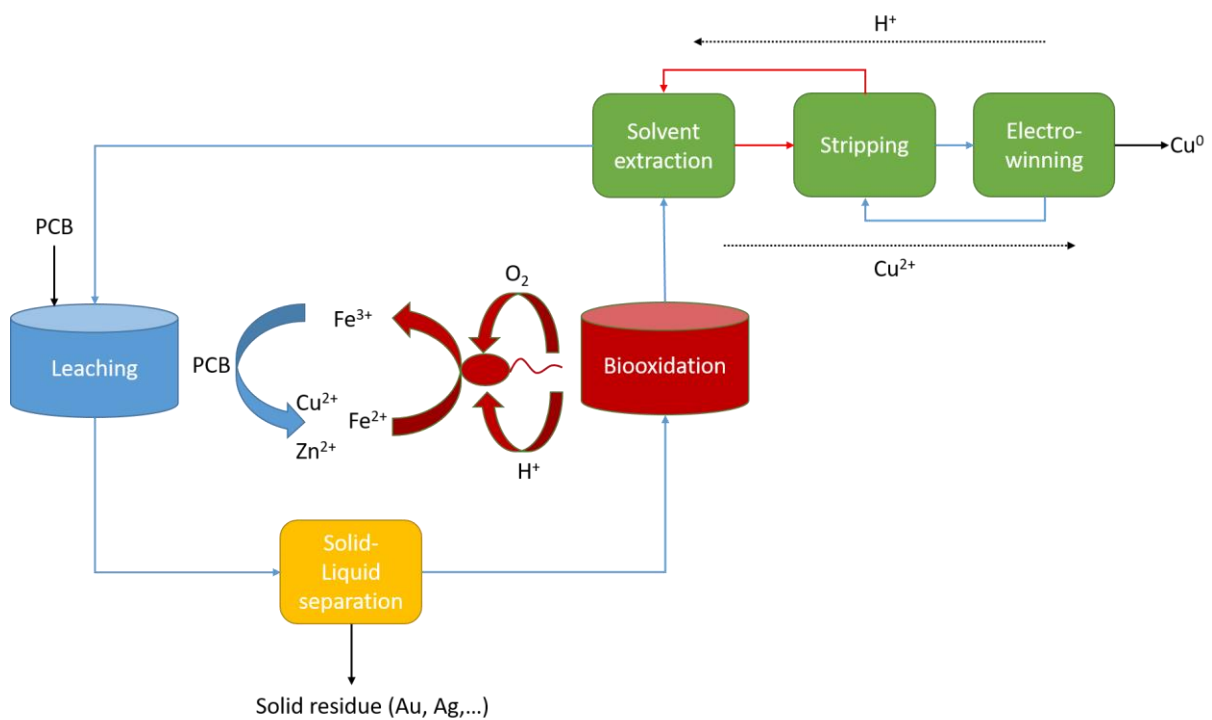


Figure 1. Conceptual flowchart of the process proposed in this work to obtain copper by biohydrometallurgical route from PCB residues.

Figure 1 shows the conceptual flowchart of the process. The process begins with a feed of the ground PCBs to the chemical leaching reactor. In this reactor, the dissolution of copper will take place by iron leaching (apart from copper, other minority metals of the PCB, such as Zn and Ni, will go into solution). The kinetics of this process is fundamentally influenced by 3 factors: size of the PCB particles; concentration of leaching agent (Fe^{3+}) and temperature. To achieve high extraction copper kinetics in this work, ground PCBs in a range of sizes, a concentration of Fe(III) in the feed to the reactor of 40 g/L and a temperature of 60°C have been used. Another parameter to control in the process is the pH, which must be less than 1.5

to avoid precipitation of Fe^{3+} . The output of the reactor, a mixture of liquid and solid, passes to a filtration stage to separate the solid part from the liquid. In this stage, a solid practically free of copper, zinc and nickel is obtained, but with a high concentration of precious metals (gold, silver, etc...). The liquid stream containing the copper and part of the Fe^{3+} converted to Fe^{2+} is passed through a biooxidation column in order to regenerate the leaching agent. In a recent study, it has been shown that the use of a flooded packed bed bioreactor is capable of biooxidising Fe^{2+} to Fe^{3+} at concentrations of up to 50 g/L and pH below 1 with a volumetric productivity greater than 3g/Lh. In this way it is possible to regenerate the ferric iron consumed in a circular process. For this, the iron-oxidizing extremophile microorganisms adsorbed in the biooxidation reactor use oxygen and protons to transform Fe^{2+} into Fe^{3+} .

The output of the bioreactor is fed to the solvent extraction process in which the aqueous phase containing copper is brought into contact with an organic phase (15% solution of LIX 973 NS-LV in kerosene) which allows a highly selective extraction of copper from the aqueous phase to the organic one. In this process, there is an exchange of Cu^{2+} ions from the aqueous phase for protons from the organic phase, which makes it possible to compensate for the consumption of acid in biooxidation. The organic phase loaded with the copper extracted from the PCB is placed in contact with an aqueous solution from electrodeposition with a high concentration of acid (2 M), causing the copper ions to pass into the aqueous solution entering the electrodeposition while the phase organic is recycled to solvent extraction. Subsequently, copper is deposited on the cathodes of an electrolytic cell applying a current density of 350 A/m^2 and recovered in metallic state with high purity. Finally, the recirculation of all streams generated in downstream processing leads to theoretically zero reagent consumption and no emission of any liquid effluent.

2. MATERIALS AND METHODS

2.1 Material

The material under study comes from end-of-life mobile phones (EoL mobiles) from which the casing and battery have been removed. This material was shred to sizes between 800-2000 micrometers by means of a cutting mill consisting of three concentric knives which creates a 200 mm diameter action circle. The rotational speed used was progressively increased from 1500 to 3000 rpm. Two screening sizes of 2 and 7 mm mesh size were installed creating a recirculation system until achieving the objective sizes.

The sample was divided by a rotatory cone sample divider (Laborette 27, Fritsch) to guarantee representative subsamples for analysis and testing. The metal composition was determined by atomic absorption spectrophotometry (PinAAcle 500, Perkin Elmer) previous acid digestion with aqua regia. Table 2 shows the percentage of copper, target metal of this work, determined in each replicate, with a mean of 35.71% and a standard deviation (sd) of 4.16.

Table 2: Copper composition of PCBs studied

<i>Sample</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>mean</i>	<i>sd</i>
<i>% Cu</i>	38.89	30.66	37.50	30.02	33.32	41.08	40.83	33.22	35.85	35.71	4.16

Other base metals and gold and silver were analyzed in quadruplicate. Table 3 shows the average metal content and the standard deviation. From both tables it can be observed that Cu is the main component of the sample, other base metals such as Zn, Pb, Fe, Ni and Al represent slightly more than 1% by weight of the sample each. The high content of noble metals stands out, 1043 g/t of gold and 1.06% of silver on average. However, the standard deviation is high in all cases, revealing the heterogeneity of the material.

Table 3. Chemical composition of the PCBs studied.

	<i>Cu %</i>	<i>Pb%</i>	<i>Al%</i>	<i>Fe%</i>	<i>Ni%</i>	<i>Zn %</i>	<i>Ag g/t</i>	<i>Au g/t</i>	<i>Co g/t</i>
<i>Average</i>	35.71	1.90	1.53	1.69	1.64	1.09	10614	1043	83
<i>sd</i>	4.16	0.49	0.31	1.31	0.52	0.09	5748	149	15

2.2 Experimental procedure

Batch ferric leaching

In order to study the leaching kinetics a batch leaching test was carried out. Batch ferric leaching test was performed in a 1L-stirred tank reactor. Reactor was stirred with a four-blade impeller at 800 rpm by an overhead stirred (IKA RW20). The working temperature was kept

constant at 60°C thanks to an immersion thermostat (DIGITERM S-150) that pumped water into the reactor jacket at a flow rate of 12 L/min. Solid/Liquid ratio was 1%, that is, 10 g of pieces of EoL mobiles and 1L of biogenic leaching solution composed of 37 g/L of Fe(III) at pH 1.0 in sulphate media. The test lasted 24 hours and during this time samples were taken for the analysis of dissolved copper and Fe(II) generated.

Continuous ferric leaching

In order to determine the behavior of the leaching stage in the system once all the stages were connected, a continuous test was carried out with a leaching solution similar to the one that would come from the bioreactor. The continuous ferric leaching was carried out in a jacketed glass reactor with a useful volume of 965.7mL. Reactor was stirred with a four-blade impeller at 800 rpm by an overhead stirred (IKA RW20). The working temperature was kept constant at 60°C thanks to an immersion thermostat (DIGITERM S-150) that pumped water into the reactor jacket at a flow rate of 12 L/min. The loss of water by evaporation in the system was estimated and compensated by pumping 2mL/h of water to the reactor. Reactor was fed on the one hand, with a biogenic ferric solution by a peristaltic pump, and, on the other hand, with pieces of EoL mobiles by a vibratory feeder (LABORETTE 24, Fritsch). The solid/liquid ratio varied in the range 0.25-1.75%. The biogenic ferric solution was composed of 40g/L of Fe(III) and 5 g/L of Cu(II) and pH 1, and filtered before being fed to the reactor. Daily, liquid flow rate was controlled (about 135 mL/h), pH was measured, and samples were taken for Cu(II) analysis. The output of the reactor was collected by overflow in a tank for its subsequent filtering and biooxidation.

Biooxidation

Continuous biooxidation was conducted in a flooded packed bed bioreactor (Mazuelos et al., 1999). This bioreactor consists of a column (8.4 cm in diameter and 17.8 cm in height) randomly packed with siliceous stones (7 mm) as support of biofilm. The protocol for starting up was described by Mazuelos et al., 2000. The culture used as inoculum was obtained from the Rio Tinto Mine in Huelva, Spain. It mainly consists of *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* (Mazuelos, et al. 2010).

This bioreactor was operated at 31°C. Liquid and air were fed at the bottom of the bioreactor at flow rates 100 mL/h and 750 mL/m, respectively. Both fluids went up through the bed

occupying all the voids between particles (porosity 0.42). Air was introduced by a pipe of 1 mm of internal diameter. The working volume was 0.55 L.

Solvent extraction tests

In order to recover copper from the pregnant leach solution, solvent extraction tests were carried out with a 15% (v/v) solution of LIX 973 NS-LV in kerosene. The extraction isotherm was determined by mixing different volumes of the organic and aqueous phases, in the proportions 5:1, 2:1, 1:1, 1:2 and 1:5, until reaching equilibrium at 20°C. The solution at the outlet of the bioreactor, containing copper (6.8 g/L) and iron(III) (38.8 g/L), and pH=1.1 (aqueous phase) was placed in contact with the organic phase by manual shaking for 2 minutes in a 250mL-separation funnel. Likewise, the stripping isotherm was found by mixing 5 mL of the loaded organic phases, obtained in the determination of the extraction isotherm, with 2.5 mL of a solution simulating the acidity of the electrolyte from the electrowinning stage (200 g/L of H₂SO₄) in a 50 mL-separation funnel.

Also, a stripping test was carried out by contacting the loaded organic phase with a solution simulating an electrolyte composed of 10 g/L of Cu and 200 g/L of H₂SO₄. Copper and iron were analyzed by AAS in the aqueous phase before and after extraction and stripping. The concentrations of copper and iron in the organic phase were calculated by mass balance.

Electrowinning

A synthetic solution of 15 g/L of Cu and 155 g/L H₂SO₄ was prepared to simulate the solution resulting from solvent extraction. This solution was conducted to an electrowinning unit to recover Cu using an experimental setup with polished 316 L stainless steel anodes and cathodes in a self-made cuboidal Teflon tank of 200 mL of capacity. Anode and cathode, each measuring 2 cm x 4.1cm, were connected to a DC source (Model: FAC-622 Promax, Spain) and the resulting voltage and current intensity were monitored. The interelectrode space was fixed at 2.5 cm. Electrowinning tests were carried out at a current density of 350 A/m². The average electrical potential was 2V. Cu concentrations were measured by Atomic Absorption overtime and the deposited Cu was analyzed using scanning electron microscopy (SEM). The cathode was weighed before and after the test to check mass balance. H₂SO₄ concentration was determined by acid-base titration using 1 M NaOH-standardized and phenolphthalein as visual indicator.

Current efficiency was calculated using Faraday's equation:

$$\%CE = \frac{m(Cu) \cdot n \cdot F}{M(Cu) \cdot I \cdot t} \cdot 100 \quad (\text{eq. 2})$$

The energy required for electrowinning was determined as:

$$E(Kwh/Kg) = \frac{I \cdot V \cdot t}{m(Cu)} \cdot \frac{1}{3600} \quad (\text{eq. 3})$$

Where, $m(Cu)$ is the mass deposited on the cathode in g, n is the number of transferred electrons (in this case =2), F represents Faraday's constant (96.485 C/mol), $M(Cu)$ is the atomic weight of Cu, I is the current passed in amperes, V is electrical potential in volts and t is the time in seconds.

3. RESULTS

3.1 Batch ferric leaching.

The study of the ferric leaching kinetics of copper from PCB have been studied in several papers (Deveci and Yazici 2014; Becci, et al. 2020; Iglesias-González, et. al. 2021). It is shown that, apart from PCB size, temperature and ferric iron concentration are key parameters leading to increasing copper extraction rates when increasing either of the two parameters. Furthermore, copper extraction kinetics can be modeled as a heterogeneous reaction limited by mass transfer where two distinct processes occur simultaneously, on the one hand the leaching of the copper exposed to the solution and on the other hand the leaching of the internal copper (Iglesias-González, et al. 2021). For the experimental conditions used in the present work (40 gL⁻¹ and T = 60°C) it can be assumed that the external copper is converted almost instantaneously, therefore at $t = 0$, $X_{Cu} = X_{Cu,0}$, where X_{Cu} and $X_{Cu,0}$ are the copper conversion and the instantaneous copper conversion, respectively. Since a pulp density of 1% was used the ferric iron concentration is expected to be higher than 30 g/L during all the leaching experiments, and, therefore the influence of ferric iron concentration can be neglected. With these assumptions the kinetics of copper leaching is given by the following equation:

$$\frac{dX_{Cu}}{dt} = k \cdot (1 - X_{Cu}) \quad (\text{eq. 4})$$

Integration of equation 4 with initial conditions $t = 0$ and $X_{Cu} = X_{Cu,0}$ gives:

$$\ln(1 - X_{Cu}) = \ln(1 - X_{Cu,0}) - k \cdot t \quad (\text{eq. 5})$$

Therefore, a linear plot was obtained when $\ln(1-X_{Cu})$ vs. t was plotted as shown in Figure 2. From the slope of the linear regression of the experimental data the kinetics constant was obtained with a value of $k = 8.5 \cdot 10^{-3} \text{ min}^{-1}$, whereas $X_{Cu,0}$ was obtained from the value of the intercept of the linear regression with a value of $X_{Cu,0} = 0.505$. Once these values were obtained the copper conversion as function of time is obtained by rearranging equation 5:

$$X_{Cu}(t) = 1 - (1 - X_{Cu,0}) \cdot e^{-k \cdot t} \quad (\text{eq. 6})$$

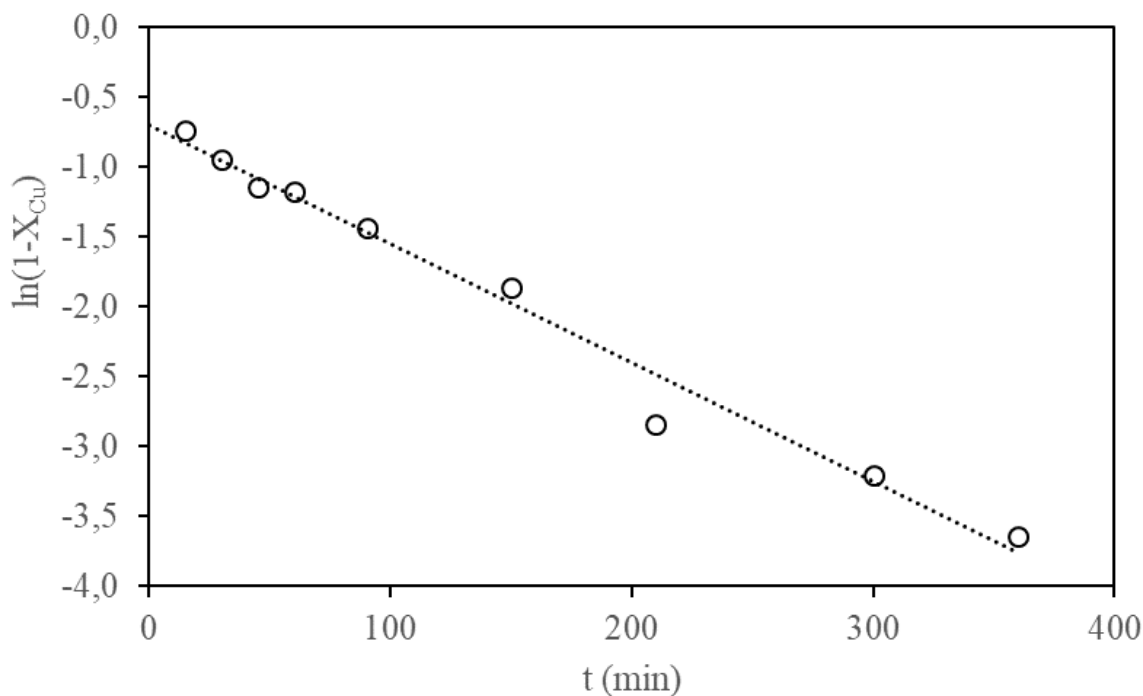


Figure 2. Plot of $\ln(1-X_{Cu})$ vs. t from the experimental values of copper extraction for the batch ferric leaching experiment. Experimental conditions were: $[\text{Fe}^{3+}]_0 = 37 \text{ g/L}$; $\text{pH} = 1.0$; $T = 60^\circ\text{C}$; $\text{p.d.} = 1\%$; agitation speed = 800 r.p.m. Dotted line is the linear regression of the experimental data according to equation 5, with $k = 8.5 \cdot 10^{-3} \text{ min}^{-1}$ and $X_{Cu,0} = 0.505$.

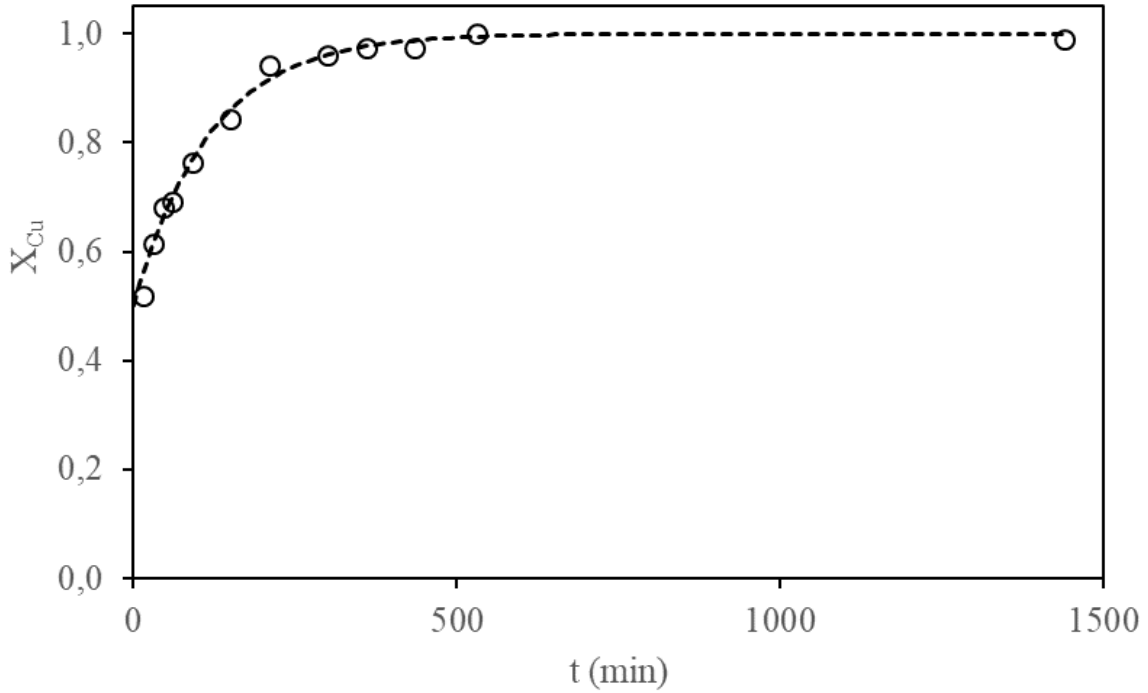


Figure 3. Experimental values of X_{Cu} vs time for the batch ferric leaching experiment. Experimental conditions were: $[Fe^{3+}]_0 = 37$ g/L; pH = 1.0; T = 60°C; p.d. = 1%; agitation speed = 800 r.p.m. Dashed line is obtained by equation 6 with the parameters of k and $X_{Cu,0}$ obtained with the linear plot of Figure 2.

3.2 Continuous ferric leaching.

A continuous test was carried out as explained in the experimental section. The hydraulic retention time (HTR) was set to 6 hours. In the limiting case where the solid retention time (SRT) was equal to the HRT the mean copper conversion can be evaluated by the expression for the segregation model:

$$\underline{X} = \int_0^{\infty} X(t)E(t)dt \quad (\text{eq. 7})$$

with $X_{Cu}(t)$ given by equation 6 and the residence time distribution, $E(t)$ for a perfectly mixed continuous stirred tank reactor:

$$E(t) = \frac{e^{-t/\tau}}{\tau} \quad (\text{eq. 8})$$

being τ the HRT.

Solving eq.7 for the values of k , $X_{Cu,0}$ obtained in the previous section and $\tau = 6$ h a mean copper conversion of 88% would be expected if CSTR model in steady state was reached. Since the most likely scenario implies a higher SRT than the HRT value a higher copper conversion would be expected.

The continuous ferric leaching test was carried out for 96 hours. Every 24 hours, which corresponds to 4 times the HRT, the copper extraction and productivity was determined and the solid feed was modified in order to study the influence of the solid/liquid ratio of the feed in the daily productivity of the continuous reactor. Figure 4 shows the value obtained for the copper extraction and productivity every day for the different solid/liquid ratio of the feed.

The daily volumetric productivity was obtained from the following equation:

$$Q_{Cu} = \frac{\%Cu_{ex} \cdot m_{PCB} \cdot \%Cu_{PCB}}{V_R \cdot t_f} \quad (\text{eq. 9})$$

m_{PCB} , being the mass of PCB fed, $\%Cu_{PCB}$, the fraction of copper in the PCB, $\%Cu_{ex}$ the copper extraction, t_f , the feeding time and V_R , the volume of the reactor.

It is observed that despite the different solid/liquid ratio fed to the reactor copper extraction was always almost complete (only the third day the copper extraction was of only 90%). It is clearly observed that Q_{Cu} increases when increasing solid/liquid ratios, since the copper extraction remains practically the same for all experimental conditions. On day four when the solid/liquid ratio was increased to 1.8 % an extraction rate as high as 1 g/Lh of copper was obtained. This value is much higher than extraction rates obtained in most of the previous studies in copper bioleaching from PCB (see Table 1).

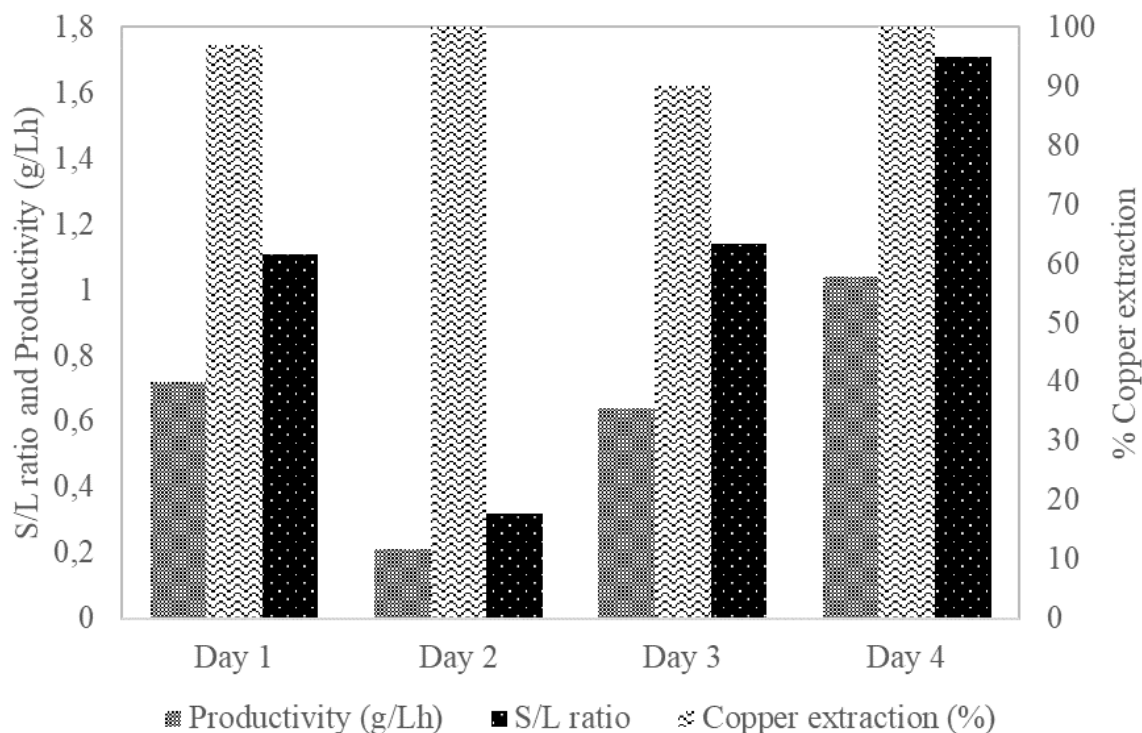


Figure 4. Results of ferric copper leaching in the continuous stirred tank reactor. Operation conditions: $T = 60^{\circ}\text{C}$; stirring speed = 800 r.p.m. Liquid inlet stream: volumetric flow rate= 135 mL/h, $[\text{Fe}^{3+}] = 40 \text{ g/L}$; $[\text{Cu}^{2+}] = 5 \text{ g/L}$; $\text{pH} = 1.00$. Solid inlet: crushed PCB. Red bars are the solid/liquid ratio of the feed; green bars are the daily copper productivity and blue bars represent the percentage of copper extracted with respect to copper fed each day.

Once the continuous operation was finished, the total amount of solid filtered in the outcoming stream was 21.93 g, whereas the weight of the solid that remained in the reactor was 53 g. Therefore, at the final part of the process the pulp density of the reactor reached a value of 6.3%. In addition, the weight loss of the PCB after the ferric leaching was 44.5% of the solid feed. Both solid fractions, the one recovered in the filtration as well as the one that remained inside the reactor, were digested with aqua regia to determine their copper content and other metals of interest. Table 4 lists the copper, zinc, silver and gold content in the feed and the solid fractions collected, as well as the weighted concentration in the final solid residue. The copper concentration in the solid residue was approximately 0.4%, therefore a copper extraction of 99% was obtained. In addition, 96% of the initial zinc has been recovered and a gold-enriched solid is obtained. Regarding silver, it is worth noting the difference in silver concentration between the filtered solid and the solid retained in the reactor. This difference could be explained by the decrease in the solubility of silver sulfate with the drop in temperature, as

occurs in this system in which the silver ions would dissolve inside the reactor, but they would precipitate out of the reactor upon cooling.

Table 4: Initial and final solid composition

<i>Solid</i>	<i>m(g)</i>	<i>Cu (%)</i>	<i>Zn (%)</i>	<i>Au (ppm)</i>	<i>Ag (%)</i>
<i>Feed</i>	135.01	35.71	1.03	1043	1.06
<i>Filtered</i>	21.93	0.66	0.06	1440	1.77
<i>Inside reactor</i>	53	0.31	0.07	1420	0.17
<i>Weighted</i>	74.93	0.41	0.06	1426	0.64

3.3 Biooxidation

Before receiving Pregnant Leach Solution (PLS) from ferric leaching of PCB, the bioreactor was fed with an iron solution containing 6.12 g/L of Fe(II), 25 g/L of Fe(III) and pH 1 at a flow rate of 100 mL/h. The Fe(II) concentration in outlet solution was 0.15 g/L and pH 1.07. Therefore, the volumetric ferrous iron productivity reached was 1.1 g/L·h. After that, the bioreactor was fed with PLS. Ferrous iron bio-oxidation results are shown in table 5.

Table 5: Continuous ferrous iron bio-oxidation test. Liquid flow rate 100 mL/h, air flow rate 750 mL/min, temperature 31 °C, total iron concentration 37 g/L. *Liquid flow rate 37 mL/h.

<i>Time (h)</i>	<i>[Fe(II)]_{in} (g/L)</i>	<i>[Cu]_{in} (g/L)</i>	<i>pH_{in}</i>	<i>[Fe(II)]_{out} (g/L)</i>	<i>pH_{out}</i>
0	4.67	7.8	1.06		
24	4.78	7.8	1.01	0	1.14

45	4.64	7.8	1.01	0.04	1.10
67	4.73	7.8	1.02	0.05	1.10
95	9.29	10.45	1.08	2.37	1.22
168*	9.29	10.45	1.08	0	1.24

Despite the very extreme operational conditions (high total iron concentration at low pH in the presence of about 10g/L of Cu), high conversion of ferrous iron contained in PLS from continuous ferric leaching of PCB was achieved. No inhibitory effect for microbial population was observed. For total conversion, biooxidation rate is limited by Fe(II) availability, thus obtaining the higher biooxidation rate (1.3g/Lh) at 95 h of operation when conversion of Fe(II) was lower than 75%. From these results, it can be stated that there is no technical hindrance for biological ferric iron regeneration for the continuous flow sheet proposed.

3.4 Solvent extraction

The solution at the outlet of the bioreactor, containing copper (6.8 g/L) and iron(III) (38.8 g/L), and pH=1.1, is treated by solvent extraction in order to separate the copper for its recovery as a cathode, from the ferric iron that will be reused as a leaching agent in the reactor. Figure 5 shows the extraction isotherms for LIX 973 NS-LV in kerosene 15% v/v.

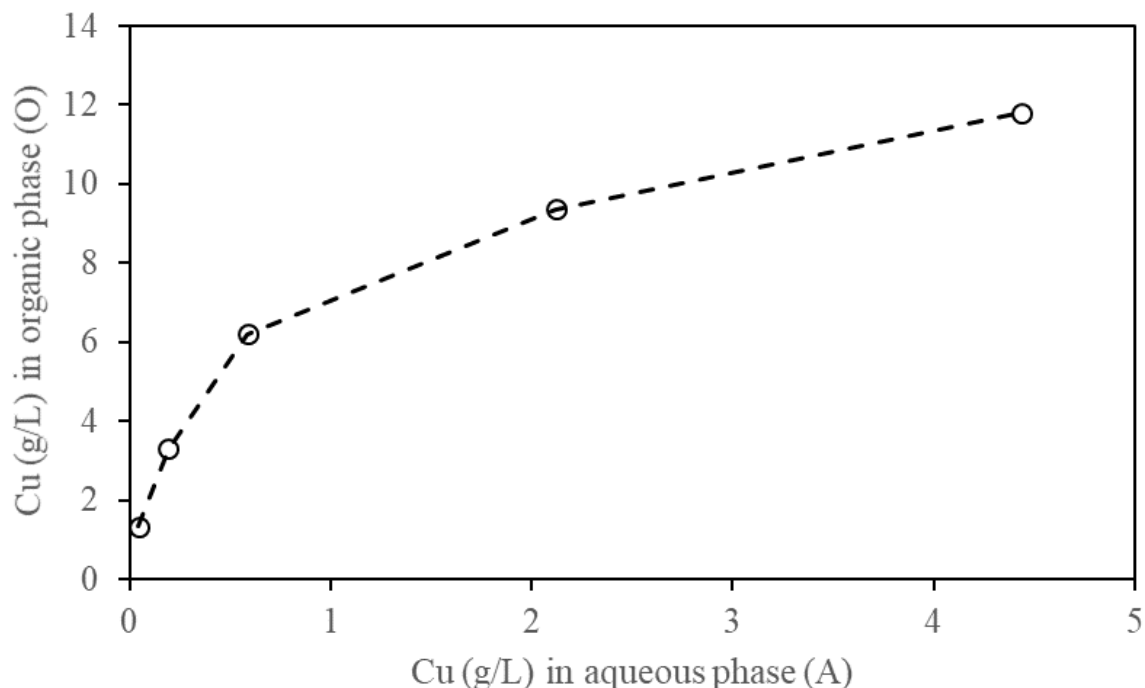


Figure 5. Copper extraction isotherms for LIX 973 NS-LV in kerosene 15% v/v at 20°C.

From Fig.5 high distribution coefficients for the different aqueous/organic volumetric ratios (A/O) employed are observed. At the same volume of aqueous and organic phases (A/O=1), the distribution coefficient is 10.57 and only one solvent extraction stage is necessary for 91.4% of Cu to pass into the organic phase and all the iron remains in the aqueous phase. Therefore, it can be said that the extraction under the studied conditions is efficient and selective since the copper passes mainly to the organic phase and the iron remains in the aqueous phase. Figure 6 shows the stripping isotherm for a 200 g/L H₂SO₄ solution, in which a saturation of the aqueous phase of around 14 g/L of Cu is observed. Subsequently, a stripping test was carried out putting in contact the exhausted electrolyte containing 9.8 g/L of Cu and 200 g/L of H₂SO₄, and an organic phase containing 6.21 g/L of Cu in the volumetric ratio 20/4 (O/A). A concentration of 24.68 g/L of Cu was obtained in the aqueous phase. Therefore, the copper transfer from the organic to the aqueous phase was 14 g/L which is in consonance with equilibrium data.

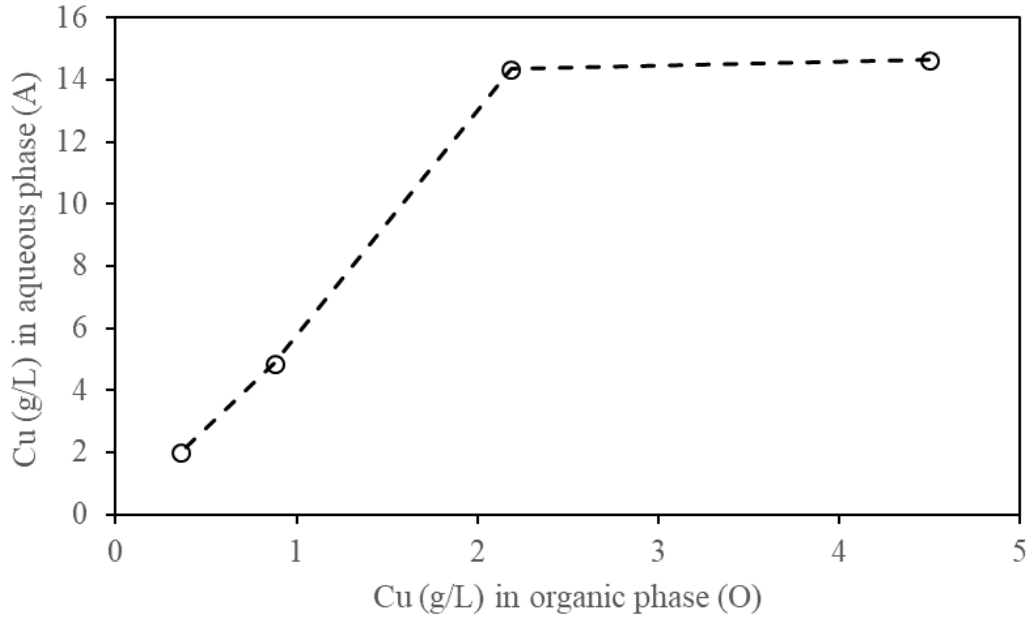


Figure 6. Copper stripping from LIX 973 NS-LV in kerosene 15% v/v at 20°C with a solution simulating an electrolyte composed of 200 g/L of H₂SO₄

3.5 Electrowinning

A synthetic solution of 15 g/L of Cu and 155 g/L H₂SO₄ was exposed to the electrolytic cell described in section 2.2 at a current density of 350 A/m². The concentration of Cu in the solution was monitored over time (refer to Figure 7), and the rate of electrodeposition observed was 3.35 g Cu/L/h. The copper electrode deposited was checked by Scanning Electron Microscopy (Figure 8). At the conditions tested the current efficiency was 99.2% and the energy consumption was 1.7 Kwh/Kg. After 2 hours of operation, the resulting solution of this step was 8.9 g/L of Cu and 177 g/L of H₂SO₄. Therefore, electrowinning at these conditions is efficient and suitable for the recovery of copper at the concentrations and conditions obtained from the extraction step and can be coupled to the circular global process defined in the work presented herein closing the loop.

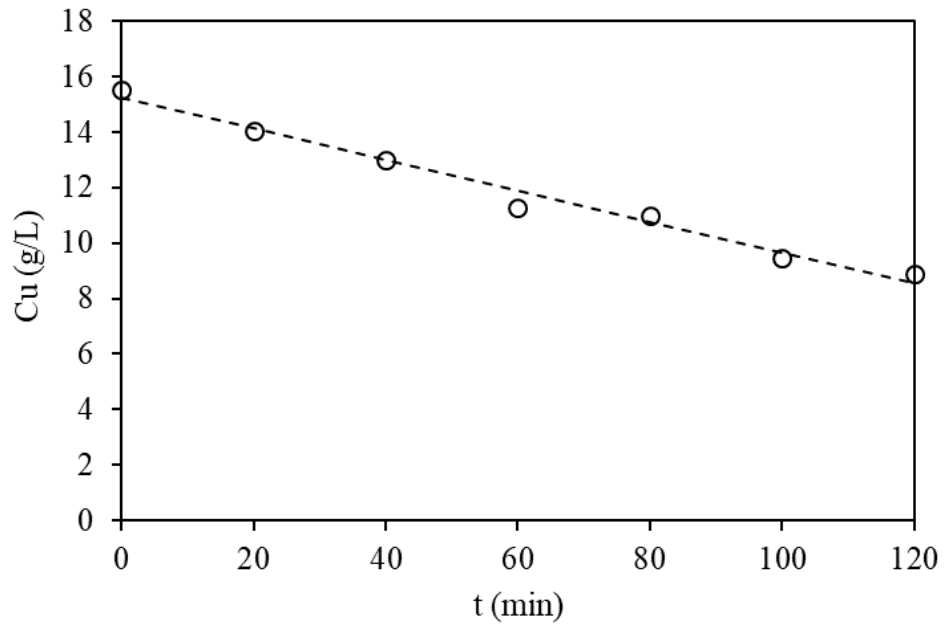


Figure 7: Cu concentration in solution over time in the electrolytic cell (hollow dots) and linear regression in dashed lines.

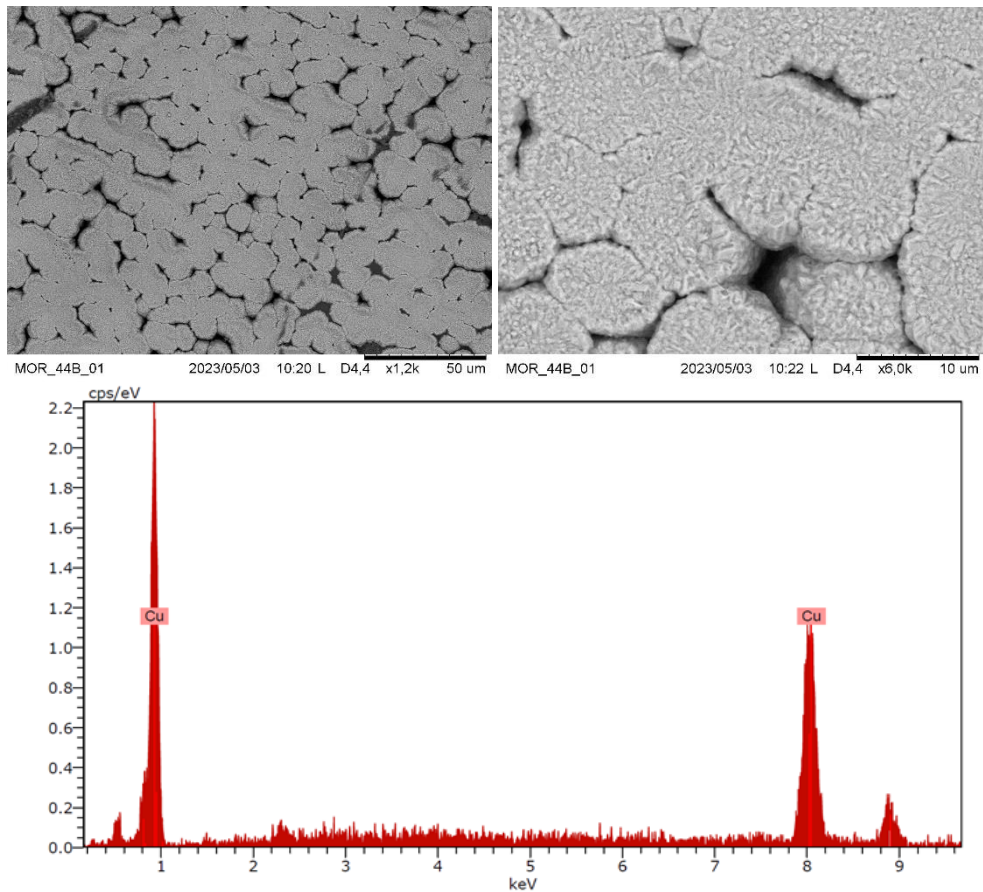


Figure 8: Electron micrograph of copper deposits above on the left (x1,2k), on the right (x6k) and below EDS spectrum by Scanning Electron Microscopy.

4. CONCLUSIONS

In the present work it has been tested a hydrometallurgical process to obtain copper metal from PCB waste in a continuous operation as shown in Figure 1.

First, a continuous iron leaching process of ground PCB waste was carried out, reaching a copper dissolution rate higher than 1g/L·h and a yield of 99%. It has been shown that high copper recovery can be achieved if working at a high ferric iron concentration (40 g/L), and at a temperature of 60°C.

Once the reactor outlet stream was filtered, the solid obtained had a weight loss of 44% and the gold and silver of the PCBs were concentrated in this solid residue. The filtrate liquor with concentrations of up to 10 g/L of copper was passed through a biooxidation column to regenerate the consumed iron. A biooxidation rate of 1.3 g/Lh was achieved and no inhibition was observed.

It was also studied the recovery of the dissolved copper from the outlet stream of the bioreactor by means of liquid-liquid extraction. It was shown that more than 90% of copper could be extracted from the pregnant leach solution in a single stage. From the stripping experiments it was observed that at the experimental conditions tested in the present work, the maximum copper concentration that was transferred from the organic to the aqueous phase was 14 g/L. Finally, copper was obtained efficiently by electrowinning at the conditions obtained in the extraction step. These results show that it is feasible to develop an efficient circular biohydrometallurgical process for obtaining metal copper from PCB waste minimizing the reagent consumption and obtaining a leaching residue less-pollutant with a reduction up to 44% in weight.

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