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Copper Electrowinning from Supercritical Leachate of Printed Circuit Boards

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Abstract: The technological development propitiates the rapid replacement of electrical and electronic equipment, which makes it indispensable to develop recycling processes for the treatment of this equipment when discarded. Printed circuit boards (PCBs) are fundamental components of electrical and electronic equipment. PCBs are composed of ceramics, polymers, and metals. Copper is the metal that is present in the greatest percentage of mobile phone PCBs. The objective of this study was to recover copper in the form of metallic deposits from a copper solution extracted from comminuted PCBs through supercritical CO_2 in the presence of cosolvents (H_2O_2 and H_2SO_4). A synthetic $CuSO_4$ solution was employed to determine the ideal current density in the range of 250 to 540 A/m^2. The electrowinning of the leachate solution from PCBs was performed at the determined current density. Using the current density of 250 A/m^2, pH equal to 4, and temperature of 25 °C, a current efficiency of around 100% was achieved for the real solution. The deposit obtained showed a copper concentration of 95.97 wt%, recovering 40% of the copper contained in the solution in 300 min of electrowinning. It was observed that for a longer electrowinning time, the percentage of copper recovery could increase.

Keywords: CO_2 supercritical; acid leaching; PCBs; metallic copper

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Citation: Calgaro, C.O.; da Silva, M.D.C.R.; Tanabe, E.H.; Bertuol, D.A. Copper Electrowinning from Supercritical Leachate of Printed Circuit Boards. *Metals* **2023**, *13*, 395. https://doi.org/10.3390/met13020395

Academic Editor: Man Seung Lee

Received: 28 December 2022
Revised: 6 February 2023
Accepted: 13 February 2023
Published: 15 February 2023

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1. Introduction

The rapid advances in technology and availability of electric and electronic equipment (EEE) over the past two decades shorten the life cycle of EEE and generated a large amount of waste electric and electronic equipment (WEEE) [1]. Among different components of EEE, printed circuit boards (PCBs) are the major component inside of EEE [2,3].

PCB support the electronic components mechanically and connect them together to function correctly [4]. This component is responsible for 4–7% of total mass of EEE [5] and it is composed by metals (40%), ceramic (30%) and polymeric materials (30%) [6,7]. Copper is the predominant metal in mobile phone PCBs [8]. However, the metal composition of electronic waste varies considerably with its age, origin, and manufacturer [9]. According to Yamane et al. [8], the average composition of metals in cell phone PCBs is 34.49 wt% Cu, 10.57 wt% Fe, 5.92 wt% Zn, 3.39 wt% Sn, 2.63 wt% Ni, 1.87 wt% Pb, 0.26 wt% Al, and 0.2 wt% Ag determined by leaching with aqua regia. Additionally, metal contents are much higher than those in ore, indicating its economic potential for the recovery of precious metals (e.g., Au, Ag, Pd) and base metals (e.g., Cu) [10]. However, the difficulties in processing of PCB are due to its multicomponent nature and heterogeneity, which limits metal recovery [11].

Several techniques have been studied in past years for the recycling of PCB: hydrometallurgy, pyrometallurgy, biometallurgy, electrometallurgy and combinations of these

procedures. Hydrometallurgy has been used for the recovery of metals from primary and secondary resources worldwide due to its high recovery rates, low costs and simple process control [4]. In this process, mineral acids (e.g., sulfuric acid) and oxidizing agents (e.g., hydrogen peroxide) are usually applied for metal leaching [12,13]. Supercritical fluids are an alternative for the conventional solvents providing fast kinetics, high reaction rates and efficient yield, along with recycled and reused solvent in process [14]. Using supercritical carbon dioxide combined with cosolvents, previous works showed feasibility to recover cobalt from spent lithium-ion batteries [15], neodymium from hard disk drives [16], indium from liquid crystal displays [17] and copper from mobile PCB [18].

CO_2 is one of the most used supercritical solvents because it has moderate critical conditions (Tc = 31.1 °C and Pc = 7.38 MPa), it is cheap and environmentally acceptable, it has high mass diffusivity, it is gaseous at room temperature and pressure (easy recovery and solute separation), it can be recycled and reused, and it can be modified with solvents. However, the main disadvantage of supercritical CO_2 is its low polarity, and it is often necessary to add modifiers [19]. The efficiency of metal recovery using supercritical CO_2 is because it has a similar gas-like mass transfer rate and a liquid-like solubility, whose high diffusivity and low viscosity facilitate its penetration into porous solid matrices and the extraction of solutes by transferring to the liquid phase. However, the application of supercritical technology research on metal extraction is mostly concentrated in the laboratory stage. The high cost of manufacturing high-temperature and high-pressure vessels for industrial production still limits the scale-up of this process [20].

Metals leached after hydrometallurgy techniques are further processed to produce the respective base metals. In the case of copper, electrowinning and electrorefining are used to produce high-purity copper [21]. Sivakumar et al. [22] achieved 89.1% copper recovery by electrowinning acid-leachate derived from fine ash PCB obtained by pyrometallurgy. Rajahalme et al. [23] demonstrated 92% copper recovery from PCB leachate with sulfuric acid with hydrogen peroxide using electrowinning. Baniasadi et al. [24] reported 75.8% copper recovery from PCB using an electrowinning process combined with bioleaching.

Different mechanical treatment steps can precede the hydrometallurgical and electro-obtaining process. Veit et al. [25] used the comminution, magnetic and electrostatic separation before acid leaching and electrometallurgical technique. The copper obtained by electrowinning is above 98% in most of the tests. Guimarães et al. [26] cut PCBs into pieces, ground them in a knife mill, and concentrated the metals with a pneumatic method before acid leaching. The copper had no impurities obtained after 15 h of electrolysis at 25 °C.

In a previous study, supercritical CO_2 and ethanol were used and approximately 70% of the polymers from cell PCBs were extracted at 170 °C and 7.5 MPa, and in the extracted liquid phase, organic compounds such as bisphenol A, 1,3-dimethylbenzene, and hexadecanamide were obtained [27]. Hsu et al. [28] demonstrated that the application of supercritical CO_2 with sulfuric acid and hydrogen peroxide improved copper leaching from PCBs due to the creation of morphological changes in the surface of PCBs. Additionally, the supercritical CO_2 with sulfuric acid promoted a process of induced crystallization of the polymers [28].

Using supercritical CO_2 in the presence of water, Sanyal et al. [29] achieved the delamination of PCBs scraps into copper foil, glass fiber, and polymeric portions. Xing and Zhang [30] identify the presence of the following compounds during using sub- and supercritical conditions during the treatment in the presence of water: phenol, 4-(1-methyl ethyl)-phenol, 2-bromo-phenol, 2-methyl-phenol, 2-methyl-benzofuran, and (Z)-9-octadecenamide. Therefore, the process of copper leaching under supercritical CO_2 with sulfuric acid and hydrogen peroxide has the potential to simultaneously extract copper from PCBs and other components from the polymeric portion during the process.

However, in the present literature, there is an absence of research involving copper electrowinning from solutions obtained by supercritical leaching of PCB. The electrowinning was applied by Bertuol et al. [31] to recover cobalt from a solution obtained by the supercritical leaching of discarded cell phone batteries and achieve a current efficiency

of 96% and a deposit with cobalt concentration of 99.5 wt%. These promising results motivate the application of electrowinning after the supercritical extraction of copper from PCBs. Furthermore, organic compounds can be extracted from the PCB polymeric matrix during leaching with supercritical CO_2, so it is important to verify their influence on Cu electrowinning. In this scope, the aim of this study was to study copper electrowinning of solutions extracted by supercritical fluids combined with cosolvents from the obsolete PCBs of obsolete mobile phones. In addition, this study determined the adequate conditions for copper electrowinning with a current efficiency close to 100%. It also determined at what concentration of the copper-containing solution it would no longer be possible to maintain this current efficiency.

2. Materials and Methods

2.1. Mechanical Processing

Waste PCBs used in this work were obtained by manual disassembly of discarded mobile phones. The PCBs were reduced into less than 2 mm diameter particle through a hammer mill (Tigre, A4 model, Itaquera, Brazil) with a 5 mm screen and knife mill (Rone, N-150 model, Carapicuíba, Brazil) with a 2 mm screen [18].

2.2. PCBs Characterization

The chemical composition of the comminuted PCBs was determined by energy-dispersive X-ray fluorescence spectrometry (model EDX-720, Shimadzu, Kyoto, Japan) under vacuum. The Cu present was quantified by leaching with aqua regia, using 5 g of comminuted sample obtained by quartering. The leaching conditions were a solid:liquid ratio of 1:50, temperature of 90 °C, stirring at ~600 rpm, for 60 min. The solution was separated from the solid material by filtration, and analysis was performed by flame atomic absorption spectrometry—FAAS (200 Series AA, Agilent Technologies, Santa Clara, CA, USA) [18].

2.3. Supercritical Leaching

The supercritical extraction system used is described in Calgaro et al. [18]. The comminuted PCBs and cosolvents were placed in a reactor constructed of 304 stainless steel and internally coated with Teflon. The reactor was jacketed, enabling temperature control using an ultra-thermostatic circulator bath (model Q214M2, Quimis, Diadema, Brazil). A flask containing a NaOH solution was connected after the extraction valve and the collecting flask to wash the CO_2 that was separated (under ambient conditions by expansion) from the extracted solution. CO_2 (99.5%) was provided to the pressurized system, and the required pressure was achieved using a high-pressure syringe pump (model 500D, Teledyne ISCO). The supercritical extractions were performed at 35 °C and 7.5 MPa, which was slightly above the minimum pressure and temperature required for CO_2 to behave as a supercritical fluid [32]. Sulfuric acid (H_2SO_4, 2.5 M) and hydrogen peroxide (H_2O_2, 30%) were used as the leaching and oxidizing agents, respectively, and/or as cosolvents. They were added at a solid:liquid ratio of 1:20, where from 0 to 25% of the solution volume was H_2O_2, and the rest was H_2SO_4. Cu contained in solutions was determined by F-AAS. These conditions were chosen based on the best results obtained by Calgaro et al. [18].

2.4. Copper Electrowinning

The electrowinning tests were performed in a cell describe in Figure 1. The cell was composed by two distinct compartments separated by an anionic membrane (PCacid 60/PCA Ion Exchange Membranes GmbH, Heusweiler, Germany) with 25 cm^2. The electric current was supplied by a source (PS-7000, iCEL Manaus, Manaus, Brazil). This cell was used based on a previous study by Bertuol et al. [33], which the applied membrane promoted an increase in current efficiency through the separation of anodic and cathodic reactions and reduction in pH variations. An anode of platinum/iridium cover with

titanium with 10 cm^2 of area was inserted into the anodic compartment where sodium sulfate solution (1 M) was circulated. A polished stainless-steel cathode with 9 cm^2 of area was inserted into the cathodic compartment where cathodic solutions (synthetic: $CuSO_4$ 15 g/L; supercritical leachate) were circulated. Centrifuge pumps were used to circulate the solutions in the compartments with flow rates of 1.4 L/min and 2.2 L/min for the anodic and cathodic solutions, respectively.

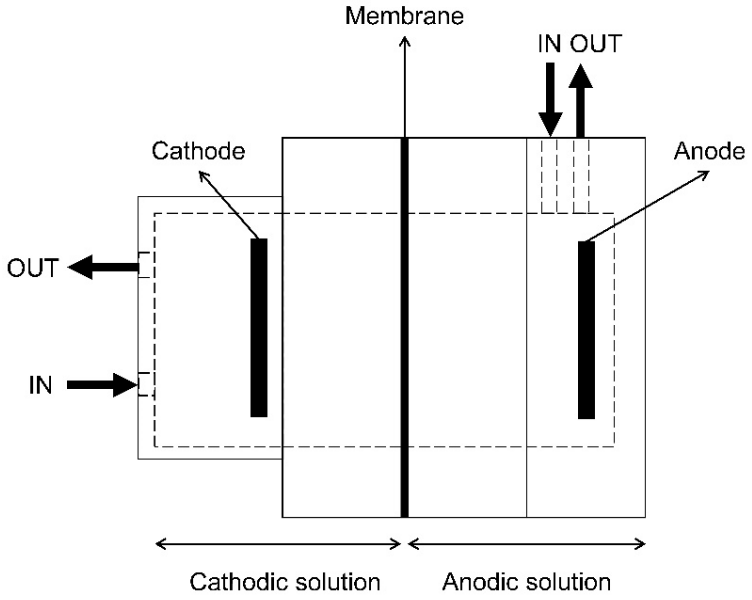


Figure 1. Two compartment electrowinning cell.

The experiments were performed at pH 4.0 in both solutions based on the best results obtained by Bertuol et al. [33]. The pH was monitored and adjusted during the experiments with NaOH (1 M, 2 M and 4 M) and H_2SO_4 (4 M) at room temperature. The tests to determine the ideal current density for electrowinning were performed for 2 h. After determination, the tests were performed for 5 h.

The cathode was weighted before and after each test, and the deposit mass was used to calculate current efficiency. The usable cathode area was determined before the experiments. Cathodic solutions concentrations were determined by F-AAS. The current efficiency was calculated using Faraday's equation (Equation (1)) and the experimental deposit mass obtained by electrowinning (Equation (2)) [34]. In Equation (1), "M_{Cu}" is equal to 63.55 g/mol and "n" is equal to 2, for the case of copper, and "F" is the Faraday constant equal to 96,485.34 C/mol. After the ideal current was determined, the test was carried out at the best current for 5 h and 5 h 30 min to evaluated current efficiency according to the reduction in copper concentration in the solution determined by F-AAS.

$$m_{theoretical} = \frac{M_{Cu}\, i\, t}{n\, F} \quad (1)$$

$$Current\ efficiency\ (\%) = \frac{m_{deposit}}{m_{theoretical}} 100 \quad (2)$$

2.5. Experiments Using Synthetic Solution

Electrowinning tests were used to evaluate the performance of copper electrodeposition from the leachate obtained with supercritical CO_2 and cosolvents (H_2SO_4 and H_2O_2). Thus, the possibility of copper recovery was verified by this methodology. A synthetic solution of $CuSO_4$ (15 g/L) was used to determine the adequate current density for copper recovery based on the resulted current efficiency. The current density range of 370–540 A/m^2 was investigated according to Schilesinger and Paunovic [34] for copper

electrowinning in traditional processes. The concentration of 15 g/L was used due to the maximum recovery obtained in the supercritical copper extraction from PCBs (15.46 g/L) at the following conditions: 1:20 solid/liquid ratio; H_2SO_4 (2.5 M) + 20% H_2O_2; 20 min; 35 °C; 7.5 MPa. The use of 20 min of acid leaching with supercritical CO2 was the optimal time for recovery of Cu, which is 9 times faster than conventional leaching. More details are available in Calgaro et al. [18].

2.6. Experiments Using Supercritical Leachate

The leachate used for electrowinning was obtained by supercritical leaching in the conditions of higher percentage of copper extraction: 1:20 solid/liquid ratio; H_2SO_4 (2.5 M) + 20% H_2O_2; 20 min; 35 °C; 7.5 MPa. The software Hydra/Meduza [35] was used to determine the pH where copper precipitation begins. Through Hydra/Meduza [35], it was possible to select the adequate pH for electrowinning. NaOH (2 M and 4 M) was added to supercritical leachate until the pH was 4.0 and copper concentration was determined by F-AAS. When pH reached 4.0, a filtration was carried out to remove the precipitate, which was further dried and characterized by X-ray Diffraction (XRD, Shimadzu, Kyoto, Japan, Miniflex 300) at 30 KV and 10 mA using a Cu Kα source.

Copper was obtained by electrowinning from the supercritical leachate in 5 h experiments, and the current efficiency was calculated based on the mass of copper removed from the solution and determined by F-AAS. The metallic deposit was characterized by energy-dispersive X-ray fluorescence (EDS-XRF; Bruker, Billerica, MA, USA, S8 Tiger), scanning electron microscopy and energy-dispersive spectroscopy (SEM-EDS, Philips, Amsterdam, The Netherlands, XL-30 FEG). A deposit fraction (0.3072 g) was dissolved in nitric acid at 60 °C for 1 h under 600 rpm. The copper present in the solution was determined by F-AAS.

3. Results and Discussion

3.1. PCBs Characterization

Figure 2 shows the chemical composition of the comminuted PCBs, which was obtained by analysis using energy-dispersive X-ray fluorescence spectrometry (XRF), from which it can be seen that Cu was the metal present in the greatest mass percentage (31.95 wt%). In addition, the Ag (0.34 wt%) detected by XRF indicates the possibility of recovering precious metals from this waste in future studies.

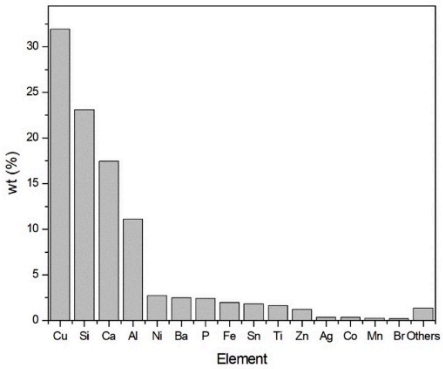


Figure 2. Chemical composition of PCB specimen determined by XRF.

The average Cu weight percentage determined from the aqua regia leaching in time of 60 min was 35.78%, which was close to the value obtained by XRF (31.95 wt%). This value (35.78 wt% of Cu) resulting from aqua regia leaching were considered as the total amounts of the metal in the mobile phone PCBs.

3.2. Supercritical Leachate

Based on a previous study using supercritical CO_2 with H_2SO_4 and H_2O_2 as cosolvents, it obtained kinetics nine times faster for copper recovery in comparison to acid leaching at

atmospheric pressure [18]. The optimum time for supercritical extraction was 20 min. That is interesting in terms of the process, since with a faster extraction, kinetics could recover a greater amount of copper and the size of the equipment also could be reduced, despite the power consumption required to maintain the CO_2 in supercritical conditions. The use of H_2O_2 as cosolvent along with H_2SO_4 was significant for copper supercritical leaching: 20% of H_2O_2 and H_2SO_4 2.5 M resulted in the highest yield for copper extraction (88.79%) [18]. The chemicals reactions involved in the Cu supercritical extraction are similar to chemical reactions involved in the Cu leaching at atmospheric pressure (Equation (3)) because the CO_2 should not take part in the reaction; it just assists in mass transfer and helps in the separation of the polymer layers from the copper [18]. Supercritical CO_2 possibly weakened the structure of PCBs, and it created pores, cracks, and delamination, thus improving the solvent transport to the buried metal interfaces [28]. In addition, supercritical CO_2 may cause partial dissolution of the constituent polymers of the PCBs, which makes the leached solution different from that obtained by the conventional method at atmospheric pressure. Therefore, five supercritical extractions were performed at the highest yield conditions to constitute the supercritical leachate for electrowinning.

$$Cu + H_2SO_4 + H_2O_2 \rightarrow CuSO_4 + 2H_2O \quad (3)$$

3.3. Copper Electrowinning

3.3.1. Copper Electrowinning from Synthetic Solutions

Copper deposits were obtained from synthetic solutions (15 g/L $CuSO_4$) to determine the optimum current density as a function of the current efficiency in four different current densities based on the information present in the literature for the traditional copper electrowinning process [34]. The current efficiency in different current densities is displayed in Figure 3. It can be observed that at 250, 370 and 450 A/m^2, the current efficiencies were above 94%. However, at 540 A/m^2, the current efficiency presented the lowest value (approximately 87%). The highest current efficiency (99.3%) was obtained at 250 A/m^2. Therefore, the current density of 250 A/m^2 was adopted in the further experiments.

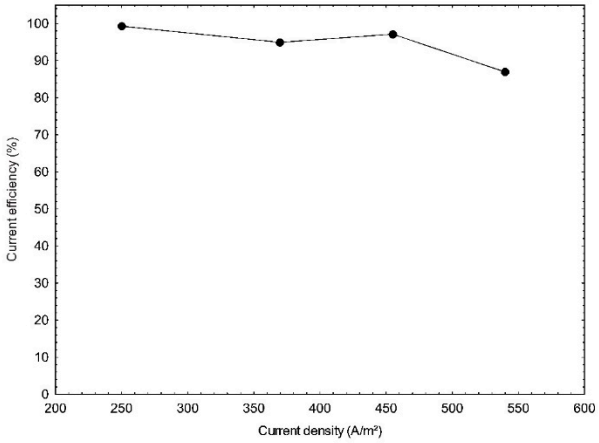


Figure 3. Determination of ideal current density. Conditions: pH = 4; room temperature; 120 min; $CuSO_4$ synthetic solution.

After the first 120 min of electrowinning at 250 A/m^2 using the synthetic solution, three sequential electrowinning tests using the same solution were performed. The first test (Figure 4) was performed in 300 min. The second test had 330 min (Figure 5) and the third was performed in 300 min (Figure 6), adding up to 930 min of electrowinning. This test sequence was realized aiming to remove the maximum copper from the solution.

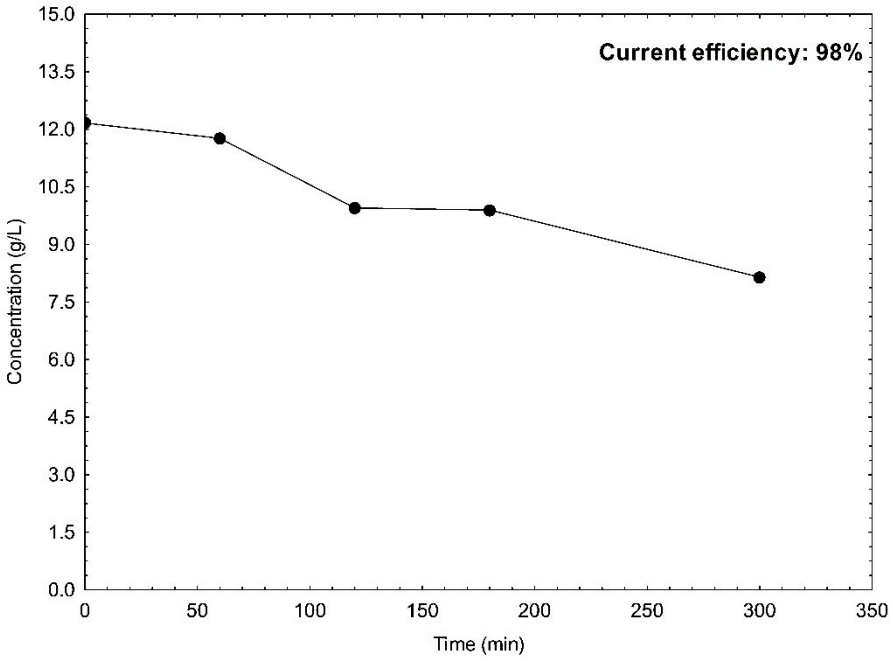


Figure 4. Variation of copper concentration as a function of electrowinning time at 250 A/m^2, pH = 4 and room temperature for the $CuSO_4$ synthetic solution.

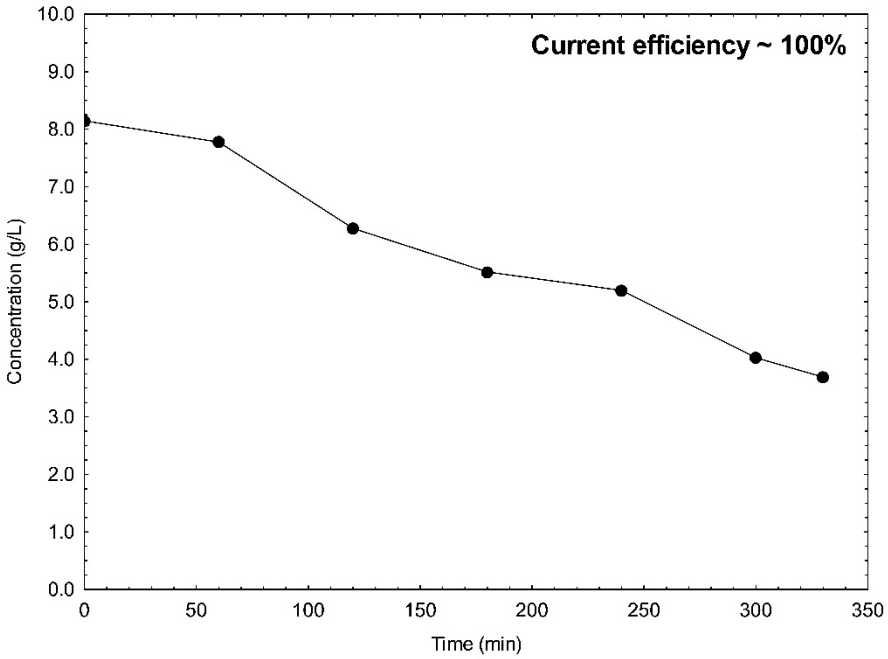


Figure 5. Variation of copper concentration as a function of electrowinning time in the sequential test, presented in Figure 3, at 250 A/m^2, pH = 4 and room temperature for the $CuSO_4$ synthetic solution.

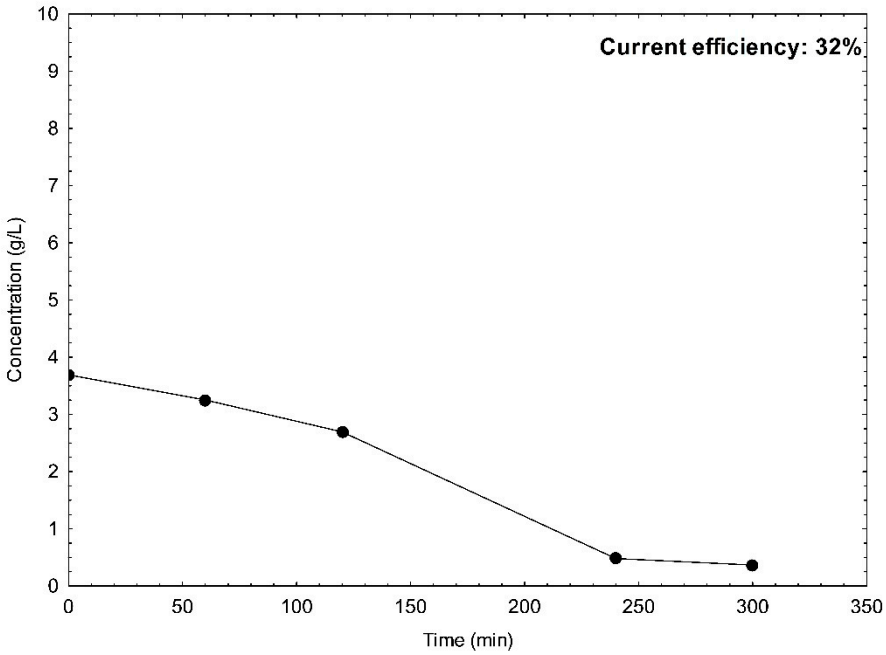


Figure 6. Variation of copper concentration as a function of electrowinning time in the sequential test, presented in Figure 4, at 250 A/m^2, pH = 4 and room temperature for the $CuSO_4$ synthetic solution.

From Figures 4 and 5, it can be observed that copper concentration was progressively reduced along with time, and current efficiencies were maintained approximately at 100%. Those current efficiencies were in agreement with the efficiency obtained in 120 min. In addition to the reduction in copper concentration to 3.69 g/L at 630 min, the current efficiency was maintained at 100% approximately.

However, in Figure 6, it can be observed that even though copper concentration was reduced to below 0.4 g/L, the current efficiency obtained from the deposit mass was only 32%. This can be attributed to a decrease in copper ions in solution as result of the reduction of copper ion to metallic copper. Therefore, the ion transport toward the cathode was a limit factor, and it favored another electrochemical semi-reaction: the reduction of H^+ to form H_2 [36].

The decrease in copper concentration in solution to 0.4 g/L was possibly associated with the formation of other less soluble copper compounds in aqueous solution after 240 min. The formation of a precipitate containing Cu can be evidenced by the formation of the metallic Cu deposit that was of significantly lower mass than that corresponding to the reduction in the concentration of copper in the solution. The cathodic pH, which was reduced before 240 min and was adjusted every 30 min, increased to 5.85, and the solution became turbid. The pH continued to increase with time, reaching 11.26 in 270 min and 11.85 in 300 min, and the copper concentration was reduced to 2.69 approximately (Figure 5). Therefore, it was not possible to obtain metallic copper, since other less soluble compounds were formed and precipitated.

The diagram obtained by Hydra/Meduza software (v1, Stockholm, Sweden) (Figure 7) identified the following copper forms: $Cu_3SO_4(OH)_{4(c)}$ between pH 4.8 and 5.4, $Cu_4SO_4(OH)_{6(c)}$ between pH 5.6 and 7.5, $Cu(OH)_2$ from pH 5.9, and $CuO_{(cr)}$ from pH 7. The formation of these compounds in these values of pH can justify the decreased of copper in solution even without metallic copper deposition. The increased pH in the cathodic solution was possibly associated with the reduction in copper ions in solution, taking place over other predominantly electro-chemical reactions, as hydrogen evolution.

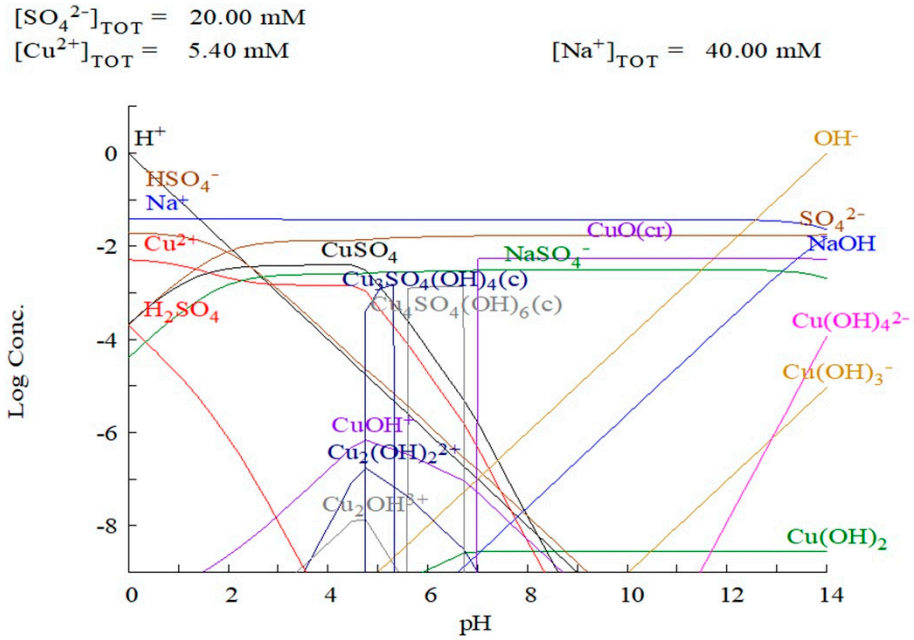


Figure 7. Chemical speciation diagram for copper, generated from Hydra-Medusa software.

The rise of pH solution from 4.0 to 5.85 and then to 11.85 was driven by the reduction in copper concentration in solution, favoring the hydrogen evolution [37]. Furthermore, Haghighi et al. [38] reported copper precipitation in leachates with sulfuric acid at pH 5.5 and 25 °C, which is a factor that also justified the results obtained in solution with copper concentration below 2.69 g/L, where the pH was 5.85 and it was not possible to obtain metallic copper by electrowinning anymore. Experimentally, we observed the solution cloudiness in pH above 5.85, which can be attributed to copper precipitation and the formation of identified compounds. Thus, considering the concentration of 12.16 g/L of copper present in Figure 4, at the zero electro-obtaining time, after 750 min of electro-obtaining, the concentration of 2.69 g/L of copper in solution was reached and a recovery of 78% of the copper contained in the solution in the form of solid deposit was obtained.

3.3.2. Purification of Supercritical Leachate

When the leachate pH was adjusted by NaOH addition to 4.0, a precipitate was formed. This precipitate was further analyzed by XRD along with chemical equilibrium diagrams for copper and other metals identified in the sample. The chemical speciation diagrams generated for copper, iron and aluminum (Figures 7–9) were obtained using Hydra-Medusa software. From Figure 7, it is observed that copper does not tend to precipitate at pH values below 4, it is precipitated only from pH higher than 4.8 in the form of $Cu_3SO_4(OH)_4(c)$. Meanwhile, iron, with the oxidation state of 3+ tends to precipitate from pH around 2 in the form of $Fe_2O_3(cr)$ (Figure 8) and aluminum tends to precipitate from a pH around 3 in the form of $AlOHSO_4(c)$ (Figure 9).

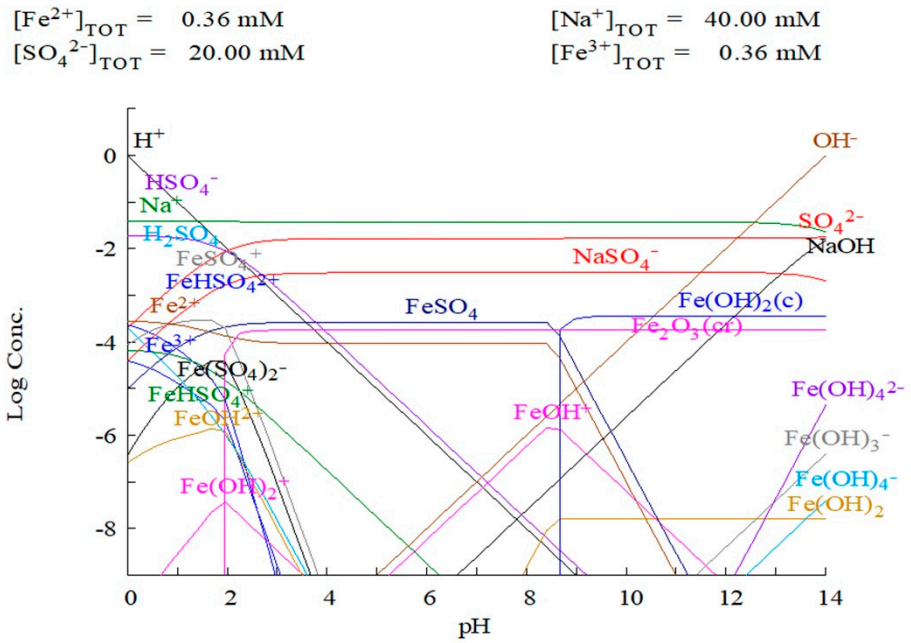


Figure 8. Chemical speciation diagram for iron, generated from Hydra-Medusa software.

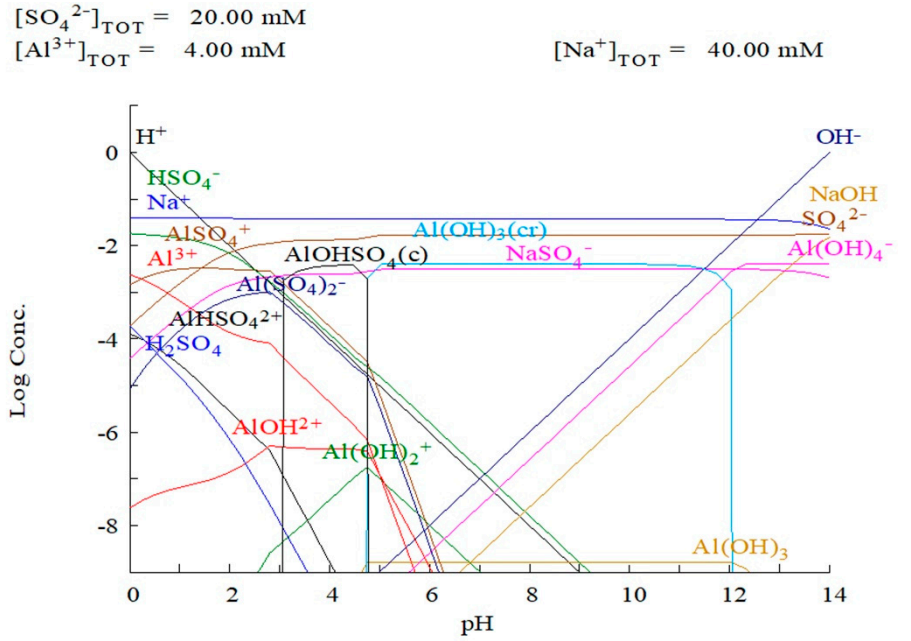


Figure 9. Chemical speciation diagram for aluminum, generated from Hydra-Medusa software.

Figure 10 present the XRD diffractogram, where there was an absence of copper. However, only iron and aluminum structures were identified. Therefore, copper was not present in the precipitate, which is interesting for the conditions used in electrowinning. In addition, the precipitation of iron and aluminum up to pH 4 also contributed to purifying the leachate and consequently to the purity of the electro-obtained copper deposit.

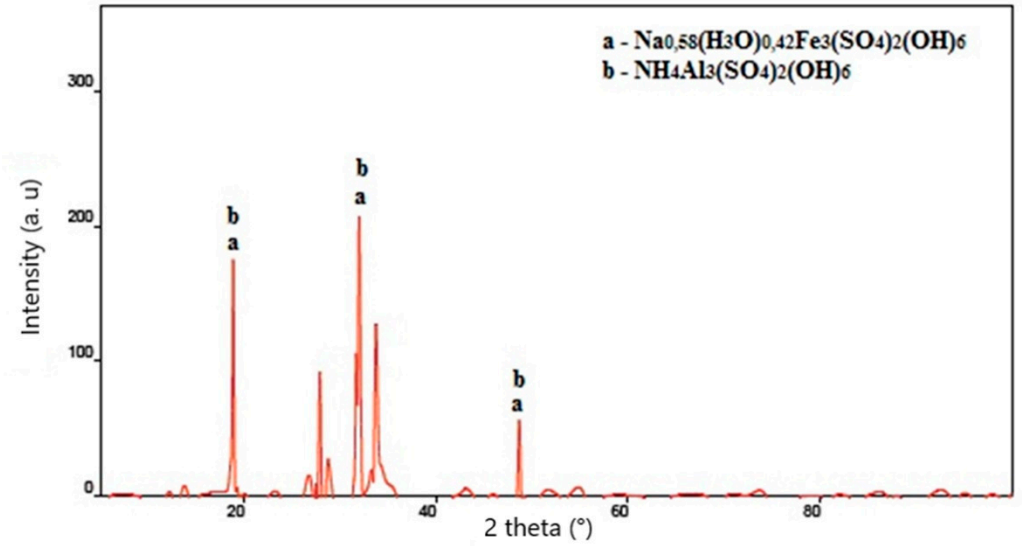


Figure 10. Precipitate XRD diffractogram formed at pH = 4 in the supercritical leachate.

3.3.3. Copper Electrowinning from Supercritical Leachate

Figure 11 presents the variation of copper concentration during the electrowinning tests using the supercritical leachate. The initial copper concentration in the beginning was 5.11 g/L, which was below the 15.46 g/L obtained by supercritical extraction. This is associated to the addition of NaOH (2 M and 4 M) to correct the pH to 4.0, which diluted the leachate.

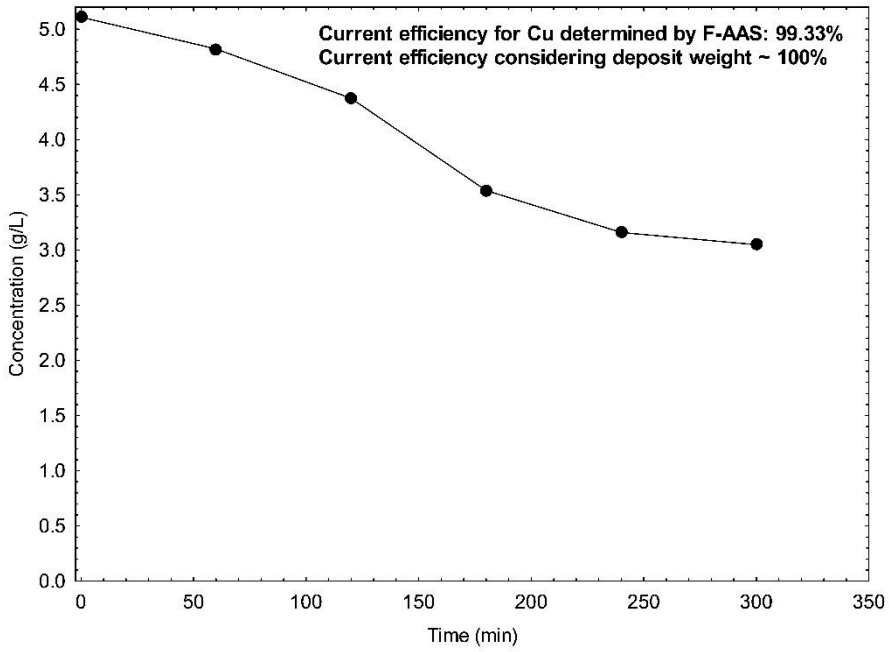


Figure 11. Variation of copper in the supercritical leachate with electrowinning time. Conditions: 250 A/m^2; pH = 4; room temperature (25 °C).

The current efficiency determined by the mass of copper deposited was 99.33%. This result demonstrated that the conditions tested with synthetic solutions could be applied to supercritical leachate. The current density of 250 A/m^2 selected based on the experiments carried out with synthetic solution also achieved current efficiency near 100% for copper recovery.

The copper deposit was analyzed to determine its purity since PCBs had other metals in the composition. Nitric acid leaching was performed using a deposit fraction, and it was further analyzed by F-AAS. The results showed 95.97% of copper in the deposit. Additionally, FXR was performed in the deposit (Table 1), identifying 92.77% of copper and other elements in small quantities, such as iron and zinc, and other impurities (mainly Na) due to deposit handling and the absence of water washing after electrowinning. The metals present in small amounts, such as Zn, Fe and Ni were leached out together with the copper from the PCBs and also deposited by electrowinning.

Table 1. Copper deposit XRF obtained by electrowinning of supercritical leachate.

Element	Si	Fe	Cu	Zn	Ni	Impurities
Weight percentage (%)	0.05	0.06	92.77	0.11	0.04	6.97

Deposit surface was evaluated by SEM-EDS. A fraction of the deposit was analyzed in three points and the whole area. The results obtained in all SEM images were similar. In Figure 12a, it can be observed that the deposit is homogeneous with some pores in the surface. The EDS (Figure 12b) showed the presence of copper in the deposit along with aluminum and iron. Although aluminum and iron precipitated during the pH increase to 4 of the supercritically leached solution, possibly these metals did not precipitate completely, because aluminum can precipitate as $Al(OH)_3(cr)$ only from pH = 4.8 and iron as $Fe(OH)_2(c)$ from pH = 8.7. It was not possible to further increase the initial pH of the solution, since from pH = 4.8, the precipitation of copper as $Cu_3SO_4(OH)_4(c)$ already starts (Figure 7).

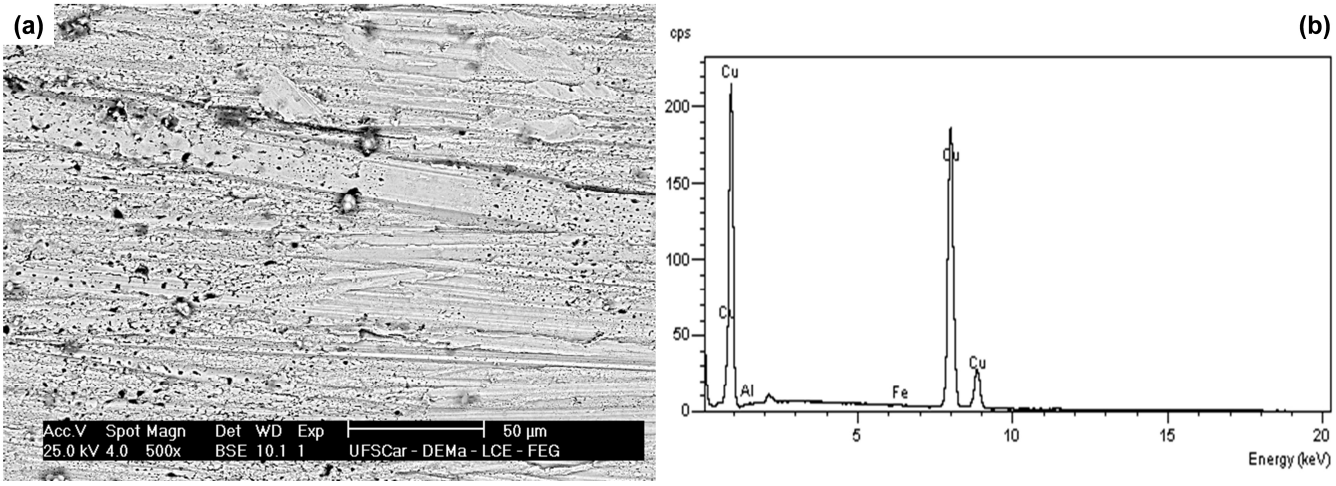


Figure 12. (**a**) Copper deposit micrography obtained by electrowinning of supercritical leachate; (**b**) Deposit EDS spectrum (**b**).

Therefore, it was possible to recover metallic cooper by leaching PCBs with supercritical CO_2 and cosolvents (H_2SO_4 and H_2O_2) combined with electrowinning. The current efficiency was near 100%, and the deposit obtained was composed of 95.77% copper (determined by F-AAS). When considering the initial concentration of the leached solution shown in Figure 11 of 5.11 g/L of copper at time zero, after 300 min of electro-obtaining, the concentration in solution reduces to 3.05 g/L of Cu, totaling electro-obtaining of 40.3% of the copper in the form of a metallic deposit.

In the literature, several studies reported the recovery of copper from PBCBs applying electrowinning as one of the processes or the main process. Fogarasi et al. [39] used two reactors in series, one for leaching and the other for high-purity copper electrowinning (99.04%). The current efficiency obtained was 63.84% for copper electrowinning from waste PCBs using a current density of 40 A/m^2 and 0.37 M of $FeCl_3$ for 12 h. Kasper et al. [40] applied various mechanical techniques to concentrate copper from cell phone PCBs, which

was followed by leaching with aqua regia and electrowinning. The copper obtained had purity similar to the result presented in this work (>95%) at 600 A/m^2 current density and 90 min.

However, through this study from the synthetic solution with a current density of 250 A/m^2, it was possible to obtain 78% of Cu contained in the solution, after 750 min of electrowinning, in the form of a metallic deposit. Applying these conditions to the supercritically leached solution of the PCBs obtained 40% of the copper that was in the solution in the form of a metallic deposit with 95.97% purity after 300 min of electrowinning. If the electro-obtaining of the leached solution was extended for more time, this percentage of recovery would increase; however, when reaching the concentration of 2.69 g/L, the cathodic solution should go through some concentration process to avoid the pH increase and copper precipitation observed in the synthetic solution.

Figure 13 shows the mass balance for obtaining copper as a metallic deposit from the copper supercritical leaching step. In this balance, to obtain the amount of copper present in the solution leached with supercritical CO_2 and the cosolvents H_2SO_4 and H_2O_2, the percentage of copper contained in the PCBs (35.78 wt%) determined by aqua regia was considered, and the percentage of 88.79% of copper was recovered under the following conditions: solid:liquid ratio of 1:20, H_2SO_4 (2.5 M) and 20% H_2O_2, during 20 min of extraction at 35 °C and 7.5 MPa. In the electrowinning step, it was considered that copper was electro-obtained from the leached solution until a copper concentration of 2.69 g/L was reached (minimum threshold concentration determined with the synthetic $CuSO_4$ solution). The mass of copper corresponding to the concentration of 2.69 g/L was determined with the total volume of the leaching solution for the mass of 1000 kg of PCBS in the solid:liquid ratio of 1 g:20 mL. The weight of copper obtained in the form of a deposit represented 95.97% of its weight (purity percentage determined by F-AAS), the remaining weight was impurities (other metals such as Fe and Al). Thus, from Figure 13, it can be inferred that from 1000 kg of comminuted PCBs, 263.89 kg of copper could be obtained in the form of metallic deposit containing only 11.08 kg of impurities, which represents 73.75% of the total amount of copper present in 1000 kg of already comminuted PCBs.

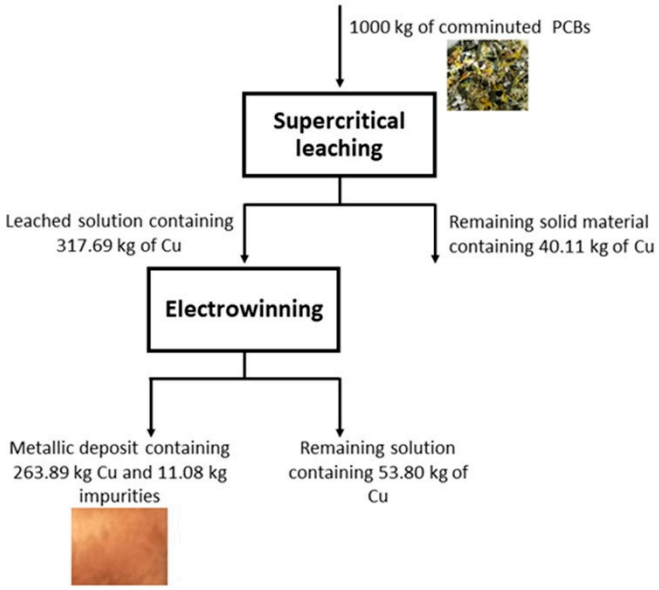


Figure 13. Mass balance for copper recovery from supercritical leaching to electrowinning under the best conditions.

4. Conclusions

The electrowinning experiments in a two-compartment cell with the synthetic $CuSO_4$ solution showed that the current density of 250 A/m^2 led to the highest current efficiency for copper deposition among the tested current densities (250, 370, 455, and 540 A/m^2).

The tests performed with the synthetic solution at a current density of 250 A/m^2 and pH 4 allowed the recovery of 78% of the copper contained in the solution after 750 min of electrowinning. The concentration of 2.69 g/L of copper in the solution was limiting for the process, because from this concentration, the cathodic reaction of H_2 release was favored and the pH of the solution increased to over 5.85, causing the copper to precipitate.

From the study with the synthetic solution containing copper, the conditions of current density of 250 A/m^2, pH 4, and room temperature (25 °C) for the electrowinning of the supercritically leached solution from PCBs were determined. The electrowinning of the leached solution with supercritical CO_2 and the cosolvents H_2SO_4 and H_2O_2 enabled the recovery of copper in the form of a metallic deposit. This metallic deposit was made up of approximately 96% copper and was obtained with a current efficiency of approximately 99%. After 300 min of electrowinning, it was possible to recover 40% of the copper contained in a solution with a concentration of 5.11 g/L copper in the form of metallic deposit. Therefore, electrowinning performed after a supercritical extraction of copper from PCBs can be an alternative to obtain copper in the metallic form with high purity because from the best determined conditions, it would be possible to recover approximately 74% of the copper contained in comminuted PCBs in the form of metallic deposit. The copper that would remain in the solution after the electrowinning could go through additional purification steps or even be obtained as a precipitate and used for other purposes. In addition to the process steps studied for the recovery of copper that comprised the supercritical extraction followed by electrowinning, intermediate steps can be employed for the separation of other metals that were extracted along with copper, indicating the importance of the sequence of the study of this recycling route.

Author Contributions: C.O.C.: investigation, methodology, writing—original draft and editing; M.D.C.R.d.S.: investigation and methodology, writing—original draft and editing; E.H.T.: investigation, conceptualization, supervision, Writing—reviewing; D.A.B.: investigation, conceptualization, supervision, writing—reviewing. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to thank CAPES (Brazilian Agency for Improvement of Graduate Personnel) and CNPq (National Council of Scientific and Technological Development) for financial support (Project: 06/2011–Casadinho/Procad), and would like to thank FAPERGS (Foundation for Research Support of the State of Rio Grande do Sul) for master's scholarship and financial support (FAPERGS/CAPES 014/2012).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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