

Development of Innovative and Sustainable Methodologies Applied To the Recovery of Copper in Integrated Circuit Boards

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Abstract

The high demand for electronic devices is increasing drastically, raising concerns about the generation of spent printed circuit boards, which contain a significant amount of semi-precious and precious metals. The so-called digital and energy transition creates additional stress in the raw materials supply chain, requiring innovative approaches to extract critical raw materials from waste.

The present research focuses on studying the physical and hydrometallurgy process to extract copper from integrated circuit boards. So far, it was possible to perform the physical process in order to obtain a sample mainly composed of metals to proceed with the hydrometallurgical process. The results from the hydrometallurgical process demonstrate that selective leaching is achievable. Preliminary studies indicate that it is possible to extract more than 70% of Cu.

Keywords: printed circuit boards, copper extraction, electronic waste, green leaching

1. Introduction

In 2024, the estimated global electronic waste (e-waste) is 63.3 million metric tons, and it is expected to reach 74.7 million by 2030 [1]. By 2050, the demand for several metals will increase - 35% copper (Cu), 45% silicon (Si), 100% nickel (Ni), and 3.5% lithium (Li), among others. To comply with the global net carbon emissions goals, it will be necessary to build more than 50 Li mines, 60 Ni mines, and 17 Cu mines [2]. Therefore, the increasing demand for electronic devices containing precious metals and other valuable materials has raised concerns about the supply chain, the sustainability of mining practices, and the safe dismantling and disposal of e-waste [3].

Recycling printed circuit boards (PCBs) allows for the recovery of semi-precious and precious metals, reducing the need for extracting and processing primary resources. This conserves natural resources and reduces the environmental impact of mining and processing raw materials. As visualized in Table 1, PCBs are present in all electronic devices, representing 30.3% of mobile phones, 11.6% of televisions and 13.7% of laptops [4,5]. Additionally, Cu and iron (Fe) are the most representative metals in e-waste, along with aluminium (Al), Ni and lead (Pb).

Table 1 Average weight, percentage of PCBs, semi-precious metal content in e-waste and precious metal content of PCBs.

	Average weight (kg/unit)	Percentage of PCBs (%)	Semi-precious metal content in e-waste (%)					Precious metal content of PCB (mg/ kg)			Reference
			Cu	Fe	Al	Ni	Pb	Au	Ag	Pd	
Mobile phone	0.125	30.3	13	5	1	0.1	0.3	1500	3800	300	[4,6]
Television	16.8	11.6	10	28	10	0.3	1.0	250	500	-	
Laptop	2.46	13.7	22	37	0.3	0.3-2	3.7	240	570	150	[4,5,7,8]

Regarding their values as waste, semi-precious and precious metals are potential resource to develop novel products with a high impact on society [9].

This work highlights the potential for Cu extraction. In Figure 1, illustrates the PCBs processing and the hydrometallurgy process that have been studied to extract the required metal.

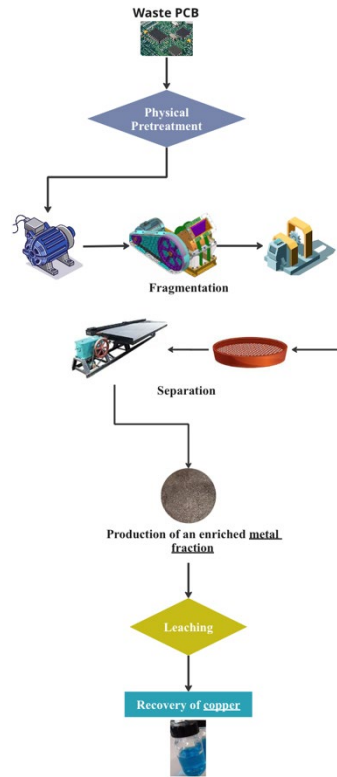


Figure 1 E-waste processing and metallurgical process.

The focus of the present research was divided in two phases. In the first phase, PCBs pre-treatment was performed, involving physical methods that rely on mechanical techniques. Disassembly and mechanical processes are required to liberate and separate the metallic parts from PCBs to deliver a metallic-enriched product to the subsequent hydrometallurgy processes [9]. Following dismantling, the next stage involved size reduction, where crushers and grinders equipment were used. Then, a shaking table was utilized to separate materials with different densities due to their different relative movements against gravitational forces. In the second phase, the hydrometallurgy process was executed, where the selective leaching using appropriate lixiviants for Cu extraction was studied.

2. Materials and Procedure

2.1 Materials

The PCBs samples (52 0500 mg/kg of Cu, 85 000 mg/kg of Fe, 12 350 mg/kg of Ni, 62 047 mg/kg of Zn) were obtained from ARG company. Hydrogen peroxide 30% brought from VWR Chemicals (batch 22A254127). Sulfuric acid 95-98% (batch 0002307670) purchased from PanReac AppliChem (ITW Reagents). Nitric acid 70% pure, in water purchased from Thermo Scientific.

2.2 Equipment

Samples separator (PT 100), grinding mill and sieves from Retsch company. Shredder acquired from Erdwich company. Overhead stirrer from Hei-TORQUE 100. Chemical analysis of Cu, Fe, Zn and Ni were performed by atomic absorption in an Analytik Jena ZEEnit70 equipment. X-ray fluorescence (XFR) from Oxford instruments.

2.3 Procedure

2.3.1 Samples preparation

In Figure 2, the schematic process for obtaining the required samples to perform the leaching experiments is presented. First, the PCBs samples were transformed into small pieces using a guillotine. After using the shredder, a total of 10 kg of sample was obtained. Then, out of the 10 kg, 8 kg were subjected to a grinding mill to liberate the plastic matrix and achieve a significant size reduction. The samples with sizes between 2.36/0.106 mm were separated using a shaking table (based on density). This allowed for the separation of concentrates from the middle and tailings samples. The concentrated samples, which are mainly composed of metal fractions, were then subjected to XFR analysis.

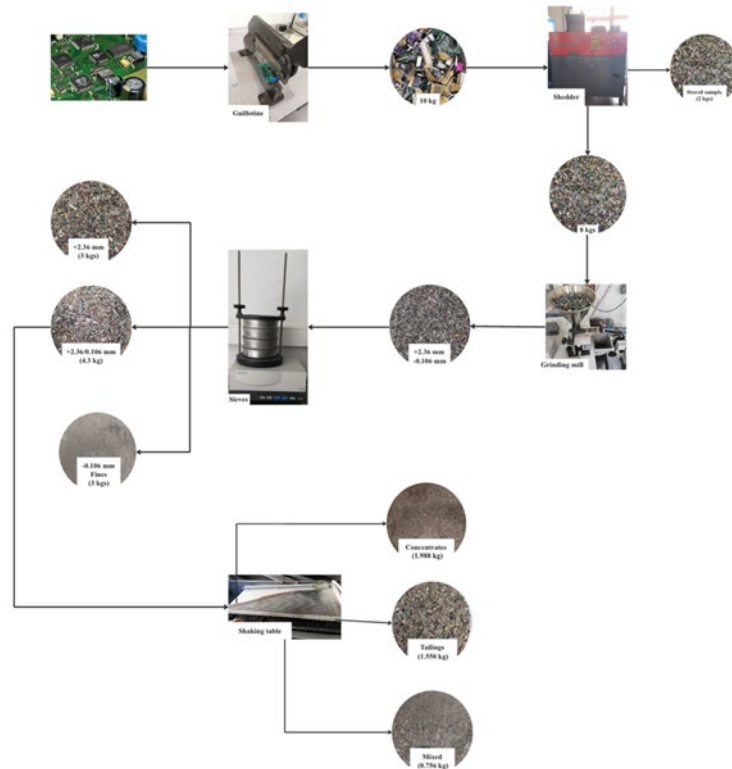


Figure 2 Schematic representation of the samples preparation.

2.3.2 PCBs Leaching using sulphuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂)

Four experiments were conducted using H₂SO₄ at different concentrations - 1, 2, 3 and 4M – as visualized in Table with a Solid/Liquid (S/L) ratio of 1/10. Initially, H₂SO₄ was added to approximately 25g of PCBs residue, followed by addition of 15 V% H₂O₂ (30%) in relation to the H₂SO₄ concentration.

Table 2 PCBs leaching using H₂SO₄ and H₂O₂.

Experiment	Ratio (S/L)	Stirring speed (rpm)	Reaction time (h)	H ₂ SO ₄ (M)	H ₂ O ₂ (M)
1	1/10	300	4	1	4.4
2				2	
3				3	
4				4	

3. Results and Discussion

3.1 Samples preparation

The XFR analysis was performed to define the chemical assay of feed material and the following size fractions: (+)2.36 mm, between 2.36 and 0.106 mm (2.36/0.106mm), and less than (-)0.106mm. In the fractions with a size +2.36 mm, a significant presence of plastics materials was observed (Figure 3).

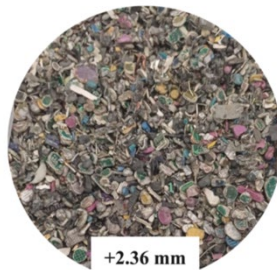


Figure 3 Fraction with a size +2.36 mm.

The fraction 2.36/0.106 mm was submitted a gravity concentration method using a Wilfley shaking table (Figure 4), to separate particles of different specific gravity, in order to obtain a final sample containing only heavy particles - metals without any plastic material – light particles. This method allows for the separation of three types of samples: concentrates (high density), the middles (intermediate density) and the tailings (low density). As expected, the middles and tailings samples contained a lower metal content because they are primarily composed of plastic materials. The concentrates contain a significant amount of Cu (43%) because it is mainly used as electric current conductor [10]. This is followed by Fe (9%), Sn (4.1%), Zn (3.8%), Pb (2.9%), Ni (0.8%) and Ag (0.081%) as illustrated in Table 3. Consequently, this specific fraction was selected for use in the subsequent experiments.

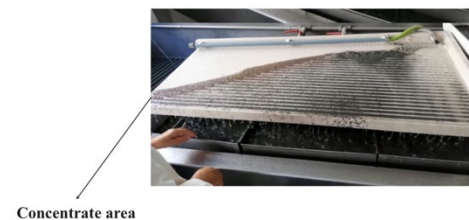


Figure 4 Shaking table.

Table 3 XFR analysis of the concentrates.

Wilfley Shaking Table	Cu	Fe	Zn	Pb	Ni	As	Sn	Ag	Au
	%								
Concentrates	43	9	3.8	2.9	0.8	0.42	4.1	0.081	n.a

3.1.2 PCBs Leaching using sulphuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂)

Initially, a sample characterization was performed using aqua regia in order to determine the approximate content of Cu in the samples.

Following, the main target of these experiments was to study the ideal concentrations for the selective extraction of metals. Therefore, the purpose of the 1st step was to extract Fe by varying the H₂SO₄ concentration. The 2nd step consisted of extracting Cu by applying the previous procedure in order to determine the concentration that allows the highest Cu extraction rate. In addition, the differences in Cu leaching efficiency were studied by varying the concentration of H₂SO₄ from 1 to 4M for 4 hours of leaching time. In Figure 5, is represented the schematic procedure, applied for Fe and Cu extraction. Additionally, for the performed experiments it was possible to observe that a green solution was obtained from the 1st step and blue leaching solution from the 2nd step, which suggests that Fe was obtained in 1st step and Cu in 2nd step.

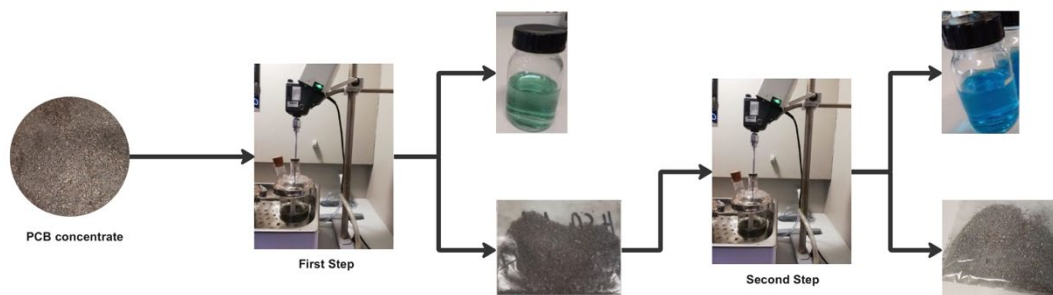


Figure 5 Schematic leaching procedure.

As depicted in Table 4, for experiment 1 it was possible to extract 51% of Fe for the 1st step. As expected, a higher content of Cu and Zn was extracted in the 2nd step, 40% and 33%. These are low extraction efficiencies when compared with the total quantity in the feed.

For the experiment 2 a significant amount of Fe was extracted after the 1st step, 76%. Although, for the 2nd step, a low content of the remaining Cu, Zn and Ni was achieved, 48%, 54% and 23%.

In experiment 3, 70% of Fe was extracted after the 1st step, thus, with a significant reduction in other metals such as Cu, Zn and Ni, with extraction rates of 44%, 69% and 41%. The 2nd step allowed the extraction of 72% of the remaining Cu and a lower content of Zn and Ni, 37% and 18%.

In the last experiment, only 28% of Cu was extracted in the 1st step, with higher contents of Fe, Zn and Ni, 87%, 59% and 44%. In the 2nd step, 25% of Ni was extracted, despite the extraction of 60% of Zn, only 40% of the remaining Cu was extracted. Therefore, these results indicate that the concentration at 4M of H₂SO₄ does not allow for a higher extraction of Cu compared to the other concentrations of H₂SO₄, especially when compared with experiment 3, where was obtained the highest Fe and Cu extraction.

Table 4 AAS analysis of the leaching solution from the 1st and 2nd step for the experiment 1, 2, 3 and 4.

Experiment	Step	Extraction, %				
		Metal	Cu	Fe	Ni	Zn
1	1 st		2	51	14	8
	2 nd		40	3	11	33
2	1 st		8	76	25	18
	2 nd		48	14	23	54
3	1 st		44	70	41	69
	2 nd		72	6	18	37
4	1 st		28	87	44	59
	2 nd		40	20	25	60

The results metal content of the residues produced during the leaching tests is portrayed in Table 5. The experiment that evidenced better extraction rate was experiment 3. For the 1st step, there is a significant Cu amount in the PCBs residue, it only changed from 43% to 32%. In addition, it occurred a higher modification for Fe (9% to 2.9%), Zn (3.8% and 0.70%) and Ni (0.8% to 0.33%). The 2nd step, the obtained values using XRF are in accordance with AAS, as it detected only 2.7% of Cu in the residue.

Table 5 XRF analysis of the PCBs (feed) sample and the final residue from the 1st and 2nd step.

Sample	Cu	Fe	Zn	Pb	Ni	Sn	Ag	Au
	%							
PCBs	43	9	3.8	2.9	0.8	4.1	0.081	-
Residue from 1 st Step	32	2.9	0.70	3.9	0.33	1.7	0.16	0.10*
Residue from 2 nd Step	2.7	2	0.12	2.5	0.24	0.79	0.15	-

*value detected only in one measure

4. Conclusion

The applied physical process made it possible to obtain an enriched-metal product composed by semi-precious and precious metals.

PCBs residue is composed of a highly heterogenous material, requiring two steps in order to obtain a final pregnant solution enriched in one type of metal. The performed leaching indicates that selective leaching can be feasible to extract different metals from PCBs. Until the moment, using a concentration of 3M of H₂SO₄ and 4.4M of H₂O₂, with a S/L ration of 1/10 and a stirring speed of 300 rpm for 4h of leaching time, it was possible to extract 70% of Fe after the 1st and 72% of the remaining Cu from the 2nd step. Although, more studies need to be performed in order to increase the Cu recuperation after the 2nd step. Towards this end, as future work, it will be studied the influence of H₂SO₄ and H₂O₂ concentrations, along with various parameters such as S/L ratio, stirring speed and leaching time. Additionally, triplicates for the optimized operating conditions need to be performed.

This is a promising process for the industry, because it is efficient, easy to operate and control, and allows a selective extraction of Cu. Therefore, it is vital to foster sustainable and innovative ways to recycle PCBs to mitigate its impact on the environment and people's health, respecting the principles of a linear economy and overcoming the limitations of traditional supply chains. Additionally, it is critical to develop different pathways for the extraction of metals, encouraging the development of new methodologies to take profit from the existing metals. Additionally, H₂SO₄ is considered less harmful to the environment than other reagents such as cyanide. Also, it does not present the same acute health risks to workers and is less prone to accidental spills or exposure incidents.

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