Copper Extraction from Waste Printed Circuit Boards

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Abstract: The quick development in the electronics industry has allowed an increase in e-waste generation; which cannot be disposed of a traditional way due mainly to the content of hazardous and polluting elements. This has given rise to a social and environmental problem in terms of handling and end disposal. Further, these wastes have become a source of heavy metals, posing challenges for recovering them and development of efficient and environmentally responsible extraction methods. An extraction process to copper extraction from printed circuit boards has been proposed. This method consists on a size reduction, concentration by magnetic and electrostatic separation, leaching of copper in sulfuric acid solution with hydrogen peroxide and oxygen and electrowinning and copper oxychloride precipitation. Concentrates with up to 63% copper and 85% maximum recovery were obtained. Copper extraction over 95% in 100 mL of 2.3 M sulfuric acid solution with 18 mL of hydrogen peroxide during 60 min of process was achieved. Metallic copper with purity over 99% and copper oxychloride as a value-added product also were obtained. This process represents a viable alternative for the recovery of copper from e-waste, contributing to management and end disposal problems, closure of the metals cycle and global sustainable development.

Key words: Electronic waste, copper recycling, copper oxychloride, solid waste management, sustainable development.

1. Introduction

Electrical and electronic equipment (EEE), especially those related to telecommunications and information technology, have presented a quick development in recent decades and its usage time is reduced increasingly [1], proportionally, increased the amount of EEE that are discarded in the world. Thus the flow of waste electrical and electronic equipment (WEEE) is growing, being the components of waste faster growth. Between 20 and 50 million tons are annually generated in the world, with an annual increase of 3%-5% [2]. The enormous volume of WEEE generated today is an emerging environmental problem and a challenge in terms of storage/disposal and solid waste management [3]. First, they content hazardous elements [4], and second, it is not possible to dispose them in the traditional way. Due to simple handwork for metal extraction, large amounts of

poisonous gas are released, and wastewater containing toxic substances is discharged into environment [5]. Improper disposal of WEEE can create both health and environmental hazards [6]. They are even considered as “the largest toxic waste problem of the century XXI” [7].

The printed circuit boards (PCB) are the base of the electronics industry, being an essential part of almost all EEE [8]. The PCB contain up to 20% by weight of Cu [2]. Given its varied metallic composition, various methods have been proposed for the recovery of different metals. Mechanical processes are usually used as a pretreatment step previous to the application of metallurgical techniques, which consist on dismantling, removal of hazardous elements, size reduction and concentration of the metal fraction. These processes are performed in order to release the metal bonded or encapsulated with resin and ceramics. Physical methods such as magnetic and electrostatic separation, flotation, pneumatic separation, have been studied for concentration [9-11].

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PCBs are also processed by incineration and smelting that allows effective recovery of copper and an amount of precious metals. However, the process has the disadvantages of producing some contaminants and a slag with a complex metal content which presents complications for the final extraction [12]. In this process, the copper is oxidized, which facilitates subsequent dissolution in non-oxidizing acid environments.

Recent researches study the extraction of metals from PCB through bioleaching processes, especially for gold and copper [13, 14]. Copper extractions of the 93%, 86% and 100% are achieved [15, 16], in different microbial environments and times of process to 280 days.

Hydrometallurgical process are a promising option for use in the treatment of waste PCB. Compared to pyrometallurgy, hydrometallurgical processes offer relatively low capital cost and are particularly suitable for small-scale installations. An added advantage is flexibility, offering a possibility for selective extraction of base and precious metals of interest in waste PCB [2]. As the metals present in the waste PCB are in elemental form or in alloys, it is necessary an oxidative leaching process for the effective extraction of the metals of interest. Leaching techniques of precious metals consist of processes using cyanide, halides, thiourea and thiosulfate [17]. Different processes have been studied in aqueous solution using sulfuric acid [18] and hydrogen peroxide as oxidant [8, 19, 20], chlorine [21, 22], nitric acid and solvent extraction [12, 23], solutions of ammonium sulfate, ammonium [24, 25], by mediated electrochemical oxidation [26, 27], 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim] HSO₄) [28], for the extraction of copper. These processes studied have disadvantages in terms of recovery and some use unsuitable reagents for scaling at the industrial level.

The development and implementation of a process for recovering copper and/or byproducts of copper from electronic waste are presented in this paper. It was

performed using physical processes together with chemical techniques used in extractive metallurgy. The process was proposed as a viable option for copper recovery from WEEE.

2. Materials and Experiments

The process shown in the flowchart of Fig. 1 was developed for copper extraction from electronic waste with a minimum emission of pollutants species.

4,300 g of printed circuit boards of different types and trademark, as a representative sample, were processed. At each stage of the process three samples were taken for chemical analysis. Samples were dissolved in aqua regia with a subsequent filtration process. The copper content in the solution was measured by atomic adsorption equipment with the AA Spectrometer iCE 300 Series Thermo Scientific.

Manual size reduction using a cutter for cutting of metal sheets to obtain maximum particle size 2 cm was made. Then, the material was passed once for a pulverizer Braun Direct Driven Pulverizer UD32, which works at 400 rpm. The material was reduced in size in the pulverizer by abrasion due to friction between the particles themselves and the plates of the pulverizer. The aim was to obtain a maximum particle size of 2 mm to achieve release of 99% of copper according Zhang and Forssberg [29].

Fig. 1 Process flowchart.

The material was classified into three particle sizes: $T_1 < 0.3 \text{ mm}$, $0.3 \text{ mm} < T_2 < 0.85 \text{ mm}$ and $0.85 \text{ mm} < T_3 < 2 \text{ mm}$. Size grading was carried out using sieves of the series ASTM-E-11 by Ro-Tap. A concentration process was performed by magnetic and electrostatic separation to remove some species of little importance and obtain a suitable material for good extractive metallurgical process. Each size fraction was processed in the magnetic separator, yielding a stream of magnetic and other of non-magnetic materials. The non-magnetic stream was subsequently processed on the electrostatic separator. Non-conductive and other conductive material fractions were obtained. The fraction conductive material, enriched in metals, corresponds to final concentrate.

To test the magnetic separator Carpc Model MIH(13)111-5 Laboratory High-Intensity Induced-Roll Magnetic Separator was used operated at a roll speed between 120 rpm and 125 rpm and vibration control in 50 units, with a current of 1.0 A. A Carpc Laboratory Electrostatic High-Tension Separator was used in the electrostatic separation with an intensity of 20 kV DC, 10 kV DC and roll rotation speed of 50 rpm.

2.1 Copper Leaching

Copper leaching in aqueous sulfuric acid with hydrogen peroxide as oxidizing agent, by magnetic stirring at room temperature and atmospheric pressure was studied. The $0.3 \text{ mm} < C_2 < 0.85 \text{ mm}$ fraction of the concentrate obtained was taken.

A sequential experimentation starting with a completely randomized 2^{4-1} fractional factorial design with 4 replicates at the center, and subsequent central composite design, were made in order to determine operating conditions. The effect of the concentration of sulfuric acid (A), volume of hydrogen peroxide added to the solution (B) amount of solids (C) and agitation speed (D) was studied. The response variable (Y) for the experiment was the percentage of copper extraction.

An amount of solids of 4 g and 8 g, which is equivalent to 40 kg/m^3 and 80 kg/m^3 was initially studied. The factors and levels studied in the leaching process are summarized in Table 1 and the design matrix is shown in the Table 2. Experimental tests were performed in a solution of 100 mL in a glass beaker of 250 mL capacity on a RCT basic Ikamag® Safety control magnetic stir plate during a time of 60 min. The design and analysis of experiments were performed with the help of the Minitab® 16 software.

Copper extraction for each experimental test was calculated taking into account the copper content in the solid sample and the amount of copper in the solution according to the Eq. (1).

$$\text{Extraction (\%)} = \frac{\text{Copper in solution}}{\text{Copper in the solid sample}} * 100 \quad (1)$$

The amount of copper in solution was measured by complexometric titration using Titriplex® III 0.01 M.

2.2 Obtaining Copper and Copper Oxychloride

Copper oxide (II) (CuO) was precipitated from the copper sulphate solution by adding sodium hydroxide

Table 1 Factors and levels of the experimental design.

Factors	Levels		
	Low	Base	High
A: Sulfuric acid concentration (M)	1	1.5	2
B: Hydrogen peroxide added (mL/100 mL)	5	10	15
C: Solids (g/100 mL)	4	6	8
D: Agitation speed (rpm)	350	400	450

Table 2 Experimental results.

# test	A	B	C	D	Extraction (%)
1	1	5	4	350	45.67
2	2	15	8	450	77.96
3	1.5	10	6	400	69.30
4	1	15	4	450	87.88
5	1.5	10	6	400	67.20
6	1	5	8	450	29.92
7	1.5	10	6	400	69.30
8	1	15	8	350	68.98
9	2	15	4	350	94.49
10	2	5	8	350	37.33
11	1.5	10	6	400	69.09
12	2	5	4	450	66.46

and with subsequent heating to a maximum temperature of 90 °C. The precipitate was filtered and dried at room temperature. The CuO was dissolved in 1M hydrochloric acid solution at room temperature. The solution of CuCl₂ obtained was neutralized by adding sodium hydroxide in order to obtain a precipitate of copper oxychloride.

For the electrowinning process, an electrolysis cell, with acrylic and capacity of 270 cm³ was constructed. A steel plate 304 with a total area of 36 cm² was used as the cathode. Lead plates were used for the anodes. For this process, the richest copper solutions obtained in the leaching tests were taken. The test was performed with a fixed current density of 250 A/m² supplied by a *BK PRECISION* High Current DC Regulated Power Supply Model 1796.

3. Results

The results obtained in the concentration process by means of magnetic and electrostatic separation are summarized in the Fig. 2. It also shows the copper content in each of the three particle size fractions. An initial concentration of copper of 23.15% in the fraction less than 2 mm was calculated.

As a result of magnetic and electrostatic separation, three copper concentrates of 44%, 63% and 58% for T₁, T₂ and T₃ fractions respectively were obtained. It is possible to work with two different size fractions, a size fraction less than 0.3 mm and a size fraction greater than 0.3 mm and less than 2 mm. The copper recovery was 63%, 73% and 85% for size fractions T₁, T₂ and T₃, respectively, which shows that the concentration for magnetic and electrostatic separation is a good alternative for the recovery of copper from PCBs. However it is necessary to improve the process to obtain higher recoveries.

3.1 Copper Leaching

The results of the experimental tests carried out according to the design of experiments are shown in the Table 2.

The first-order model in coded variables, Eq. (2), was obtained. This model presents a lack of fit according to an analysis of variance (P-value = 0.019 < 0.05).

$$\text{Extraction (\%)} = 41.53 + 10.94A + 3.75B - 5.02C \quad (2)$$

A second order design, more specifically a central composite design was performed to model the curve. For this new experimental design a constant stirring speed was maintained at a value of 400 rpm. The experimental design matrix and results are shown in the Table 3.

From an analysis of variance for the experimental results, the second-order model of Eq. (3) was determined. It has a $R^2 = 81.00\%$ and $R_{adj}^2 = 77.44\%$, which is satisfactory to accept the model.

$$\text{Extraction (\%)} = -14.331 + 13.804A + 8.916B - 0.244B^2 \quad (3)$$

This model fits the data satisfactorily. Better extraction of copper achieved in the experimental region is 95.2% at a concentration of 2.32 M sulfuric acid and a volume of 18 mL of hydrogen peroxide.

3.2 Precipitation

Copper hydroxide (II) is precipitated from the copper sulphate solution by neutralization by adding sodium hydroxide to the solution as the reaction (4).

M: magnetic, NC: non conductive, C: conductive

Fig. 2 Results of physical processes.

Table 3 Central composite design results.

# Test	A	B	C	Extraction (%)
1	1	5	4	45.67
2	2	15	8	77.96
3	1.5	10	6	69.30
4	1	15	4	87.88
5	1.5	10	6	67.20
6	1	5	8	29.92
7	1.5	10	6	69.30
8	1	15	8	68.98
9	2	15	4	94.49
10	2	5	8	37.33
11	1.5	10	6	69.09
12	2	5	4	66.46
13	1.5	10	2.73	92.30
14	1.5	10	6	71.40
15	2.32	10	6	87.35
16	1.5	10	9.27	62.93
17	1.5	10	6	71.40
18	1.5	1.835	6	20.58
19	0.68	10	6	57.75
20	1.5	18.17	6	93.23

Fig. 3 Diffractogram of the precipitate.

The solution with $\text{Cu}(\text{OH})_2$ precipitated was heated to obtain the most stable copper oxide (II) (CuO). The precipitate was filtered and allowed to dry at room temperature. CuO was dissolved in 1 M hydrochloric acid solution at room temperature in order to obtain the copper chloride (II) according to Eq. (5).

The CuCl_2 solution was neutralized by adding sodium hydroxide in order to copper oxychloride obtaining, according to Eq. (6).

Finally, filtration and drying were conducted at room

temperature to obtain the desired product. An analysis of X-ray diffraction shown in Fig. 3 confirms that indeed copper oxychloride was obtained in the process described above. Atacamite and paratacamite are common form minerals as the copper oxychloride is found in nature [30].

3.3 Copper Electrowinning

The copper deposit obtained was subjected to XRF analysis. Average copper content of 99.3%, which is a good percentage and shows the selectivity of the process developed.

3.4 Copper Leaching with O_2 as Oxidant Agent

A copper leaching test was performed, using the same sample as in the previous process, using O_2 as an oxidant. The test was done in a glass beaker of 600 mL with 200 mL of 2.32 M sulfuric acid solution and 8 g of sample on a RCT basic IKAMAG® safety control magnetic stirrer for 24 h. The process was conducted with a stirring speed of 400 rpm, room temperature and injection of oxygen (O_2). It was found that after 18 h of process a copper extraction of 41.59% is achieved, and after 24 h, an extraction of 55.44% is achieved. This process is actually performed slower than using hydrogen peroxide due to the low solubility of gaseous oxygen in the water [31]. The decision to work with one or another process lies in economic and technological aspects.

4. Conclusions

The physical processes of magnetic and electrostatic concentration are shown to be effective in the recycling process and represent an excellent alternative since it does not cause pollution. An average recovery of 79% was obtained.

The copper leaching step yielded a solution rich in copper sulfate suitable for the subsequent extraction of copper. Higher copper extraction was achieved at 95% in 100 mL of 2.32 M sulfuric acid solution with 18 mL of hydrogen peroxide for 60 min. An extraction of

55.44% was also obtained after 24 h of operation in a 2.32 M sulfuric acid solution with O₂ as oxidant.

Unrefined copper with a purity of 99% by electrowinning can be obtained, this being a technique that does not generate large effluent since the solutions are recirculated to the copper leaching. Copper oxychloride, a byproduct of copper with added value that can be directly used as a fungicide for the control of pests in different crops is also obtained.

It is clear then the applicability of mineral processing techniques to separate metal fractions, ceramics and polymers of PCB and recover copper by extractive metallurgical techniques as an solution to the problem of disposal of WEEE and it is also friendly to the environment, thus contributing to the closing of the cycle of metals and sustainable development.

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