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RECOVERY OF COPPER FROM PRINTED CIRCUIT BOARD OF MOBILE PHONE SCRAP[1]

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Abstract

The printed circuit board (PCB) scrap from electronic devices, which has become increasingly abundant, has attracted attention both from an environmental perspective, with regard to the toxicity of certain components, and an economic aspect, pertaining to the presence of metals. With this aim, the present study aimed to recover copper available in PCBs of mobile phone scraps. These wastes contain large amounts of this element, particularly in the PCBs, where approximately 30% of the metal is found. Two routes were used comparatively in this study. The first used stages of mechanical processing (such as comminution as well as magnetic and electrostatic separation) combined with hydrometallurgy and electroplating. In the second route, a size-reduction step was employed followed by hydrometallurgy and electroplating. The results showed that both routes are efficient; at first, the use of mechanical processing steps allows a prior segregation of different materials and reduces the volume of leaching agent used; in addition, it reduces the quantities of wastewater generated. The second route has the advantage of lesser number of steps, with decreased power consumption and lower losses of material.
Key words: Recovery; Copper; Printed circuit board; Mobile phone.

RECUPERAÇÃO DE COBRE PROVENIENTE DE PLACAS DE CIRCUITO IMPRESSO DE SUCATAS DE TELEFONES CELULARES

Resumo

Cada vez mais abundantes as placas de circuito impresso (PCI) de sucatas de aparelhos eletroeletrônicos, tem despertado interesse pela toxicidade de alguns de seus componentes e pela presença de metais de interesse econômico. Dentro deste enfoque, este trabalho teve por objetivo a recuperação do cobre presente nas PCI's proveniente de sucatas de telefones celulares. Estes resíduos possuem uma grande quantidade deste elemento, podendo alcançar aproximadamente 30%. Neste estudo foram utilizadas, de forma comparativa, duas rotas, sendo que a primeira utilizou etapas de processamento mecânico (moagem, separação magnética e eletrostática) aliadas a hidrometalúrgia e eletrodeposição. Na segunda rota foi utilizada apenas uma etapa de cominuição, seguida de hidrometalurgia e eletrodeposição. Os resultados demonstraram que as duas rotas são eficientes, sendo que na primeira, a utilização de etapas de processamento mecânico possibilita uma segregação prévia de diversos materiais além de diminuir o volume de agente lixiviante, reduzindo geração de efluentes líquidos. Na segunda rota, tem-se a vantagem de um menor número de processos, com consumo menor de energia e com menores perdas de material.
Palavras- chaves: Recuperação; Cobre; Placas de circuito; Telefone celular.

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1 INTRODUCTION

Information presented by Gartner, an American company providing consulting services in information technology, indicates that, in 2009, worldwide sales of mobile phones exceeded 1.2 billion units. Further, they reported that, in Brazil, the number of handsets sold in 2009 reached 45.5 million units.(1) Some of these devices were sold to first-time users of mobile services, whereas others were sold to existing users who wanted to exchange defective or obsolete equipment for newer, more modern and sophisticated phones.

It is estimated that, currently, each user retains a single mobile device, on average, for 9 - 18 months; after this period, many units are forgotten in closets or discarded as household waste.(2) The main consequence of this high turnover of equipment is the large amount of scraps discarded annually, with resultant economic losses and environmental pollution.

A single mobile phone device contains more than 40 elements of the periodic table, including metals such as iron (Fe), aluminum (Al), copper (Cu), nickel (Ni), and tin (Sn), rare metals such as cobalt (Co), indium (In), and antimony (Sb), precious metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd),(3) and toxic and hazardous substances such as arsenic (As), lead (Pb), cadmium (Cd), bromine (Br), and others.(4) Most of these metals are concentrated in the printed circuit boards (PCBs).

The PCB of a mobile phone comprises, on average, between 30% and 35% of polymer, approximately 30% of oxides, and between 35% and 40% of metals.(5) Among the metallic components, 20–30% is made up of copper, 6–8% by ferrous metals, and approximately 5% of nickel, 2.5% of tin, 1.1% of lead, and 1.1% of zinc.(6) However, the percentages of some of these metals in the PCB may vary widely by model and year of manufacture.

The large amounts of copper present in PCBs of handsets have induced efforts aimed to assess the recovery of this metal. In this work, two routes were used to recover copper from the PCB of mobile phones. In Route 1, a combination of techniques for mechanical processing (such as comminution as well as magnetic and electrostatic separation) followed by hydrometallurgy and electrometallurgy were applied. However, Route 2 employed a comminution process (without separation processes), hydrometallurgy and electrometallurgy.

The techniques for mechanical processing are a good alternative to concentrate metals in a fraction and in other polymers and ceramics. Components of mechanical processing include: comminution, classification, and separation (based on differences in density, weight, texture, magnetic and electrical properties, etc.). These techniques have been successfully used by several authors such as Zhang and Forssberg,(7) Tenório et al.,(8) Veit et al.,(9,10) Duan et al.,(11) Lee et al.,(12) among others, with good results.

Frias et al.(13) studied alternatives to regenerate solutions used in the manufacture of PCBs of computers and recovery of metals, particularly copper. Regeneration was based on electrometallurgical techniques, while recovery of copper was made possible by hydrometallurgical techniques such as solvent extraction. Kinoshita et al.(14) used hydrometallurgical processes to recover metals from PCBs, chips, or industrial wastes and obtained a solution rich in nickel, with small amounts of copper and other copper-rich solutions, with virtually no impurities .

Veit et al.(9) used electrodeposition to recover copper present in PCBs of computers. The authors used mechanical processing (comminution, particle size, magnetic and electrostatic separation, etc.) to concentrate the bulk of the metal in a single fraction; thereafter the leachate was electrodeposited, thus obtaining an average recovery of 98% in most cases.

2 MATERIALS AND METHODS

Scraps of obsolete or defective mobile phones of various brands, models, and from different years of manufacturing, collected from stores and mobile service operators, were initially dismantled manually for the removal of PCBs.

After being removed from the apparatus, the PCBs had their metallic fraction assessed to verify the percentage of copper and other metals of interest in the material. From such characterization of the PCB, it was possible to devise strategies for the recovery of copper.

2.1 Characterization of Metallic Fraction of Printed Circuit Boards

To characterize the metallic fraction in the PCB, the following procedures were adopted:

- comminution of the PCB, to particle sizes less than 1 mm;
- leaching with aqua regia (HCl – HNO_3; ratio solid:liquid = 1:20), at 60 ºC, for 2 h; and
- characterization by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin–Elmer, model Optima 7300 DV).

2.2 Recovery of Copper

In this study, two routes for the recovery of copper present in PCBs of mobile phone scraps were tested.

In the first route, techniques of mechanical processing (such as comminution and magnetic and electrostatic separation) were used to obtain a concentrated fraction of copper; this was followed by hydrometallurgy and electroplating. In the second route, only comminution was used, as an initial stage, and was followed by electroplating and hydrometallurgy. It is evident that processes of comminution, hydrometallurgy, and electroplating are common to both routes of copper recovery.

2.2.1 Comminution

The PCBs were initially comminuted until they reached a particle size of less than 1 mm. Comminution was undertaken in a hammer mill for grinding to a coarser particle (particle size <10 mm), and a knife mill was used to grind the material into finer particles (particle size <1 mm).

2.2.2 Magnetic separation

The method of magnetic separation was intended to separate magnetic metals from the rest of material.

In this study, magnetic separation was conducted in a cross-belt magnetic separator using magnetic field intensities between 6000 and 6500 Gauss. To obtain a better result, the material was passed through the machine twice.

Following the stage of magnetic separation, the magnetic fraction was not sent by the electrostatic separator.

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2.2.3 Electrostatic Separation

Electrostatic separators are used to separate conductive and non-conductive materials. With regard to PCBs, the extreme difference between the electrical conductivity or specific electrical resistance between metals and non-metals ensures that metals become concentrated in the conductive fraction, whereas the rest of the materials (polymers and ceramics) separate into a non-conductive fraction.

The electrostatic separator used in this study was the model ES1010 from Equimag.

2.2.4 Hydrometallurgy

The material obtained in the conductive fraction (Route 1) following concentration or comminution (Route 2) was dissolved in aqua regia (with a ratio of solid:liquid = 1:20) at 60 ºC for 2 h.

In order to avoid dissolution of the cathode during the electrodeposition step, which occurs at the low pH of the extract obtained after the dissolution of the materials, the pH of the solution was raised to 7.

2.2.5 Electrodeposition

The recovery of copper was studied by applying the technique of electrodeposition. For this, a cell with a copper cathode and a platinum plate as anode was assembled as shown in Figure 1.

Figure 1: Electroplating cell.

Tests were performed by altering the electrodeposition current density as well as the duration of deposition. Following each current density and deposition-time interval tested, the cell was dismantled and the solutions stored for later evaluation.

Test conditions:

- current densities of 1 and 3 A/dm^2;
- ambient temperature (approximately 20 ºC);
- in a potentiostat (model PS 7000, ICEL of Manaus);
- the durations of tests ranged from 30, 60, 90, 120, to 180 min.

2.2.6 Chemical analysis

The percentages of metals in each of the fractions obtained during mechanical processing and the results obtained in the electrodeposition of copper (for each current density and deposition time) solutions were obtained by inductively coupled

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plasma optical emission spectrometry (ICP-OES), from Perkin–Elmer, model Optima 7300 DV.

3 RESULTS AND DISCUSSION

3.1 Characterization of Metallic Fraction of Printed Circuit Boards

The results obtained during characterization of the metallic fraction of PCBs (conductive fraction; presented in Table 1) indicate the presence of large amounts of metals of economic interest, such as copper, tin, aluminum, and precious metals (gold and silver); this implies that the activity of recycling these wastes is of greater economic interest. Further, the presence of metals hazardous to the environment, such as lead, makes the recycling process essential in order to protect the environment.

Information pertaining to specific percentage of copper in PCBs of mobile phones are rare; however, certain authors like Neira,(16) Hagelüken,(17) among others, have reported percentages of copper that range between 10% and 15% of the total weight of the device. This indicates a percentage between 25% and 45% of the weight of the plate. Thus, although the percentage of copper observed in PCBs during this study appears high, it is similar to those reported in other scientific papers.

Table 1: Metals presents in printed circuit boards of mobile phones

%	**Marks Mixed**
Aluminum	0.61
Copper	37.81
Lead	1.23
Iron	4.85
Tin	2.55
Nickel	2.54
Zinc	1.82
Silver	0.05
Gold	0.09
Total	**51.55**

3.2 Results of Recovery of Copper

3.2.1 Results obtained with the use of a route 1

Route 1 employed techniques of mechanical processing (such as comminution as well as magnetic and electrostatic separation) to obtain a fraction with the highest concentration of copper (conductive fraction). The results of this procedure are presented in Tables 2 and 3, while the graph shown in Figure 2 represents the concentrations of copper in solution following electrodeposition.

- *Magnetic separation* - The results of chemical analysis of metals in each of the magnetic fractions obtained are presented in Table 2.

  From these results, it can be concluded that iron was fully concentrated in the magnetic fraction because both non-magnetic fractions (data in the Table 3) showed very low levels of iron (<1% of the weight of the samples). This demonstrates the efficiency of the technique in separating ferrous metals from other materials. For nickel, although it is a magnetic material, a separation was not considered efficient, however; this was because high percentages of this metal were found in other fractions.

Table 2: Percentages of metals in magnetic fraction

%	Magnetic Fraction
Aluminum	0.04
Copper	2.12
Lead	0.88
Iron	59.17
Tin	0.54
Nickel	17.46
Zinc	0.14
Silver	0.07
Gold	0.07
Total	**80.49**

• *Electrostatic separation* - **Erro! Fonte de referência não encontrada.** presents results for samples obtained after electrostatic separation. It may be noted that most of the copper conductor was concentrated in the fraction and testifies to the efficiency of this technique in the concentration of this metal.
In addition, it is of interest that a very interesting content of nickel and zinc was present in the conductive fraction. Further, the presence of lead was more pronounced in the conductive fraction. As previously described, the iron content in these fractions was very low, and this shows that the magnetic separation was very efficient for recovery of this metal.

Table 3: Percentages of Metals in Conductive Fraction

%	Conductive Fraction
Aluminum	0.27
Copper	**65.22**
Lead	4.76
Iron	0.04
Tin	5.24
Nickel	3.54
Zinc	2.37
Silver	0.29
Gold	0.14
Total	**81.87**

Note that the sum of the percentage of analyzed metals was only 80%; this is attributed to the presence of non-conductive materials in the conductive fraction with metals. Further, one must consider the possibility that the amount of aqua regia digestion of the samples used (20:1), or the conditions used in the separation step may not have been sufficient for complete dissolution of some metals. Similarly, the presence of other metals, in addition to those determined in the analysis, may also have contributed to this phenomenon.
• *Analysis chemicals of the solutions after the electrodeposition* - Figure 2 presents results of chemical analysis of solutions, used in the electrodeposition of copper, that were obtained after employing mechanical processing techniques. The results show that the copper concentration varied with regard

to duration of current application. The current densities used were 1 and 3 A/dm^2.
The time 0 (zero) represents the concentration of copper from a concentrated fraction (conductive fraction) obtained during mechanical processing by digestion with aqua regia.
For a current density of 1 A/dm^2, the best result, in the lowest concentration of copper, was obtained with the duration of 180 min. This indicates that, after 180 min, 80.4% of copper in the solution was deposited or recovered at the cathode surface. With a current density of 3 A/dm^2, the best results for this condition were also obtained with a duration of 180 min, where 88% of copper present in solution was deposited on the cathode surface.

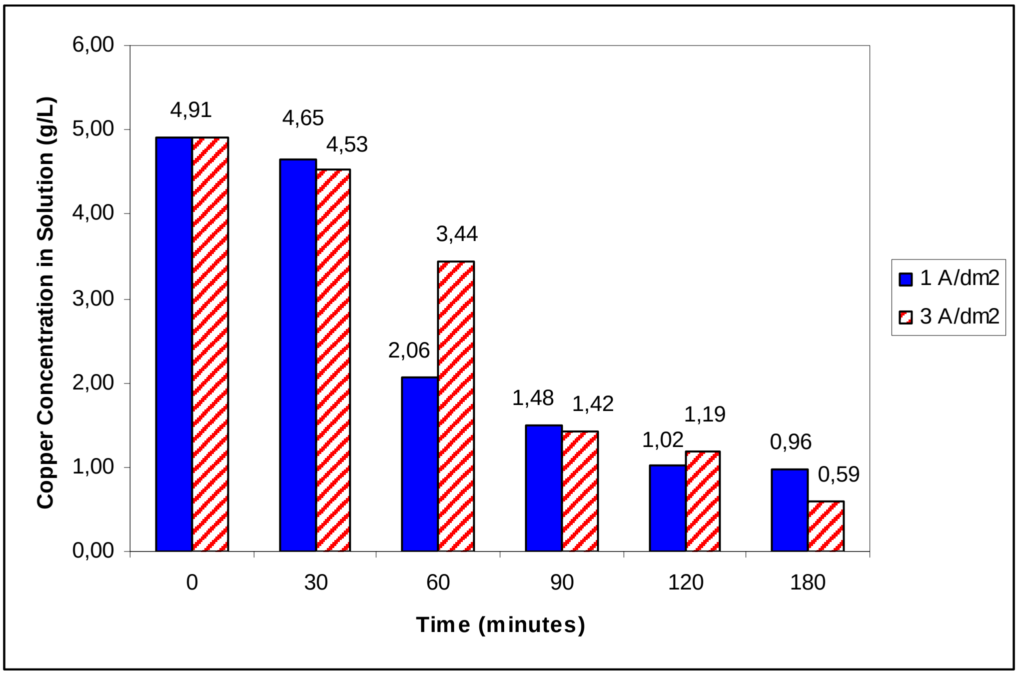

Figure 2: Variation of concentration of copper as a function of time for electroplating solutions obtained after using mechanical processing techniques.

The visual accompaniment to the process showed that when the amount of copper reached a certain level the deposited layer gave off again to the cathode, which means was not adhering, returning to the solution. This means that the amount of copper ions in the solution was too high for the size of the cathode used in the tests and therefore the percentage of recovery singe a maximum of 88% recovery. This could be solved through the use of a larger cathode.

3.2.2 Results Obtained With the Use of a Route 2

• *Analysis chemicals of the solutions after the electrodeposition* - In this route, solutions were obtained by comminution of the PCBs and without the use of mechanical processes for concentration of metals.
Figure 3 presents the results of chemical analysis in the solutions used in the electrodeposition of copper. The results show that copper concentration varied with duration of current application. The current densities used were 1 and 3 A/dm^2.

For a current density of 1 A/dm², the best result, in the lowest concentration of copper, was obtained with the duration of 90 min. This indicates that, after 90 min, 97.1% of copper in the solution was deposited or recovered at the cathode surface. At the current density of 3 A/dm², the best results for this condition were also obtained with the duration of 120 min, where 98.1% of copper present in solution was deposited on the cathode surface.

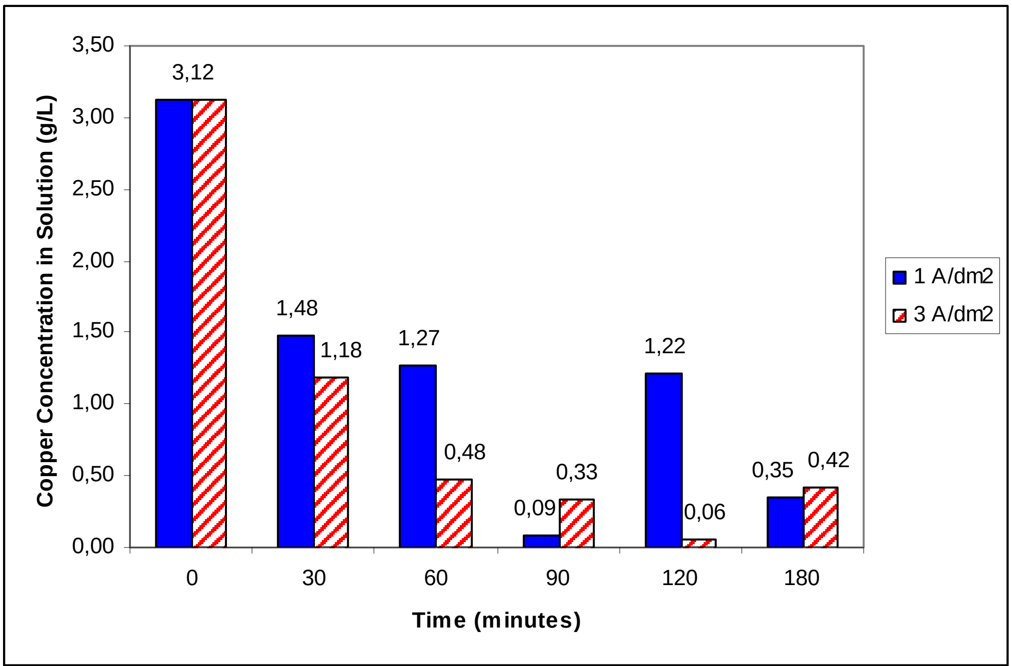

Figure 3: Variation of concentration of copper as a function of time for electroplating solutions.

4 CONCLUSIONS

Results from this study lead to the following conclusions:

- The metallic fraction of the PCB comprises large quantities of metals that are of economic interest, including copper, and small amounts of precious metals (gold and silver); this makes the recycling of this waste economically attractive. In the same fraction of metals, there are environmentally hazardous metals, such as lead, which makes the recycling process a necessity to protect the environment.
- The use of techniques of mechanical processing such as comminution and separation (particle size as well as magnetic and electrostatic) was effective in concentrations of copper.
- The results showed that the two routes are efficient, and at first, the use of mechanical processing steps allows a prior segregation of different materials; in addition, it reduces the volume of leaching agent required, and consequently, generates lesser quantities of wastewater.
- The second route has the advantage of having a smaller number of steps, with decreased power consumption, and lower losses of material.
- The concentrated fraction containing metals was dissolved in aqua regia and followed by electroplating; thus, it was possible to recover more than 88% of dissolved copper, on Route 1. Increasing the size of the cathode could raise this percentage of recovery.
- On the Route 2, the percentage of copper recovery reached 98%.

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