Abstract

Precious metal content is much higher in electronic waste than in most worldwide mines, and therefore recycling is encouraged and mostly performed by hydrometallurgical and pyrometallurgical processes. This paper addresses a combined mechanical bio-hydrometallurgical recycling process for extracting gold, copper and iron from printed circuit boards as a less expensive technology feasible for the Brazilian context. Metal recovery was carried out by combining physical, chemical and biological processes. The combined process proved to be technically viable; the microbiological route using adapted bacteria Acidithiobacillus ferrooxidans-LR is also eco-friendly. Mechanical processes recovered 97% of the iron by magnetic separation, the bioleaching extracted 99% of the copper, and 86% of the gold was recovered during the last stage of cyanidation.

Keywords: Printed circuit boards; Combined recycling route; Bioleaching; Hydrometallurgy.

1 INTRODUCTION

Recycling of WEEE warrants the extraction of metals from printed circuit boards (PCB) that have economic potential, due to the presence of metals such as copper, precious metals, and other metals that are considered critical [1]. Despite the well-known heterogeneity of PCB, copper is commonly found in greater quantities and, on average, reaches 20% by mass of typical personal computer’s PCBs [2].

Metals and/or metal compounds are recovered from PCBs at varying degrees of efficiency, depending on their value, and in the case of copper, which has lower market value when compared to precious metals, the extraction is justified by the concentration found, in addition to minimizing the extraction of non-renewable natural resources from primary sources [1,3]. Despite containing more than 90% of recyclable compounds, Brazil does not have recycling plants and a structured management system even after the approval of the Brazil’s Solid Waste National Policy that establishes the obligation of e-waste reverse logistic [4]. A fraction of the e-waste goes to informal markets; another is added to the rest of the domestic waste and landfilled despite environmental contamination concerns; and a minor portion is collected, crushed and exported to other countries for metal recovery [5]. The estimate is that just 2% of eletronic waste is recycled in the whole country [6].

According to the Technical Feasibility Study performed by the Brazilian Agency for Industrial Development, the challenge of recycling electronic waste lies in the cost of reverse logistics in a continental country with particular logistical complexities [7]. Therefore, a recycling process must be less costly and as profitable as possible to compensate transportation distances. The lack of investment in recycling plants makes the metal recovery of gold impossible, which could otherwise finance the process, and the e-waste collection companies have only exportation as a possibility after removing PCBs.

The lack of a common solution for handling electronic waste and the environmental concerns of illegal recycling practices motivate further studies to expand recycling practices and legal disposal [8-10].

In general, recycling printed circuit boards involves hydrometallurgical and pyrometallurgical processes. Despite the gains obtained, several environmental and economic considerations must be considered. In a pyrometallurgical process, a massive investment is necessary, and there are concerns regarding the energy required by the ovens and the generation of potentially polluting gases from brominated compounds used as flame retardants [11-13]. In a hydrometallurgical process, the amount of inputs such
The bacterium used in bioleaching experiments was *Acidithiobacillus ferrooxidans*, strain LR. T&K medium used for growing the bacterial inoculum was composed of two solutions (A and B). Solution A was composed of (in g L\(^{-1}\)) (NH\(_4\))\(_2\)SO\(_4\) (0.625), MgSO\(_4\).7H\(_2\)O (0.625), and K\(_2\)HPO\(_4\) (0.625), and solution B was composed of (in g L\(^{-1}\)) FeSO\(_4\).7H\(_2\)O (166.5) \([23]\). The pH of both solutions was decreased to 1.8 by adding H\(_2\)SO\(_4\) 5 M; in addition, solution A was sterilized by autoclaving during 30 min at 120 °C and 1 atm, while solution B was filter-sterilized at 0.45 μm. Therefore, both solutions were mixed at proportion of 4-A:1-B.

*Acidithiobacillus ferrooxidans* was selected for the bioleaching processes due to its tolerance to the presence of heavy metals \([15,24]\). This bacterium gets energy from the oxidation of Fe\(^{2+}\) and reduced sulfur compounds and produces important oxidant agents, such as ferric ion and sulfuric acid \([24]\).

### 2.2 Methods

Recycling of PCBs was performed using mechanical processing, bioleaching and hydrometallurgical extraction (cyanide leaching) as shown in the Figure 1.

#### 2.2.1 Mechanical processing

Mechanical processing was carried out on the collected PCBs by comminution and magnetic separation aiming to concentrate metals (especially copper and gold) and extract iron, which is prejudicial to copper bioleaching. Printed as acids and the need for installations and qualified operators make the process costly \([14-16]\).

The undeniable relevance of a final destination for electronic waste encourages research to develop cheaper and environmental friendly recycling processes to recover raw materials from the ever-increasing production of electronic equipment \([1]\), to extend landfill life \([15]\) and to contribute to the circular economy, especially in developing countries such as Brazil.

The reduction of energy and acid requirements could be achieved by optimizing the integration of mechanical, chemical and biological separation processes \([13]\).

Bio-hydrometallurgical processes involve biosorption \([17]\), biofilms \([18]\) and bioleaching with different types of microorganisms. Among the different microorganisms (fungus and bacteria) used in bioleaching processes, *Acidithiobacillus ferrooxidans* is the widest studied bacteria of all extremely acidophilic prokaryotes \([19]\). PCB bioleaching using *Acidithiobacillus ferrooxidans* is reported in several studies \([20-22]\).

This paper addresses a combined mechanical bio-hydrometallurgical process for obtaining gold, copper and iron from printed circuit board scrap as a feasible technology for the Brazilian legal and economic context.

### 2 MATERIAL AND METHODS

#### 2.1 Material

An amount of 50 kg of PCB were removed from obsolete computers for the current study. Batteries and capacitors were extracted from PCBs.

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1 Courtesy of Chemistry Institute, State University of São Paulo – UNESP, Araraquara, Brazil.
circuit boards were ground in a hammer mill to a size below 2 mm and therefore submitted to magnetic separation in a cross-belt separator to obtain magnetic and non-magnetic products. The composition of such products was previously reported in the literature [25]. The non-magnetic product was forwarded to the bioleaching experiments and bacterial adaptation; chemical composition is shown in Table 1.

As can be seen in Table 1, only 0.4% of iron remained of magnetic products from an initial concentration of 5.03%, showing the magnetic separation efficiency.

### 2.2.2 Bioleaching experiments

Bioleaching experiments were carried out to extract copper from the non-magnetic product of PCBs using pre-adapted culture of A. ferrooxidans-LR.

The bacterial adaptation process was conducted by means of sequential subcultures, and the bacteria was grown in the presence of printed circuit boards (non-magnetic product), initially in the concentration 2.5 g L⁻¹, acquiring resistance to the products of chemical and biological leaching. Successive growths were made, with a 0.5 g L⁻¹ increase in the concentration of printed circuit boards with each successive subculture, using an aliquot of 10 mL of the previous growth containing the adapted bacteria as inoculum, in this way gradually raising the bacterial tolerance to increased concentrations of printed circuit boards up to a level of 45 g L⁻¹. The bacterial adaptation process was carried out for 4 months.

The shaking experiment was carried out in sterilized Erlenmeyer flasks with 200 mL of culture medium at room temperature (25–30°C) in a rotary shaker. PCB samples (non-magnetic fraction) were added to each flask under aseptic conditions. The bioleaching system was maintained acidic (pH 1.8–2.0) with the addition of sulfuric acid (1 M) when necessary. The following conditions were studied: slurry density, inoculum volume, rotation speed and initial ferrous iron concentration.

Different slurry densities (g L⁻¹) were evaluated: 15, 22.5, 30, 45, 60, 75. Inoculum volumes evaluated were (%v/v): 5, 10, 20, 30, 40, 50, 60 at three different rotation speeds (rpm): 150, 160, 170. Three initial ferrous iron concentrations also were analyzed (g L⁻¹): 6.75, 13.57, 16.97. Abiotic controls were run in parallel. Samples (15 mL) were periodically withdrawn (1, 2, 3, 4, 5, 6, 7, 10, 13 and 15th days) for copper analyses from bioleached solution.

The aliquots from the leaching were spun during 20 minutes at 5000 rpm rotation speed. Two drops of concentrated HNO₃ were added, and the samples were preserved in amber flasks at 4 °C until chemical analysis.

### 2.2.3 Cyanidation

Insoluble material from bioleaching was leached by cyanide for gold extraction. Cyanidation was conducted in Erlenmeyer flasks (250 mL) containing NaOH solution (pH 11) with 30% of solid concentration at room temperature (25-30°C).

Erlenmeyer flasks were constantly shaken (150 rpm) to disseminate cyanide and dissolved oxygen. After pH stabilization (10 min) in alkaline condition above 10.5, sodium cyanide was added (5 g L⁻¹). Leaching was carried out for 144 h; the pH was monitored and adjusted to a value above 10.5 using NaOH 1 M when necessary to avoid formation of cyanide gas. The concentration of free cyanide was also monitored by titration and adjusted with NaCN(ω), when necessary, to keep the concentration above 200 ppm. Samples (10 mL) were periodically withdrawn (1, 4, 8, 12, 18, 36, 48, 72, 102 and 144h) for gold analyses from leached solution.

The need to replace the cyanide during experiments is due to the decomposition of the cyanide ion, which is thermodynamically unstable and has a natural tendency to degrade [26].

### 2.2.4 Analytical methods

The metal content was assessed by atomic absorption spectroscopy (AAS). The initial Cu concentration (CC) shown in Table 1 was used to calculate the copper extraction rate; the final concentration of Cu (leach CC) was analyzed in leached liquor samples collected from bioleaching experiments. The same principle was used to calculate the gold extraction.

### 3. RESULTS AND DISCUSSION

#### 3.1 Bioleaching Experiments

As shown in Figure 2, the increase in slurry density caused a decrease in copper extraction. The lower the slurry density, the greater the volume of leaching solution per mass of concentrate, which increases the metallic solubilization [27].

In addition, bacterial activity can be inhibited by higher concentrations, which vary from 0.45 to 4.45 g L⁻¹, and therefore the increase in the pulp density can significantly inhibit the activity of the microorganisms [24, 27, 28]. Guo [29] described a similar effect of slurry density on the bioleaching of melted Pb/Zn waste.

The highest copper extraction (97.2%) was achieved at a slurry density of 15 g L⁻¹ after 15 days (Figure 2).

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**Table 1.** Composition of non-magnetic product material from printed circuit boards

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cu</th>
<th>Sn</th>
<th>Pb</th>
<th>Al</th>
<th>Zn</th>
<th>Fe</th>
<th>Ni</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>28.1</td>
<td>7.8</td>
<td>4.9</td>
<td>4.5</td>
<td>3.9</td>
<td>0.4</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
More than 70% of the copper was bioleached at pulp densities of between 15 and 22.5 gL\(^{-1}\) since the bacterial adaptation had increased the bacteria’s tolerance to the ions generated in the oxidation of the metals contained in printed circuit boards. Previous studies focused on recovering copper from printed circuit boards in shaken flasks indicate similar results and copper extraction rates over than 70% [30-32].

At the highest pulp density (75 gL\(^{-1}\)), the copper extraction was less than 20%, the same level as that obtained with abiotic controls (Figure 2), showing that at this pulp density copper extraction was not influenced at all by bacterial activity, with only chemical leaching of the copper having occurred.

Few studies [30-34] note the toxicity of the printed circuit boards, and in spite of the fact that the bacterial adaptation increases the tolerance to metallic ions, probably due to the quantity of PCB added to the leaching environment, in the case of pulp densities of 30, 45, 60 and 75 gL\(^{-1}\), there may have been an increase in the lysis condition of the cells in addition to having a negative impact on the process of transfer of mass [32]. Even so, at pulp densities of between 15 and 60 gL\(^{-1}\), the extraction of copper obtained from the bioleaching was greater than that achieved with the abiotic controls.

Illyas et al. [30] suggests that the non-metallic components of the printed circuit boards also have a toxic effect on the bioleaching process due to their alkalinity, noting the increase in the initial pH when the unwashed electronic scrap was added to the leaching environment. Vestola et al. [35] suggests that the inhibition is due to the presence of organic solvent residues present in the circuit boards.

The oxidized solution is used to inoculate bacteria that are in the exponential growth phase, as follows: the lag phase (adaptation phase), the exponential phase, the stationary phase and the death phase. In the exponential phase, the number of cells increases exponentially and causes an increase in the bacterial metabolic activity involving the oxidation of the ferrous ion turning it into ferric ion and the subsequent solubilization of the copper [36].

Figure 3 presents the results obtained in the extraction of copper with different volumes of oxidated culture solution as inoculum. As can be observed in Figure 3, with a 10% inoculum a 99.2% extraction level of copper was achieved, with this being the best result obtained. The main difference observed using a 10% inoculum solution was that the exponential phase of bacterial growth occurred by the 2\(^{nd}\) day, while with a 5% inoculum this phase occurred by

![Figure 2](image-url) **Figure 2.** Copper extraction (%) from 1 up to 15 days for different slurry densities.

![Figure 3](image-url) **Figure 3.** Copper extraction (%) from 1 up to 15 days obtained using inoculum volume from 5 to 60% and abiotic control.
the 6th day. This occurred because using a 10% inoculum, a greater number of cells were introduced into the environment than with a 5% inoculum, and this increase in the number of cells meant that the available Fe^{2+} was oxidized more quickly, as observed in Figure 3, with the consequent extraction of 80% of the copper in 5 days. The increase in copper extraction from the 5th day onward was probably due to the leaching of the copper (caused by the acidic culture), and it can therefore be inferred that the bacterial growth may have entered the stationary phase, in which the number of cells remains the same or in which there is almost no replication.

With the increase in the volume of the oxidized culture solution being inoculated to the environment, consequently, the amount of Fe^{2+} available is less (in the culture environment), and how the bacterial growth is closely linked to the biological oxidization of the ferrous ion in order to obtain energy, even with the inoculation of a greater number of cells, no significant increase in the level of copper extraction was observed, when volumes in excess of 30% of the oxidized culture solution were inoculated. In addition to this, the oxidation of Fe^{2+} can be inhibited in the presence of ferric ion concentrations (10 gL$^{-1}$) [37].

In oxidized culture solution, ferrous ion was completely oxidized turning it into the ferric ion prior to the inoculation to the environment. In other words, the greater the inoculated volume, the greater the initial concentration of Fe^{3+}, which leads to a greater initial extraction of copper, as observed in the situations with between 50 and 60% of inoculum volume. From the 5th day onward, the extraction remains constant up until the end of the experiment. The leaching caused by the ferric ion was not the only factor responsible for the obtained extraction level greater than 60%. The attained results demonstrated that the direct mechanism contributed to the copper extraction better than the indirect mechanism (oxidation by the ferric ion) did.

In studies of shaken flasks, the oxygen is introduced into the leaching environment by means of constant shaking.

The availability of oxygen is fundamental, given that the bacteria A. ferrooxidans is aerobic and consumes the O$_2$ in the oxidization of the ferrous ion [21,22]. According to Lewis et al. [38], the temperature and the shaking speed have proven to be the factors that have the greatest impact on the kinetics of the copper’s dissolution.

It was argued in the earlier experiments that the effect of the chemical leaching of the metals (abiotic controls), particularly of copper, was due to the introduction of oxygen brought about by the shaking. The study using different rotation speeds was carried out to verify the possibility of reducing the rotation speed, thus eliminating the effect of the chemical leaching without compromising the extraction of the copper by bioleaching. The results obtained in relation to the extraction of copper (%) under different rotation speeds are presented in Figure 4.

As can be seen in Figure 4, the greatest extraction of copper (99%) was achieved using a rotation velocity of 170 rpm. Bioleaching studies [30,32-34,39] report extraction rates of more than 70% with shaking speeds ranging from 150 to 250 rpm, but using rotation speeds of between 150 and 160 rpm, copper extraction dropped to less than 60%, due to the reduction of the transfer of mass as the rotation speed diminished.

Due to the aerobic nature of A. ferrooxidans, the dissolved oxygen is a restricting factor for the bacterial growth, with growth not being observed for concentrations of less than 0.2 mgL$^{-1}$ [24]. Even though the oxygen dissolved in the environment was not measured, it can be observed that the reduction in the rotation speed, and therefore, in the introduction of oxygen into the environment, resulted in a decrease in copper extraction, with it being expected that slower speeds than those used may inhibit bacterial growth. Shaking the culture not only leads to the introduction of oxygen but also CO$_2$, required as a source of carbon in the bacterial metabolic activity [15].

Studies of shaken flasks are usually used on a laboratory scale, but the determination of the rotation speed occurs

![Figure 4. Copper extraction (%) from 1 up to 15 days with speed rotation of: 150 rpm (■), 160 rpm (▲) and 170 rpm (●), and the respective abiotic controls 150 rpm (□), 160 rpm (△) and 170 rpm (○).](image-url)
in an experimental way, and as in the case of the bacterial adaptation process, factors such as the biomass used and the culture environment can cause the rotation speed to vary, and therefore it is necessary to investigate this.

In previous literature using *A. ferrooxidans*, Choi et al. [39] detected that the addition of ferrous ion to the bioleaching process promotes the dissolution of copper from PCBs.

The copper extraction is shown in Figure 5 for different Fe$^{+2}$ initial concentrations. The experiment that assessed the influence of the increase in the initial concentration of Fe$^{+2}$ on the bioleaching of printed circuit boards was carried out at the same time as the study of the influence of the volume of the oxidized culture solution (Figure 4). Since the percentage of copper extracted in both the studies was one of 99%, the results presented using an initial concentration of Fe$^{+2}$ of 6.75 gL$^{-1}$ and 10%v/v have already been discussed. However, this experiment helped prove the inhibiting effect that concentrations of Fe$^{+2}$ (13.57 and 16.97gL$^{-1}$) can have on the extraction of copper.

Figure 5 shows that the increase in the initial concentration of ferrous ion did not lead to an increase in copper extraction, as expected, given that biological activity is closely linked to oxidization of the ferrous ion. However, according to previous studies [24], concentrations of Fe$^{+2}$ greater than 5 kg m$^{-3}$ present an inhibiting effect on microbial growth. In both the situations studied, the extraction obtained was in excess of 70%.

Additionally, Choi et al. [39] demonstrated that the bioleaching of printed circuit boards with different initial concentrations of Fe$^{+2}$ (0–9 gL$^{-1}$) reached a higher solubilization of copper (5gL$^{-1}$) using 7 gL$^{-1}$ de Fe$^{+2}$, which is a similar level to the one obtained in this study (6.75gL$^{-1}$).

Similar conclusions were observed by Xiang et al. [40] — the copper is better bioleached by increasing the initial concentration of Fe$^{+2}$ from 0 to 9 gL$^{-1}$, but it decreases in the concentrations of 12 and 15 gL$^{-1}$. Also in this study, the leaching rate of the copper decreased with the time of incubation, and it was suggested that this occurred due to the precipitation of Fe$^{+3}$ and formation of a passivation layer on the surface of the ground PCB, which explains the decrease in the extraction of copper at the initial concentrations of Fe$^{+2}$ (12 and 15 gL$^{-1}$).

3.2 Cyanidation

The results from the alkaline leaching with sodium cyanide of bioleaching tailings show that 86% of the gold present in the insoluble material was extracted after 144 hours of leaching (Figure 6).

Gold extraction was prominent during the first 20 hours of cyanidation reaching almost 40% of the total gold extraction. The remaining gold was slowly extracted until it reached a level of 86% over the course of 144 hours, given that gold may dissolve slowly in sodium cyanide [41]. According to Ciminelli and Gomes [26], despite being thermodynamically favored, gold extraction in cyanidic solutions is limited by the slow reaction speed.

Brittain [42], who studied the kinetics of the dissolution of gold by cyanide, describes that as the cyanidation reaction
Combined mechanical bio-hydrometallurgical recycling process of printed circuit boards in Brazil

continues and the concentration of gold in the solid fraction decreases, there is an increase in the resistance to the gold’s dissolution. Zheng et al. [43] correlates this resistance to the formation of a passivation layer on the surface of the gold. The build-up of coatings, such as AuCN, AuOH, Au(OH) (CN)$^-$, Au(OH)(CN)$^-$, Au(OH)$_2$, Au$_2$O, AgCN-AuCN, Au$_2$S$_2$, Au$_2$S-S, delays the gold’s cyanidation, as they act as passivators, blocking the reagents from the gold’s surface [44].

4 CONCLUSIONS

The combined mechanical bio-hydrometallurgical processing of printed circuit boards succeeded in the extraction of 99% of total copper content in 15 days of the bioleaching process using A. ferroxidans-LR bacteria and 86% of the gold in 144 h of cyanide leaching. Iron was recovered by magnetic separation (95%). The best conditions for copper extraction were at a slurry density of 15 gL$^{-1}$, an inoculum (adapted bacteria) volume of 10% (v/v), a rotation speed of 170 rpm, and an initial concentration of Fe$^{+2}$ of 6.75 gL$^{-1}$.

The combination of the mechanical, microbiological and chemical processes made it possible to define an alternative route for selective and sequential extraction of the iron, copper and gold even considering with slow reaction speed due to the low cost, and it can be applied as a cheaper technical solution to PCB recycling in Brazil.

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