



## A simple and nearly-closed cycle process for recycling copper with high purity from end life printed circuit boards



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### ABSTRACT

The large amount of Cu present in printed circuit boards (PCBs) residues, usually about ten times more than the Cu amount present in rich-content minerals, makes these residues an attractive secondary source of Cu. Thus, the main aim of this work was to develop a simple and nearly-closed two-step process to recover Cu from PCBs residues with high purity.

Firstly, a multi-element leaching solution, containing 78% of the total amount of Cu present in the residue together with other metals, was obtained using acidic ( $\text{HNO}_3$  2 mol/L for 210' at 50 °C) conditions. In a second step, a bispolycylamine resin was used to recover Cu with high selectivity from the multi-element (59.0% Cu) leaching solution and a final Cu solution with high purity (99.0%) was obtained after eluting, with  $\text{H}_2\text{SO}_4$  4 mol/L, the Cu retained in the column.

Additionally, the amount of Al (85%) leached from the residue, present in the raffinate, was totally recovered as a solid of  $\text{Al}(\text{OH})_3$ .

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### 1. Introduction

Printed circuit boards (PCBs) are widely used in most electric and electronic equipments. Improvements in the processing power of computers have shortened their average lifetime. Therefore, each year, the amount of waste electric and electronic equipment (WEEE) is rising three times faster than other forms of municipal waste [1].

It is estimated that between 20 and 50 million ton of WEEE are generated internationally each year and this will increase at a rate of 3–5% per annum [2,3]. The strong production of electronics increased the concerning with WEEE [4–6]. Therefore, recycling WEEE becomes a priority. Moreover, the treatment of WEEE has two main advantages: reduction of land filling and reutilization of the recovered materials [7–12]. Specifically, the recovery of metals from WEEE is important because it contributes for reducing carbon and material footprint [7].

PCBs contain approximately 30% metallic material, 40% organic resin materials, and about 30% glass materials used as resin reinforcing fibers [13]. Some of these materials are hazardous substances like heavy metals and halogenated flame retardants [14].

Although PCBs correspond to only about 6% of the total weight of the WEEE [15], they represent a significant portion of the value contained in the WEEE [4,16]. PCBs contain large amounts of precious metals, such as Au and Ag. Precious metals and Cu in PCBs account for more than 95% of its total intrinsic value [17].

PCBs contain around 20% of Cu, which is 10 times more than the Cu amount present in rich-content minerals [18–21]. This makes PCBs an attractive secondary source of this metal because it is economically interesting and contributes to the preservation of the natural resources [22–24].

Recovery of metals from PCBs is usually performed by pyrometallurgical and hydrometallurgical methods, both combined with mechanical pretreatments. Incineration of WEEE during pyrometallurgical processing releases some hazardous gases that cause severe environmental problems; in addition, this kind of process requires high investments [1,18,25].

So, it is of great interest to develop new and green technologies, with low consumption of energy and reagents, for recycling metals.

Hydrometallurgical processes are interesting due to the simplicity and less consume of energy, less capital and operating costs than pyrometallurgical ones [26,27].

The hydrometallurgical processes consist in a first step where the metals are extracted into solution by chemical leaching in acid or alkaline medium, and then a second step that consists on the solution purification. Precipitation, cementation, adsorption, ion

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exchange, electrowinning and solvent extraction are purification methods usually used [8].

Chelating ion exchangers with bispicolylamine functional groups are unique in the commercial array of ion exchange products. These resins have three nitrogen donor atoms and two of them are in the aromatic pyridyl groups (tertiary amine) (Fig. 1). Due to the electron withdrawing effect of the aromatic group, the  $pK_a$  values are quite low and these nitrogen atoms remain deprotonated even at pH of 1.5. This fact makes this kind of resins capable of adsorbing transition metal ions even at feed pH less than 2 [28]. In fact, Cu usually shows high sorption affinity for these chelating ion exchangers and literature describes that the Cu affinity for this type of resins is orders-of-magnitude greater than for Ni and Fe [28]. Moreover, these resins have proven to be highly economic and new techniques for its utilization in continuous ion exchange systems have greatly improved separation efficiencies [29].

Several hydrometallurgical attempts were tried to extract Cu from the composition of PCBs, the major metallic element in the composition of these residues. Chehade et al. [30] recovered Cu and other precious metals with high purity. However, for achieving this goal, two dissolution steps were used, followed by the application of electrowinning technology. The first dissolution step was performed with sulfuric acid ( $H_2SO_4$ ) and the second one with aqua regia that is highly corrosive and needs suitable material of construction for handling with this reagent. On the other hand, Joda and Rashchi [17] used nitric acid ( $HNO_3$ ) to leach the metals from PCBs and obtained a pure powder of Cu by electrowinning during 5 h at room temperature, after previous separation of silver by precipitation. Yang et al. [31] recovered Cu with high purity by solvent extraction using LIX 84 in querosene after a leaching step with ammonia-ammonium sulfate. Finally, Zhan and Xu [32] separated metals from mixed metallic particles by vacuum metallurgy and Cu with 98% of purity was achieved.

Since a high amount of Cu is present in PCB, its recovery is economically important (about 1400 \$ per ton of PCB) [24]. However, this economical return of Cu implies that it should be recovered with high purity. In a general way, an overall analysis of the hydrometallurgical processes, described above, to recover Cu with high purity, point out that these strategies present one or more drawbacks. Among them, the high energy consumption and/or the complexity of the steps associated are some of the disadvantages, which can be highlighted. Therefore, the main aim of this work was to develop a process for recovering Cu, as a Cu solution with high purity, from end life PCBs residues, which has fewer unit operations than the

ones described in the literature and thus, easier to scale up. For this purpose, a two-step process consisting on using a first non-selective Cu leaching step from the roasted PCBs residue followed by a purification step using a bispicolylamine resin for recovering Cu with high selectivity from the multi-metal leaching solution, produced in the first stage, was developed.

## 2. Experimental

Chemicals used in the experiments were of analytical reagent grade. The synthetic solutions were prepared by dissolving the proper chemicals in deionized water to the required concentration.

Metals (Ag, Al, Au, Cu, Fe, Pb, Ni, Sn and Zn) concentration was measured, by atomic absorption spectroscopy with flame atomization (AAS-FA) in a Perkin Elmer AAnalyst 400 spectrometer (Norwalk, CT, USA). A nitrous oxide flame was used for the determinations of Al and Sn and an acetylene flame for the remaining metals.

### 2.1. Preparation and characterization of the PCBs residue

PCBs scrap used in this work was collected from more than sixty obsolete computers from different models or brands. Only motherboards were used and the batteries and the main plastic parts were removed. All the PCBs were coarsely milled in a single shaft shredding system (M 400/1–200, Erdwich). After a preliminary study, a grain size of 0.250 mm was selected to mill the PCBs; for this purpose, a cutting mill (SM 2000, Restch) was used. This fraction was chosen based on the fact that it contains the highest amount of Cu and precious metals (data not shown), such as Au and Ag, and thus will allow later on a high recovery of these metals. The PCBs samples (fraction <0.250 mm) were roasted in air at 850 °C for 3 h in a muffle furnace (Naberthem, L5/C6) using porcelain crucibles.

The metal composition of the PCBs roasted residue was determined by aqua regia digestion, at a shaking bath with temperature control (OLS200, Grant), for 24 h at 50 °C, with a liquid–solid ratio (L/S) of 10.

### 2.2. Leaching studies

The leaching tests were performed with  $HNO_3$  at different conditions. For all experiments, unless otherwise stated, the L/S ratio was kept constant at 10, and 5 mL of leaching solution was used. The experiments were conducted using falcon tubes in a shaking bath with temperature control (OLS200, Grant) and agitation of 150 rotations per minute (RPM). Variations in the temperature (25–80 °C) and  $HNO_3$  concentration (1–3 mol/L) were studied. For the best conditions, tests with L/S of 20 and 40 were also carried out, and an experiment with 200 RPM was also tested.

The metal leaching yield was calculated by quantification of each metal in the leaching solution, after filtration, by AAS-FA. All experiments were done at least in triplicate.

### 2.3. Copper recovery

The recovery of Cu was performed using the DOWEX™ M4195 resin, purchased from Sigma Aldrich. Synthetic solutions containing Cu, Ni, Fe, Pb, Al, Zn, Ag and Sn, were prepared from  $CuSO_4 \cdot 5H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $Pb(NO_3)_2$ ,  $Al_2(SO_4)_3 \cdot 16H_2O$ , Zn standard for AAS, Ag standard for AAS and Sn standard for AAS, respectively. The initial pH was controlled through the addition of concentrated  $HNO_3$  (65%). Aqueous solutions prepared from analytical grade  $H_2SO_4$  (95%) was used in the elution studies.

#### 2.3.1. Adsorption isotherms

The adsorption capacity for Cu to DOWEX™ M4195 resin was studied in batch assays using a synthetic solution of Cu, at pH

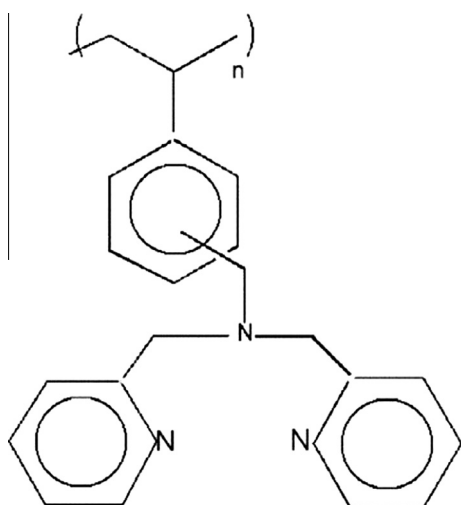


Fig. 1. Structure of bispicolylamine.

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