An innovative and eco-friendly approach to recover gold (and copper) from gold fingers of waste printed circuit boards

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Abstract Recycling waste printed circuit boards (WPCBs) is a complex problem worldwide and sustainable technologies are required. So, this work aims to offer an innovative (an European patent was submitted, EP 20216239.2 [1]) and more sustainable solution to recover high-value materials (gold and copper) from WPCBs.

The proposed process includes the following steps: (i) cutting the WPCBs´connecting terminals containing gold fingers using a mechanical tool (such as, a guillotine), (ii) swelling the cut WPCBs pieces (60 mm^2) in an appropriate organic solvent inside a low-pressure reactor (with stirring and temperature control), (iii) recovering the gold fingers from a mixture of copper foils and fiberglass using a magnetic separation process followed by sieving.

Subsequently, gold and copper were purified from the gold fingers using microwave-assisted acid leaching with nitric acid to leach copper. This process allowed recovering gold, as a solid, with high yield (99.9 wt%) and a purity grade of 74.0 wt%. Finally, leached copper was recovered by alkaline precipitation (pH around 8.8), as a solid of copper hydroxide, with high yield (99.9 wt%) and a purity grade of 85.7 wt%.

The present method has the advantages to provide an innovative and smart solution that minimizes the generation of wastes (dusts and wastewaters), energy consumption and equipment´s.

Keywords: E-waste, Printed circuit board recycling, Physical and chemical processes; Gold and copper recovery.

1. Introduction

Precious metals (PMs) (gold (Au), silver (Ag) and palladium (Pd)) are widely used in electrical and electronic equipment (EEE) such as laptops, personal computers, mobile phones, etc. due to their excellent conductivity properties. The high content of PMs and its economic revenue from these types of e-waste as raw materials represents one of the most sustainability challenges in terms of circular economy.

The PMs content in the various types of e-waste varies considerably. Wang et al. [2] summarizes several types of e-waste containing PMs; *the contain concentrations of PMs* founded in WPCBs are Au (300 ppm), Ag (2000 ppm) and Pd (110 ppm), and in waste mobile phones the PMs concentration are Au (30 ppm), Ag (2000 ppm) and Pd (1700 ppm). The main PMs containing in e-wastes, specially for Au, are found in WPCBs. Typical WPCBs comprises 40 wt% of metals, 30 wt% of plastics and 30 wt% of ceramics. The levels of PMs vary considerably depending on the age of the device from 10-1600 ppm of Au, 200-20 x 10^3 ppm of Ag and 5-970 ppm of Pd, but in most cases exceed those obtained in conventionally mined ores [3,4]. So, WPCBs are a valuable secondary source of PMs.

PCB is a thin board made of epoxy resin and glass fiber, which is coated with a layer of thin copper (Cu) film. The PCBs mechanically support the electronic components (ECs), such as resistors, capacitors etc. and connect them together to operate properly. The metals in PCB substrate are in the forms of the laminating of copper layers (10–27 wt% of PCB) and the coatings [Sn, Ni, Au, Ag, etc.] on the surface of copper layers, pins and holes that increase conductivity and oxidation resistance [5]. The non-metallic fraction (NMF) accounts for nearly 70 wt% of WPCBs [6]. NMF consists of 40 and 60 wt% of organic and inorganic substances, respectively. The common organic substance is epoxy resin (32 wt%), brominated flame retardants (BFRs), dicyandiamide curing agent, curing accelerator and so on.

Nowadays, all available technologies do not allow to recover Au and Cu in an efficient and environmentally friendly manner and with a lower carbon footprint. Milling or pulverization are common methods for that, but it generates a large amount of dusts and there is also a high energy consumption and losses of PMs [7]. Also, pyrometallurgical followed by hydrometallurgical refining processes, used in smelters, present important drawbacks (loss of PMs, generation of hazardous and toxic emissions, like dioxins and furans substances, and high energy consumption) [8].

A new friendly method for the complete delamination of WPCBs consists in dissolving the bromine epoxy resin (BER) in an appropriate organic solvent [9–11]. This dissolution allows to destruct the reinforced multi-layered PCBs structure and, thus, the enveloped metals are liberated. The main advantages of this method are that the BER does not decompose and does not produce toxic gases. However, the most critical point (not yet solved) corresponds to the subsequent efficient separation of the various metallic (gold fingers and Cu laminates) fractions from the non-metallic one, which is crucial if the desirable aim is to recycle selectively all valuable components, specially gold.

The present proposal [1] minimizes the conventional pre-treatment (crushing or pulverization) for the liberation of the plastic and the metal using organic solvent after cutting the WPCBs and separate the metal from the plastic efficiently to recover Au from the WPCBs. Further, it is possible to provide a smart process that can minimize the generation of dust, energy consumption and equipments.

2. Materials and Methods

2.1. Materials

WPCBs from personal computers and laptops were collected from a local disposer. After collection, the WPCBs were mechanically detached from the soldered components by means of a shear cutter.

All reagents used were analytical grade, sodium hydroxide (NaOH) 99% JMGS, nitric acid (HNO_3) 70% PanReac-AppliChem, dimethyl formamide (DMF) 99.8% VWR Chemicals, dimethyl acetamide (DMA) 99.0% Merck, ciclohexanone ≥ 99.0% Sociedade Portuense de Drogas, dimethyl sulfoxide (DMSO) 99.5% VWR Chemicals, *N*-methyl-*2*-pyrrolidone (NMP) Valente e Ribeiro Lda, γ–butyrolactone ≥ 99.0% Merck, ethanol ≥ 99.5% VWR Chemicals, hydrochloric acid (HCl) ≥ 37% Honeywell, bisphenol-A (BPA) 97% Alfa Aesar and naphthalene > 99.7% Sigma.

2.2. Methods

2.2.1. Delamination of the WPCBs and recovery of the gold fingers:

The proposed method to recover the gold fingers in WPCBs includes the following generic steps: **a)** Cutting the connecting terminals containing the gold fingers from the WPCBs using a guillotine, **b)** Overnight pre-swelling process with an appropriate organic solvent and agitation, **c)** Organic swelling performed in a low-pressure reactor using stirring and finally, **d)** Recovering the gold fingers from a mixture of the copper foils and the non-metallic dried fraction using a magnetic separation process (using a magnetic bar) with sieving.

After cutting the connecting terminals from the WPCBs in a size of 60 mm^2 (15×4 mm) using a guillotine as cutting tool, the cut pieces (3 g) are putted into an appropriate organic solvent (30 mL) and then stirred at a rotation of 600 rpm for 17 hours (overnight pre-swelling), which will help for the liberation of metal and non-metal components from the WPCBs in the subsequent swelling process. After the overnight pre-swelling process, the same solution is transferred into a low-pressure reactor (5100 Reactor Parr) using two helical stirrers in order to efficiently cause the dissolution of the BER. The stirring was performed at a rotation rate ranging from 600 to 1000 rpm at a temperature of 150 ºC to 180 ºC (depending on the boiling point of the solvent used) for 30 minutes to efficiently cause the optimum dissolution of the BER and consequently the delamination of the non-metal and metal layers of the WPCBs. The amount of BER dissolved in the several organic solvents used was measured by Ultraviolet-Visible spectroscopy (UV-vis) (against the absorbance versus concentration curve plotted for pure Bisphenol-A (BPA) because BPA is the major constituent of epoxy resin polymer chain. The BPA shows a maximum absorbance at 283 nm and this technique is well established and validated for the analysis of dissolved BER in organic solvents [9]. All the dissolution experiments were carried out at least twice to observe the reproducibility of the results obtained and to minimize the effect of random instrumental errors. After all experiments, the collected organic solvents were recycled and could be re-used afterwards.

The metal and non-metallic components recovered after the swelling process are subjected to a drying step in an oven (VWR Venti-Line 112 Prime) at 150 ºC for 15 h and then the gold fingers are separated from the remaining (non-metal and copper) components using magnetic separation process with sieving. The separation process is carried out using a magnetic stirrer for 120 minutes at 600 rpm. The sieving process allows the larger glass fibres to be separated, using sieves from 2 mm to 0.707 mm, remaining the recovered gold fingers separated.

2.2.2. *Gold and copper recovery from the gold fingers:*

Purification of gold from the gold fingers was performed by microwave-assisted leaching (6 mL HNO_3 4.66 mol/L /0.5 g of gold fingers, power 840 W) inside a polytetrafluoroethylene (PTFE; 23 mL) bomb for 60s. After that, samples were allowed to cool for 20 min and then a solid/liquid separation was implemented by filtration resulting in a solid phase, constituted by the purified gold layer and an acid leachate. Subsequently, the gold layers were dried for 12 h at 50 ºC in an oven. For pH adjustment of the leached solution, NaOH solutions were used using a pH meter GLP 22 (Crison, Barcelona, Spain). Metals concentrations were measured, by atomic absorption spectroscopy with flame atomization (AAS-FA) with a Perkin Elmer AAnalyst 400 spectrometer (Norwalk, CT, USA) or an Analytik Jena novAA350 spectrometer (Konrad-Zuse, Germany); nitrous oxide-acetylene flame was used for Al and Sn determinations whereas an air-acetylene flame was used for the remaining metals.

3. Results and Discussion

Our studies started with the choice of the WPCBs. We targeted the PCBs of random access memories (RAMs) and graphics boards, sound and ethernet due to their high gold content (**Table 1**). Regarding the RAMs, the specific cut of the terminals allowed the concentration of ≈65 wt% of the total gold contained in the WPCB board. The measured gold concentration contained in the several types of PCBs tested were determined after the digestion in aqua regia.

Table 1 Gold composition of selected WPCBs by weight after aqua regia digestion.

Samples	**Au composition (wt%)**
Terminals of RAM	**0.382**
RAM without terminals	0.014
Motherboard	0.001
Graphic board	**0.025**
Hard drive	0.004

Table 2 summarizes the gold fingers recovery yields achieved according to the described method (after organic swelling with each solvent followed by magnetic separation).

Results show that the best organic solvents to obtain a complete delamination and a higher recovery yield for gold fingers recovery are dimethyl sulfoxide (DMSO) and *N*-methy-2-pyrrolidone (NMP), being NMP a better solvent than DMSO. Without a pre-swelling overnight at 180 ºC, the recovery yield of gold fingers using NMP was 97.4 wt% and with DMSO under the same conditions was 96.6 wt%. This can be explained by the physical, chemical and structural properties of NMP in dissolving the BER.

Table 2. Gold fingers recovery yield at the end of the proposed method with various organic solvents studied. All experiments were performed using stirring ranging from 600 to 1000 rpm velocity with pressure for 30 minutes for a solid/liquid (S/L) ratio of 1:10 g/mL (* solid/liquid ratio of 1:5 g/mL).

Organic Solvents	**Gold fingers recovery rate (wt%)**	**T (°C)**	**Overnight**
DMF	60.6	180	Yes
DMA	85.5		
Cyclohexanone	78.8		
γ – butyrolactone	73.3		
DMSO	97.1		
	96.6		No
	89.6*		
	95.1	150	
NMP	98.3	180	Yes
	97.4		No
	94.1*		
	94.4	150	

At the end of this proposed method, total delamination of the non-metal and metal layers of the WPCBs was achieved as it can be observed in **Figures 1A** and **1B**. Metal characterization of gold fingers was performed using aqua regia and the metal content in weight (wt%) is summarized in **Table 3.** The results evidence that the gold fingers contain significant content of Ni, which enables the separation of the gold fingers from the fiber glass and the copper laminates by magnetic separation followed by sieving.

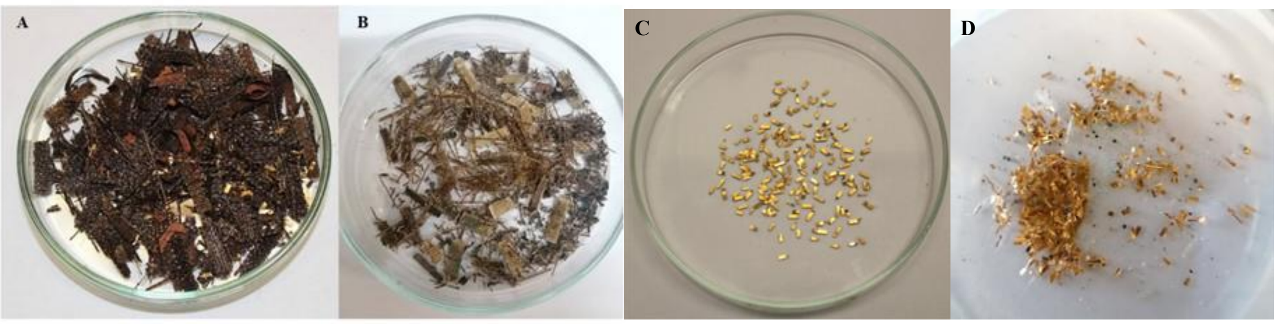

Figure 1. A) Separated components obtained after the NMP swelling of the WPCBs constituted by glass fibers, gold fingers and copper laminates. The experimental conditions were S/L ratio of 1:10, WPCB area/size of 60 mm^2/15×4 mm, at 150 ºC for 30 min, without overnight swelling and a stirring velocity of 1000 rpm. **B)** Separated components obtained after the DMSO swelling of the WPCBs constituted by glass fiber, gold fingers and copper laminates. The experimental conditions were S/L ratio of 1:10, waste PCB area/size of 60 mm^2/15×4 mm, at 180 ºC for 30 min, without overnight swelling and a stirring velocity of 1000 rpm. **C)** Photography of the gold fingers after magnetic separation followed by sieving. **D)** Photography of the thin layer of purified gold after microwave-assisted leaching with HNO_3 for 60 s.

Table 3. Metal composition of the gold fingers after aqua regia digestion.

Element	Cu	Ni	Au	Sn	Zn	Al
Content (wt%)	62.53	6.03	0.65	0.46	0.04	0.04

After magnetic separation of the gold fingers from the mixture of copper laminates and fiber glass with sieving, the final recovered gold fingers can be observed in **Figure 1C.**

Since gold fingers contain a low amount of gold (< 1 %) plus a huge content of base metals (**Table 3**), subsequent purification of gold was performed by microwave-assisted acid leaching using mild oxidized-acid conditions (nitric acid was used) in just one minute of reaction. A thin layer of gold with high recovery yield (99.9 wt%) and a purity of 74.0 wt% was achieved as shown in **Figure 1D**.

Subsequently, precipitation of Cu at pH 8.8 from the leachate closes the recycling process and Cu is totally recovered (99.9 wt%) with a purity of 86,7 wt%.

4. Conclusions

The present method has the advantages to provide a smart process that minimizes the generation of wastes (namely, dusts and wastewaters containing metals), energy consumption and equipment's . Furthermore, the combination of the physical and chemical processes proposed in this invention leads to an easily scale-up technology for industrial application.

The optimum condition of complete separation of WPCBs using NMP and DMSO solvent was S/L ratio of 1:10, WPCB area/size of 60 mm^2 /15×4 mm, at 180 ºC for 30 min with a velocity of 1000 rpm. Overall NMP proved to be best solvent for gold fingers recovery with a yield of 97.4 wt% in comparison to DMSO with a yield of 96.6 wt%. Additionally, in order to increase the purity of gold, we propose a fast and efficient process using microwave-assisted acid leaching with nitric acid to leach base metals (mainly copper) from the gold fingers. This process allowed recovering gold, as a solid, with high yield (99.9 wt%) and a purity of 74.0 wt%. Finally, copper was recovered from the leachate by alkaline precipitation (pH around 8.8), as a solid of copper hydroxide, with high yield (99.9 wt%) and a purity of 85.7 wt%.

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