# Optimization of Sustainable Processes for the Extraction of Precious Metals from End-Of-Life Printed Circuit Boards

Alessandro Becci [*], Alessia Amato, Matteo D'Arcangelo, Giulia Merli, Francesca Beolchini

Department of Life and Environmental Sciences-DiSVA, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona, Italy
a.becci@univpm.it

The technology advancement and innovation has been very significant and fast, in the last decades. This aspect is particularly evident in the electric and electronic equipment (EEE) field, where new devices are produced every year. The manufacture development is translated in two main issues: the highest metal required and the greatest waste flows to manage. To solve this double criticality, the old linear management method, in which every product became a waste, must evolve in a circular approach based on the principle "resource-product-regenerated resource" (urban mining). The end-of-life printed circuit boards (PCB) represent one of the most significant wastes from electric and electronic equipment (WEEE). In addition to their availability, the interest for these scraps is mainly justified by the high precious metal concentration (e.g. gold, silver, and palladium), which makes them a promising secondary resource. Several approaches are developed for precious metal recoveries from PCB, mainly by pyrometallurgy or hydrometallurgy. Biohydrometallurgical and green hydrometallurgical processes, using more sustainable reagents, are gaining increasing prominence, for their possibility to decrease the environmental costs, compared to the most traditional hydrometallurgy with chemical cyanide lixiviant. The present work aims to supply two innovative solutions: biotechnology by *Pseudomonas aeruginosa* for the biological cyanide production, and a green-hydrometallurgical process, using the thiosulphate as lixiviant agent for precious metal (i.e. Au and Ag) recovery. The central composite design of a response surface methodology (CCD-RSM) is used to optimize the cyanide production by *P. aeruginosa* evaluating the influence of both initial pH and glycine concentration. The same statistical approach (CCD-RSM) is used to find the best operative conditions for the precious metal leaching from PCB by thiosulphate, assessing the interaction among sodium thiosulphate, total ammonia/ammonium, particle size and time. The experimental results are further enhanced by the carbon footprint assessment which has quantified the possible environmental advantages of the developed solutions of PCB recycling, able to integrate the circular economy principles.

## 1. Introduction

Our world is a hyperconnected system, which needs electronic devices to ensure communications and the operation of all the most important activities. The manufacture of these devices requires many important materials from a few countries in the world. These materials, defined strategic raw materials (SRM), are also used to manufacture printed circuit boards (PCB) the hearth of all the electronic devices. PCB reach the up 3-5% of total WEEE and represent the most relevant category of e-waste (Becci *et al.*, 2020). The effective management of e-waste represents a key factor, when a device is incorrectly disposed, all the materials inside are lost. Nowadays, traditional methods for e-waste management include a separated collection and their exploitation, mainly by pyrometallurgical techniques (Merli *et al.*, 2022). The greatest attention for e-waste management would allow the recovery of the valuable materials inside, reducing the primary raw materials demand. Currently, Europe almost completely dependents on the SRM (and precious metals) import from few countries, mainly China and Africa (European Commission, 2023). Gold has a concentration of about 80-1000

g/t (Montero, Guevara and De La Torre, 2012), higher than that in ore, where the content does not exceed 20-40 g/t (Wu *et al.*, 2017; Frimmel, 2018). Thus, the recovery of gold and other metals from e-waste could generate benefits for both the environment and the economy, making the EU supply chain safer. As an alternative to the most common pyrometallurgy, hydrometallurgy allows metal extraction from e-waste by chemicals for leaching processes. The most widely used leaching agent for Au extraction is cyanide. Nevertheless, it is toxic for leaving things and it causes significant environmental impacts (Merli *et al.*, 2023). For these reasons, research has focused on alternative lixiviants, such as thiourea, thiosulphate and halides. Thiosulfate ($S_2O_3^{3-}$) is a non-toxic alternative agent, it's low toxicity makes it useful in several sectors (Cui and Zhang, 2008). Another alternative to chemical-origin cyanide concerns implementation of biotechnologies (Chi *et al.*, 2011; Merli *et al.*, 2022).There is a growing interest for this approach for the lowest leaching costs (both environmental and economic) that make, it a sustainable solution for e-waste metal extraction (Cui and Zhang, 2008). In this context, the goal of the present paper was the optimization of innovative processes for the extraction of gold from PCB by thiosulphate and biotech-cyanide. Once the best conditions were found, the most sustainable option was identified by life cycle assessment (LCA) methodology.

## 2. Materials and methods

### 2.1 Printed circuit boards

Waste PCB were shredded to obtain a granulometry lower than 2mm, in agreement with the conditions described by Becci et al. (2020). A preliminary washing with water saturated with NaCl (210 g/L) allowed to separate metal fraction from plastic (Merli *et al.*, 2023). Cu must be removed since the formation of complexes between cyanide and precious metals can be impaired by the presence of Cu with a decrease in the leaching rate. For this reason, PCB were pretreated using *At. ferrooxidans* bacteria in the presence of 10 g/L $Fe^{2+}$, resulting in a Cu removal of 90% (Pham and Ting, 2009; Becci *et al.*, 2020). Metal concentrations in PCB, after the pre-treatment are reported in Table 1.

*Table 1 PCB concentration after pre-treatment (Merli et al., 2022)*

| Metals | Concentration after pre-treatment |
|--------|-----------------------------------|
| Cu | 5% w/w |
| Au | 200 ppm |
| Ag | 300 ppm |

### 2.2 Thiosulfate leaching

To identify the best conditions in thiosulphate use for the mobilization of Au and Ag, leaching tests were carried out by varying the following parameters: sodium thiosulphate concentration (0.1, 1 mol/L), total ammonia concentration (0.2, 1 mol/L) and particle size PCB (0.1<Ø<0.25 mm; 0.5<Ø<1 mm). All the experiments were performed with a PCB concentration of 2% (w/v) at 25 °C for 24 h. The pH was kept between 10 and 10.5 by adding NaOH 10 M.

### 2.3 Cyanide production

The bacteria used for the cyanide production is *P. aeruginosa* strain (Merli *et al.*, 2022). To optimize the cyanide production by bacteria metabolism, two factors have been investigated: pH (between 8 and 10) and glycine concentration (between 0 and 7.5 g/L). The incubation lasted 48h at 30°C and cyanide production was measured every 2 h. The bioleaching is carried out under the optimal cyanide production conditions, adding PCB powder (1 g/L) after 20 hours from bacteria inoculation and he bioleaching experiment is carried out for 7 days.

### 2.4 Statistical analysis

The central composite design for Response surface methodology (CCD-RSM), was used to calculate the individual interactions of all the parameters in thiosulphate and cyanide experimental. The equation of CCD was (Eq.1):

$$Y = b_0 + \sum_{i=l}^{k} b_i X_i + \sum_{i=l}^{k-1} \sum_{j=l}^{k} b_{iJ} X_i X_j + \sum_{i=l}^{k} b_{ii} X_i^2 + \varepsilon \tag{1}$$

Where Y is the response, the concentration of cyande in mg/L in the cyanide case and the concentration of metals (Au or Ag), in the thiosulphate case. The other parameters are:$X$ is the individual factor considered in the different experimental plans, *bi* is the coefficient influencing the single parameter, *bij* is the coefficient of interaction between the parameters, *bii* is the coefficient of the single factor at the second, $\varepsilon$ is the error.
The number of the experiments required for the CCD analysis is calculated from the following equation (Eq.2):

$$N = 2k + 2k + cp \tag{2}$$

Where $K$ is the factor number and $Cp$ is central points.

## 2.5 LCA

The carbon footprint of Au recovery processes was estimated by the LCA approach performed in agreement with the ISO standards 14040 and 14044:2006 (UNI EN ISO14040:2006; UNI EN ISO 14044:2006) The selected method is EF 3.0, considering the only category of climate change. The functional unit selected for this study is 1 kg of PCB (corresponding to 0.6Kg pre-treated PCB). Figure 1 describes the system boundaries considered for the LCA, which exclude the PCB pre-treatments, common to both scenarios. As concern leaching by thiosulphate (scenario 1), the analysis considered the best conditions identified by experiments. A chemical process with cyanide (Montero et al. 2012)) was selected in scenario 2, since the treatment developed by Merli et al., (2022) showed a low concentration of both PCB and resulting cyanide, not yet suitable to hypothesize a process scale-up.
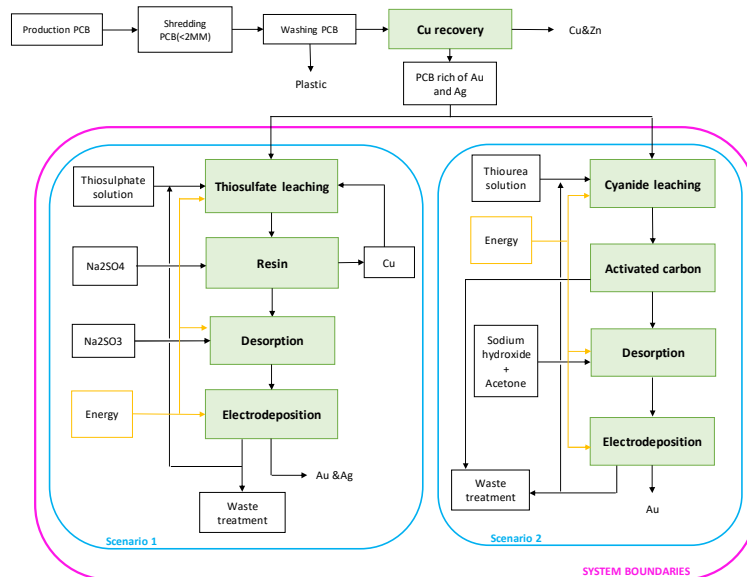


Figure 1: System boundaries considered for LCA.

## 3. Results and discussion

### 3.1 Thiosulfate process

The results in Figure 2 show that the best particle size (for both Au and Ag extraction) is the smallest one (<0.25mm) which improves the contact between the particles and thiosulfate for extraction. As proved by Eq. 3, all the factors and their interactions affected Au and Ag mobilization. Furthermore, Figure 3 shows the goodness of the model by relating the simulated data and the experimental data by indicating the residue distribution and the validity of the analysis ($R^2$ of 0.92 and 0.97 for Au and Ag, respectively).
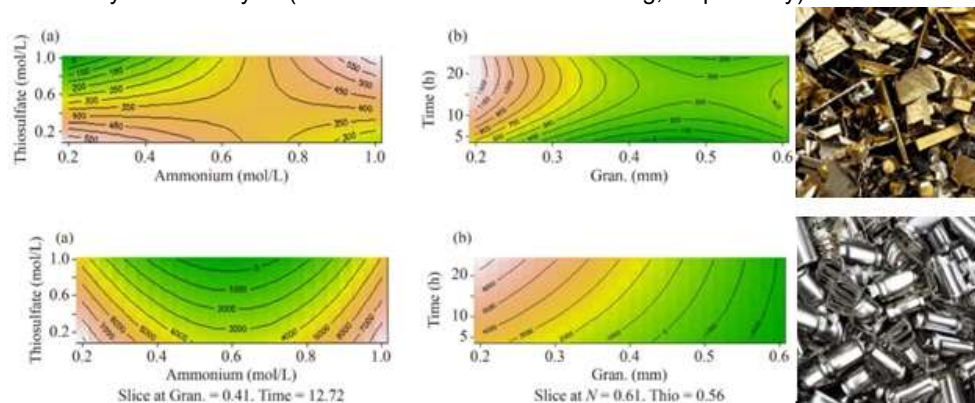


Figure 2: Au(up) and Ag (down) surface response optimization results.

The highest Au mobilization (2 mg/L) was achieved after 16 h, with 0.2 mol/L ammonia and 0.1 mol/L thiosulfate concentrations or 1 mol/L ammonia and 1 mol/L thiosulfate concentrations.

To optimize the considered factors, the results were analyzed by CCD. The Eq. 3 expresses the Au concentration in the solution, in relation to the following factors: initial ammonia concentration ($X_1$, mol/L), the initial thiosulfate concentration ($X_2$, mol/L), the PCB granulometry ($X_3$, mm) and the leaching time ($X_4$, hours).

$$Au = 353.40 + 79.16X_1 - 57.66X_2 - 360.89X_3 + 98.69X_4 + 247.15X_1X_2 - 47.91X_1X_3 + 25.00X_1X_4 + 47.40X_2X_3 - 18.46X_2X_4 + 422.34X_3^2 - 34.75X_4^2 \qquad (3)$$

Data in Figure 2 show that the 1:1 molar ratio between thiosulphate and ammonia is the best operating condition for Au leaching from PCB. As confirmed by the interaction between ammonia/ammonium and thiosulfate concentration, it is the parameter that has the greatest effect.
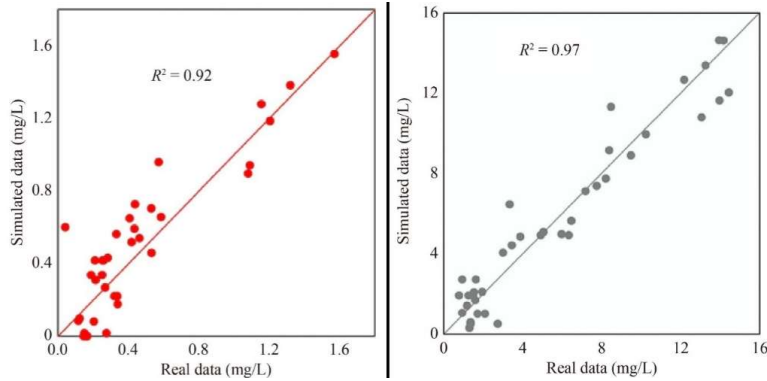


*Figure 3: Simulated data vs. real data for Au (red) and Ag (grey).*

The highest Ag mobilization (15 mg/L, Figure 2) was achieved after 8 h with 0.1 mol/L thiosulfate and 0.2 or 1 mol/L ammonia concentrations. The final equation predicted for the dissolution of Ag can be expressed in Eq.4 in relation to the same factors as the Au equation.

$$Ag = 1486.77 + 63.35X_1 - 2083.70X_2 - 3802.32X_3 + 455.44X_4 + 247.27X_1X_2 - 282.45X_1X_3 + 152.46X_1X_4 + 360.95X_2X_3 - 49.28X_2X_4 + 5473.64X_3^2 - 13.77X_4^2 \qquad (4)$$

All the factors considered had a significant impact on the predicted response, but the ANOVA showed that their interaction was not statistically significant (Merli *et al.*, 2023). The dissolution of Ag occurred with the greatest efficiency only with the smallest size of the PCB particles, especially in the first two hours, where it reached 100% of efficiency.

### 3.2 Cyanide process

Figure 4a shows a growing cyanide production until reaching a maximum, followed by a decline in relation to the time. This trend can be linked to bacteria that during the late growth phase use cyanide as a source of carbon and nitrogen. The best concentration of glycine was 1 g/L that allowed the best cyanide concentration of 10 mg/L in 20 hours.
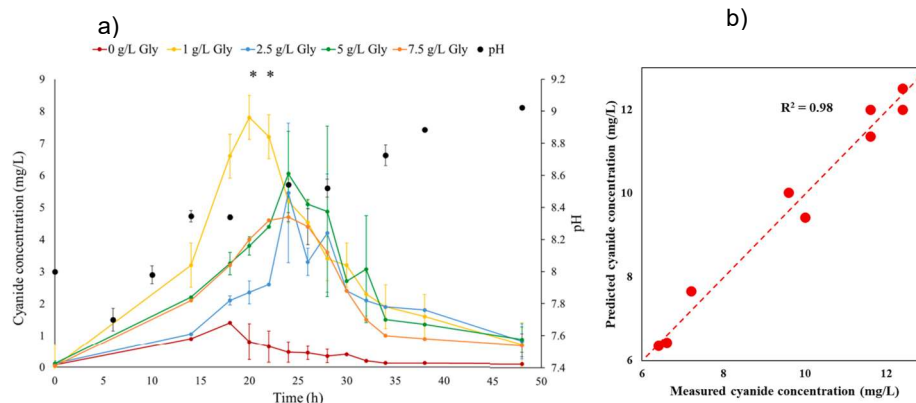


*Figure 4: Cyanide production and pH profile at different times and glycine concentration. The lines represent the average between the various real values (n = 3 replicates for each sample). The black stars identify the time conditions affected by glycine (a). Predicted vs measured plots for cyanide production (b).*

Following tests showed the best conditions for cyanide production by evaluating glycine and pH concentrations. The results were statistically analyzed using the Eq. 5 that relates the production of cyanide by the metabolism of bacteria to the concentration of glycine and pH:

$$CN = 12 - 1.74516(glycine) - 1.09207\ (pH) + 2.92229\ (glycine)x(pH) - 1.55633(glycine)^2 - 0.513831(pH)^2$$

(5)

The experimental points with a $R^2$ of 0.98 fit very well with this estimated value (Figure 4b). Both glycine concentration and pH have a negative effect on cyanide concentration. The addition of PCB highlighted the reduction of bacterial abundance later, confirming the toxic effect of e-waste. However, after about 8 h the bacteria were able to adapt and began to grow again. However, the stationary phase lasted longer, about 4 days. The bioleaching allowed extraction efficiencies of 90% for Ag and 20% for Au, after 7 days (Figure 5).
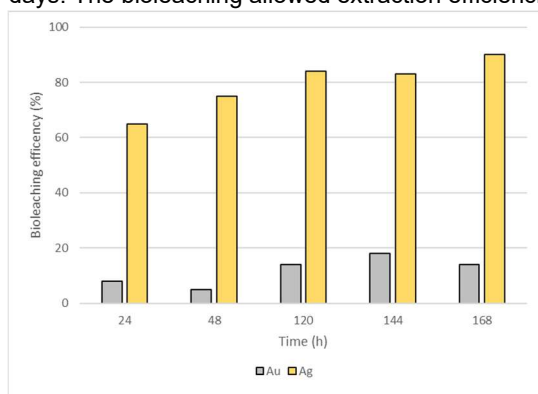


Figure 5: Leaching efficiency in the bioleaching experiment for Ag and Au.

### 3.3 Life Cycle Assessment

The results in Figure 6 show carbon footprint of the two options (expressed as Kg of $CO_2$ eq.) highlighting the most impacting phases. Negative values represent environmental credits related to the $CO_2$ eq. saving for the avoided primary production of both gold and silver.

The overall results show that thiosulfate process is 83% more sustainable than cyanide one thanks to the highest value of environmental credits, mainly connected to the recovery of Au. This result is also explained by the avoided high-impact primary production of this metal (from mining to refining).

Focusing on the detail of environmental burdens, leaching is the most impacting phase for the thiosulfate process due to the largest amounts of reagents needed. In cyanide scenario, the activated carbon produces the majority of the impact due to both its production and the disposal at the of its life.
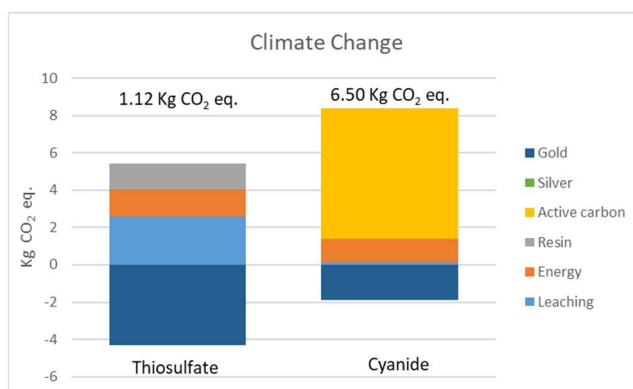


Figure 6: Climate change- Kg $CO_2$ eq.- comparison between cyanide and thiosulfate processes (functional unit 1 kg PCB, corresponding to 0.6 kg of pre-treated PCB).

## 4. Conclusions

The present work has shown all the steps for the optimization of innovative processes for the recovery of gold and silver from waste PCB, combining experimental activities with a statistical analysis of the results and a sustainability assessment. The integrations of these evaluations allowed to identify the thiosulphate leaching (operative conditions: the smallest PCB particle size, 1 mol/L ammonia and 1 mol/L thiosulfate concentrations)

as the best option. On the other hand, the results showed that bioleaching needs further improvement to hypothesize its scale-up. Additional efforts to improve bioleaching performance are desirable since it represents a promising option in the perspective of green economy, since the metabolic action of bacteria could reduce the problems associated with wastewater rich of toxic cyanide which characterizes the most traditional hydrometallurgical approaches.

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