

Selective Leaching of Precious Metals from Electrical and Electronic Equipment through Hydrometallurgical Methods

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The rapid human evolution has improved the quality of our lives through the use of technology. This not only resulted in increased raw materials extraction but also in the production of a worrying amount of electronic wastes. Indeed, in 2019 worldwide production of Electronic and Electric Equipment Waste (WEEE) was worth 50 million tons, causing several disadvantages such as the reduced space in landfills and massive shipping to countries with less restrictive regulations. On the other side, the billionaire electrical devices market is causing a significant increase in Precious Metals (PM) demand. Nowadays, the economic importance of PMs is as high as their supply risk. The answer to this problem consists of finding selective methods to extract and raffinate precious metals from disposed WEEE.

On average, WEEEs contain around 30 % of plastics, 30 % ceramics, and 40 % metals; among these only around 0.1 % is characterized by PMs, such as gold, silver, rhodium, platinum, and palladium. The separation of PMs from other non-precious components is generally obtained using pyrometallurgy, which consists of fusing the wastes at temperatures up to 1500 ÷ 1700 °C. However, this method produces toxic gaseous by-products and implies high energy costs. A possible alternative is given by hydrometallurgical processes, consisting of leaching the WEEE with solutions containing acids and oxidants at temperatures lower than 100°C. One of the main issues of the hydrometallurgical process is to leach copper and other non-precious base-metals selectively while keeping PMs in the solid-state.

In this work, we report preliminary results of equilibrium and kinetic leaching tests in a well-stirred batch reactor, aimed at the optimization of the main operating parameters of a hydrometallurgical process for selective leaching of copper and other base-metals from Wasted Printed Circuit Boards (WPCBs). In particular, experiments have been carried out at different HCl and NaCl concentrations of the leaching solutions, exploring also the effect of temperature variation (20, 50, and 70 °C).

1. Introduction

The growing market demand for Electrical and Electronic Equipment (EEE) is compensating the technological efforts toward miniaturization of electronic components, leading to the production of wastes, once these products are discarded. Although considerable efforts have been made to reduce the production of wastes and to improve recycling processes, there is still a huge lack of effective recovery technologies (Babu, 2007). The term “WEEE” is used to describe the Waste from Electrical and Electronic Equipment. The rapid expansion of technology and the “global village” philosophy drove society to the creation of a very large amount of e-waste. The final destination of end-life electronics is refurbishment, reuse, resale, or, at most, accumulation in landfills (Yeow, 2018). Since the global situation has not been regulated yet, the problem of Waste of Electrical and Electronic Equipment (WEEE) is creating a significant environmental impact (Baxter, 2016). Indeed, about 65.4 million tons of e-waste were generated in 2017 in the world (Perkins, 2014). In Europe, e-waste is generated with an increase of 16-28% every five years, which is 3 times faster than the average rate for municipal waste (Hossain, 2015). However, at the same time, WEEE can become a precious

source of plastic, glass, and metals that can be recovered and re-introduced into the production processes (Figure 1a). Amongst all the WEEE, Waste Printed Circuit Boards (WPCBs) are potentially considered as the most valuable components due to their high content of precious metals, which makes them a valid source for these metals (Huang, 2009). Therefore, WEEE could turn from problem to resource and from accumulation in landfills to recycling through an adequate treatment for the recovery of all reusable and recyclable components. However, the main problem of WPCBs is their composition (Figure 1b), since they are characterized by an upper and lower layer of plastics and base-metals, followed by a full layer of copper. On average, excluding CPU and RAM connectors, the PCBs contain their PMs in the inner core substrate (Widmer, 2005). The average of some base-metals and PMs content of Waste PCBs have been investigated several times in the literature (Pietrelli, 2018); in this work, the tested PCB metal contents are reported in Table 1. As it is possible to see, the sum of the most important Base-Metals tends to reach the 40 % w/w of the WEEEs (Figure 1a).

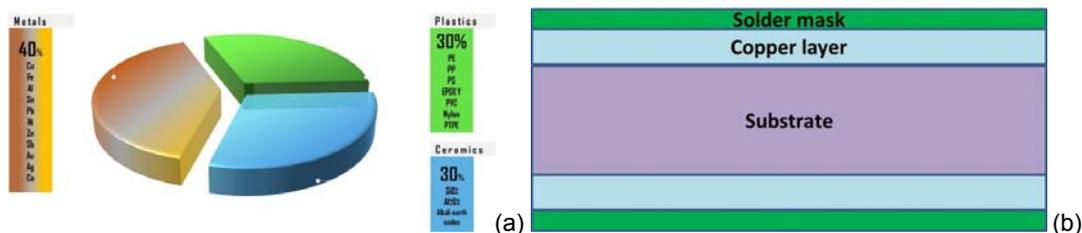


Figure 1: Overall WEEE components (a) and metal repartition in PCB (b)

Table 1: Some Base-Metal (g metals/g PCB), Precious Metals (μg metals/g PCB) content in the tested WPCB

Base-Metals	g/g	Precious Metals	$\mu\text{g/g}$
Fe	0.053	Ag	3300
Cu	0.268	Au	110
Al	0.019		
Pb	0.012		
Ni	0.005		
SUM	0.357		

PMs are resistant to corrosion and oxidation in moist air. Their physical and chemical properties, their high supply risk, and their application in industrial fields such as metallurgy, electronics, high technology, jewellery, and coinage make them some of the most valuable materials on the planet. Since noble metals concentration is limited in mineral reservoirs, the industrial production from secondary resources became particularly interesting. Moreover, previous studies found that WPCBs are richer in precious metals than the typical metal concentration in ores extracted from mines. This makes the recycling process of precious metals from WPCBs a potentially profitable business.

Since the Copper represents about 26.8 % on a mass basis of the total metal content into an average WPCB (Zhao, 2004), the main risk of a leaching reaction is to extract simultaneously copper (and other non-precious metals) together with gold, reducing the selectivity of PMs recovery. Therefore, the main idea of this work was to develop a batch-mode process to perform a selective washing of copper from this PCB matrix. The extraction was carried out by a leaching step of the PCBs components using "cleaning" acid solutions such as HCl/H₂O₂ at different volume concentrations and temperatures.

2. Materials and Methods

2.1 Materials

The materials used for the preparation of the leaching solutions are hydrochloric acid (MW 36.46 g/mol, purity 37 % v/v, CAS number 7647-01-0, purchased from Sigma Aldrich, Italy) and hydrogen peroxide (MW 34.01, 9.1 % v/v, 30 v., CAS number 7722-84-1, purchased from Titolchimica S.p.A., Italy) diluted with distilled water (CAS number 7732-18-5, purchased from Best Chemical S.r.l., Caserta, Italy). Sodium Chloride was also added in some of the programmed experiments. Concerning the solid matrices containing the precious metals, a manual dismantling of PCBs was performed, until reaching an average mean size of 2x2 cm². The experiments were carried using WPCB scraps obtained from a spent generic printer, two different brands of a motherboard, a calculator, a Wi-Fi amplifier, a modem, and a card reader. These scraps were mixed to obtain a homogeneous metal content in a solid mixture. WPCB solid mixture had a density equal to 4488 kg/m³.

2.2 Methods

The leaching process was performed in a batch-mode configuration until reaching equilibrium conditions. After the manual dismantling, scraps were weighted and put in contact with the leaching solution. For each leaching experiment, a mass of 3 g and a leaching volume of 100 mL were used. Diffusivity of precious metals ions in aqueous bulk was calculated as an average of $2.00 \cdot 10^{-9} \text{ m}^2/\text{s}$. A stirring rate of 300 rpm was set during leaching reactions.

During the reaction time, 2 mL of liquor was withdrawn at defined time intervals. The liquor sample was filtered using a $0.45 \mu\text{m}$ filters (Millipore, Burlington, United States) and collected in a glass vial. Subsequently, the metal content was measured using an Atomic Absorber Spectrophotometer (AAS), mod. SpectrAA 220, Varian Inc., Palo Alto, United States. Leaching reaction aimed at the elimination of copper; for this reason, the detection of this metal can be obtained in the wavelength working range $218 \div 328 \text{ nm}$, but this instrument has the best Cu sensitive line at 324.8 nm . In these batch-mode operating conditions, the ratio volume/mass was approximately 33 mL/g. In Table 2, the process parameters whose effects were studied in this experimental campaign have been listed.

Table 2: Operating parameters for experiments performed in this work

Experiment Scope	HCl concentration [v/v]	H ₂ O ₂ concentration[v/v]	NaCl concentration. [v/v]	Temperature [°C]
Effect of HCl concentration	3	1	0	20
	10	1	0	20
	20	1	0	20
Effect of NaCl concentration	3	1	0.1	20
	3	1	0.5	20
	3	1	1	20
Effect of the temperature	3	1	1	50
	3	1	1	70

Experimental results consisted of time courses of copper concentrations, which were modelled according to the Lagergren equation (Hossain, 2015) described in the following Eq.(1) and Eq.(2):

$$\begin{cases} -V \frac{d(C_{eq}-C(t))}{dt} = K_c [C_{eq} - C(t)] \\ t = 0 \quad C(t) = 0 \end{cases} \quad (1)$$

Eq.(1) represents a mass balance on the batch leaching reactor, where the extraction of the precious metal is performed. Then, using the boundary condition, the integration of Eq.(1) becomes:

$$C(t) = C_{eq}(1 - e^{-k_c t}) \quad (2)$$

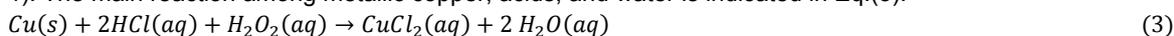
Eq.(2) is characterized by the parameters C_{eq} and K_c . The first one is determined experimentally as it is the equilibrium concentration; the second is the kinetic constant and can be calculated by best-fitting of the experimental data.

3. Results

The experimental campaign started with explorative tests to investigate the best lixiviant solution to extract metals from WPCBs scraps. Dissolution of copper was the main registered problem of the leaching processes. The amount of this metal was predominant in all types of electronic equipment, making the extraction of Precious Metals particularly difficult and not profitable. In this section, the tests regarding different operating conditions such as the effect of HCl concentration, NaCl concentration, and temperature, will be analysed to optimize the leaching of copper.

The use of hydrogen peroxide was considered a key point: it was the main reagent that made possible the leaching of metallic copper from WPCB in acidic chloride solutions (Hao, 2020). According to literature and to previously performed experiments, in this study, the concentration of hydrogen peroxide was set at 1 % v/v.

The effect of HCl concentration on copper extraction was investigated in a range of 3 to 20 % v/v (see Table 1). The main reaction among metallic copper, acids, and water is indicated in Eq.(3).



However, the concentration of copper that was indicated in the following diagrams is exactly the total amount of copper that has been measured in the leachate solutions, analysed using Atomic Absorption Spectroscopy (AAS). Therefore, the detected values did not only represent the amount of copper obtained from the

dissociation of CuCl_2 , but the total Cu amount obtained from overall leaching reactions occurred during this operation. The effect of HCl concentration in the leaching solution is shown in *Figure 2*.

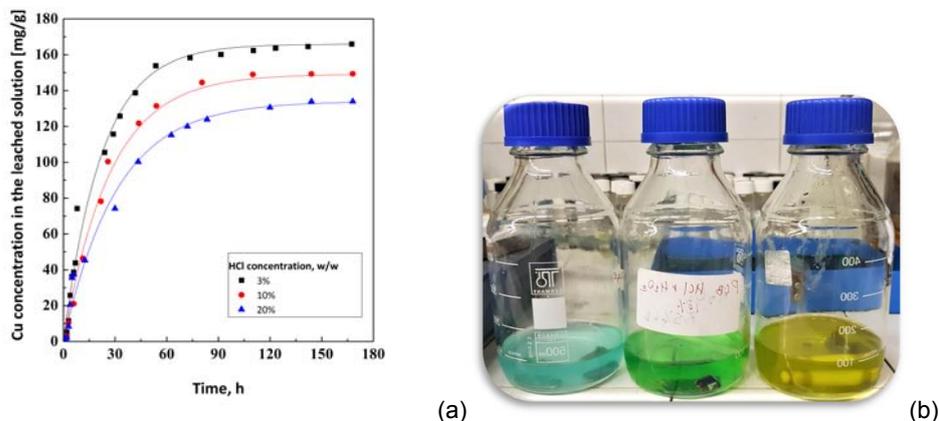


Figure 2: Total Cu concentration detected in PCB leached solutions. Tests performed varying HCl concentration in reacting solutions: modelled raw data (a) and colours of batch experiments (b)

The 3 % v/v concentration of the acid led to a higher copper equilibrium concentration (about 160 mg/g at 3 % HCl); however, the equilibrium time was reached after about 150 h for all the investigated HCl concentrations. As we can see in *Figure 2b*, different HCl concentrations led to different colour solutions. It can be explained considering the concentration of CuCl_2 produced. In particular, low concentrations of HCl (i.e. 3% v/v) results in a low concentration of CuCl_2 and the solution is blue due to the formation of the unreacted Cu^{2+} ion hexahydrate ($[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$). Instead, a higher concentration of HCl (i.e. 10% v/v) means a high concentration of $[\text{Cl}^-]$ ions which are responsible for the green colour of the solution. A much higher concentration of HCl (i.e. 20% v/v) and the excess of $[\text{Cl}^-]$ ions led to the formation of halide complexes, that have a formula $[\text{CuCl}_{2+x}]^x$ which gives a yellow colour to the solution.

The effect of NaCl concentration on copper extraction was then investigated at 0.1 M, 0.5 M, and 1 M, keeping the other process parameters constant and setting the HCl concentration at 3 % v/v (*Figure 3*). As a comparison, the curve obtained in absence of NaCl at 3 % HCl, extracted from *Figure 2* and cut at 30 h of observation, was added to the diagram.

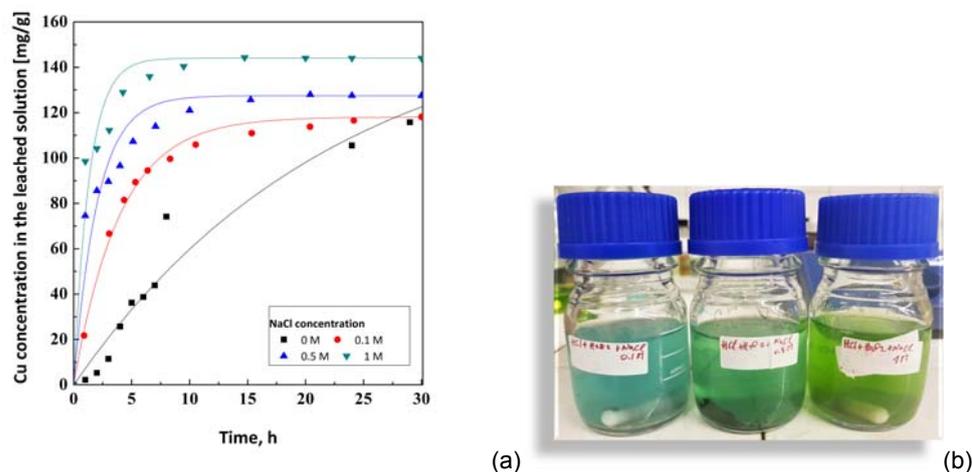


Figure 3: Total Cu concentration detected in PCB leached solutions. Tests (at 3 % v/v HCl) performed varying NaCl concentration in reacting solutions: modelled raw data (a) and colours of batch experiments (b)

Figure 3 shows that leaching kinetics completely change with the addition of Sodium Chloride, that results into an increase of Cu equilibrium concentration by increasing the NaCl concentration. The solubilized NaCl also reduces the time to reach equilibrium concentration (about 140 mg/g at 1 M NaCl) to an average of 25 h for

the three investigated concentrations. Indeed, the dissociation of NaCl into sodium and chloride ions provided the solution with sufficient chloride ions for the formation of the tetrachlorocuprate ion, following Eq.(4).



In particular, NaCl 0.1M provided a low amount of [Cl⁻] ions and the solution colour was light blue because of the predominant presence of CuCl₂, which reacts with water producing Cu²⁺ hydrate ([Cu(H₂O)₆]²⁺). The addition of an excess of [Cl⁻] ions (0.5 M) tends to shift the reaction to the formation of the tetrachlorocuprate ion, responsible for the green colour (as indicated in Figure 3b). The copper extraction rate increased significantly adding NaCl at 1 M in leaching solutions due to the increase of H⁺ and Cl⁻ ions concentration.

The third effect that was studied regarded the solution temperature, which was enhanced to have an improved copper leaching efficiency (Upadhyay, 2013). In this case, the concentration of HCl was set at 3 % v/v, and the concentration of NaCl was set at 1 M, as indicated in the previous experiments. In Figure 4, all the other process parameters were kept constant. Experiments at 50 °C and 70 °C were performed and compared to the previously performed experiment (extracted from Figure 3 and cut at 4 h) at 20 °C.

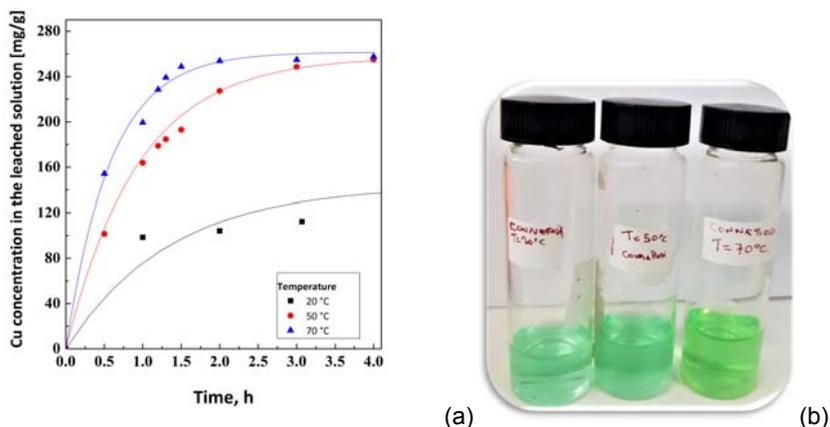


Figure 4: Total Cu concentration detected in leached PCB solutions. Tests performed varying the reaction temperature: modelled raw data (a) and colours of batch experiments (b)

By changing the temperature, equilibrium concentration was reached around 4 hours (see Figure 4a). The chemical equilibrium in CuCl₂ solutions caused the transition of part of the [Cl⁻] ions that belonged to a dissociated CuCl₂ mole to a Cu²⁺ ion, finding both [CuCl₄]²⁻ and [Cu(H₂O)₆]²⁺ complexes in a competitive co-existence, as indicated by Eq.(5) and Eq.(6) heterogeneous reactions.



In this last effect-study, the solution appeared bluish-green, which turned in full green with the increase of the temperature (Figure 4b). After 30 minutes, the solutions at 50 °C and 70 °C were characterized by a significant increase in leaching rate if compared to 20 °C solutions, demonstrating that the increase of temperature to enhance the efficiency of the process.

In the following Table 3, kinetic constants obtained with the indicated model and their mean square roots were listed, together with copper and gold recovery percentages

Table 3: Equilibrium concentrations, kinetic constants, Cu and Au recovery percentages

Process parameters	C _{eq} [mg/g]	K _c [1/h]	R ²	Cu, %	Au, %
3 % HCl	166	0.0447	0.9803	61.92	n.d
10 % HCl	149	0.036	0.9939	55.73	n.d.
20 % HCl	134	0.0323	0.9861	50.00	n.d
0.1 M	118	0.2525	0.994	44.06	n.d
0.5 M	128	0.4897	0.9225	47.57	0.19
1 M	144	0.7475	0.9443	53.74	6.00
50 °C	255	1.064	0.9671	95.15	15.45
70 °C	258	1.7148	0.9935	96.12	19.09

Recalling *Table 1*, the average content of copper and gold in the WPCB scraps are 0.268 g(Cu)/g(PCB) and about 110 µg(Au)/g(PCB), respectively. The study performed on the HCl concentration lead to the highest recovery of copper (about 62 %) but after very long reaction times (150 h). By the addition of sodium chloride, the reaction was slightly less efficient (from 44 % to 53 % copper removal) but with a still negligible gold loss and only 5 h of reaction. At 1 M NaCl concentration, copper removal was 53 % and gold loss 6 %, still acceptable in terms of selectivity. However, at increased temperatures (50 °C and 70 °C), even if the copper removal reached 96 % after a few hours, the leaching tests eliminated almost 20 % of gold from the WPCB scrap. This reduced significantly the selectivity of copper with respect to gold.

4. Conclusions

The effect of three process parameters was investigated during the leaching test for the selective extraction of copper from WPCB. The leaching solution which allowed the best selectivity is composed of HCl at 3 % v/v and an oxidizing agent, H₂O₂, at 1 % v/v, with the addition of NaCl 1 M. An increase of copper leaching efficiency was registered with the decrease of the HCl concentration. The increase of the temperature enhanced the leaching efficiency but decreased the selectivity of copper with respect to gold.

In the objective of sustainable process development, this could be the key point to reduce the operative costs and the environmental impact using low-acid hydrometallurgical selective extraction methods. For this reason, the temperature will be set at 20 °C for future experiments.

As it is possible to see, 3 % v/v HCl concentration increased the reaction kinetic constant, as well as the increase of the NaCl concentration and temperature. However, as indicated above, a too fast reaction rate could improve copper extraction, but worsen significantly the selectivity in terms of gold. The experimental results indicate that the proposed leaching process earns a chance for a further investigation aimed to optimise the process in terms of selective copper extraction.

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