

Article

Metal Extraction and Recovery from Mobile Phone PCBs by a Combination of Bioleaching and Precipitation Processes

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Abstract: Bearing in mind the metal rich composition of printed circuit boards (PCBs), this material represents a secondary source of valuable metals and offers an entrepreneurial opportunity in the metal sales market. Based on the ability of microorganisms to regenerate and produce the chemical oxidants that are responsible for metal leaching, bioleaching has become an efficient and affordable alternative to conventional metal recycling technologies, although further research is still necessary before industrial implementation. This study focuses on the recovery of metals contained in mobile phone PCBs through a combined process. Two different PCB pre-treatments were evaluated: grinding the whole piece and removing the epoxy cover from the piece without grinding. The benefit of *A. ferrooxidans* activity on the metal solubilization rate was analyzed. Additional chemical leaching assays were also conducted for comparison purposes and the reagents ferric iron (Fe^{3+}) and sulfuric acid (H_2SO_4) were selected for these experiments. The copper extraction results obtained in Fe^{3+} experiments with and without bacteria (*A. ferrooxidans*) were similar after 260 h of operation, indicating the need for alternative strategies to ensure a controlled and continuous metal biodissolution rate. The contribution of H_2SO_4 to the leaching processes for copper and nickel was almost negligible during the first 50 h, and more significant thereafter. The recovered metals were precipitated from a synthetic solution simulating a real ferric leaching by adding sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The combination of both precipitants allowed an effective removal of metals from the leachate.

Keywords: mobile phone PCBs; pretreatment; bioleaching; *A. ferrooxidans*; chemical precipitation; recycling



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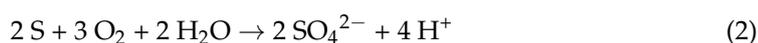
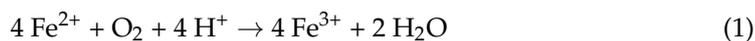
1. Introduction

Electrical and electronic equipment (EEE) includes all devices that require electric currents or electromagnetic fields in order to function properly, as well as units that generate, transmit and measure the aforementioned currents and fields. Since 2018, all EEE are classified within the six categories set out in Annex III of the Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on Waste Electrical and Electronic equipment (WEEE) [1]. Among them, the group whose widespread use across the globe has led to an exponential growth in recent decades is that of small information technology and telecommunication equipment. This group includes gadgets, such as mobile phones (smartphones, phablets, etc.), GPS and navigation equipment, personal computers, printers or telephones. Accordingly, the amount of e-waste generated by their consumption has also increased dramatically. In Spain alone, 32,726 t of e-waste were collected in 2018 (equivalent to 0.70 kg inhabitant⁻¹), which was 8057 t more than in 2017 and represents an increase of 105% since 2009 [2].

Waste printed circuit boards (WPCBs) are generated in the dismantling of this type of e-waste. A functional PCB comprises the integral component of any electronic equipment, as it electrically connects and mechanically supports the other electronic components [3]. It is essentially an electronic circuit laminated with copper, a glass-reinforced epoxy resin and flame-retardants, ceramic materials and a number of metallic materials, including base, precious and heavy metals [4,5]. In the case of mobile phone PCBs, the average composition by weight comprises metals 40–60%, polymers 13–30% and ceramics 24–30% [6,7]. Therefore, the WPCBs act as a rich secondary source of valuable metals, either because of their relatively high concentration (Cu, Al, Ni, Zn and Sn), or due to their high market price, even in extremely low concentrations (Au, Ag, Pt and Pd). In addition, hazardous metals, such as lead (Pb), mercury (Hg) and cadmium (Cd) can be also found in these devices, especially in those manufactured before 2006, when the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoSH) 1 Directive came into force and restricted the use of certain hazardous substances in the EEE [8]. In conclusion, despite their complex composition, metal recovery from WPCBs should be a priority in order to avoid the environmental impact of this waste that could, surprisingly, become a long-term profitable business.

Metal recycling technologies, such as pyrometallurgical and hydrometallurgical processes, have been extensively investigated in the literature. Chemical leaching prevails among the latter ones, employing mineral acids (hydrochloric acid, sulfuric acid or nitric acid) together with strong oxidants (hydrogen peroxide, ferric chloride or chlorine) for metal extraction from WPCBs [9]. However, given the environmental impact caused by the high consumption of reagents, industries are increasingly forced to move toward greener extraction technologies, such as bio-metallurgical processes [10].

Bearing in mind its capacity to carry out an environmentally safe regeneration of the oxidant agents, bioleaching has become a solid alternative, both from a sustainable and economic point of view, among biotechnologies with a potential for implementation [11,12]. Two commonly used microorganisms involved in this process include the sulfur-oxidizing bacterium *A. thiooxidans* and the sulfur- and iron-oxidizing bacterium *A. ferrooxidans* [12,13]. Both bacteria need the energy generated by the oxidation of elemental sulfur (Equation (1)) or ferrous iron (Equation (2)), rendering the reagents responsible for metal leaching.



Despite the promising results reported in the literature [10], bioleaching is still an immature technology, according to the technology readiness level scale [14]. There are many aspects to optimize before overcoming the “Valley of Death” and achieving Technology Readiness Level (TRL) 7 (system prototype demonstration in relevant environments). Thus, while several authors have demonstrated the efficiency of the bioprocess, only a few of them have studied the treatment of depleted solutions containing high concentrations of the dissolved metals that are responsible for bacterial inhibition [15–17].

Regarding metal recovery by chemical precipitation, several examples have been reported in the literature concerning the treatment of valuable metals in hazardous effluents of acid wastes. Tabak et al. (2003) [18] selectively recovered metals as hydroxides and sulfides from acid mine drainage impacted water by using potassium hydroxide (KOH) and biologically produced hydrogen sulfide (H₂S), respectively. Yang et al. (2017) [19] employed sodium sulfide (Na₂S) to precipitate fractionally Cu, Zn, Cd, Pb and As from Cu smelter dust after an acid leaching process.

Sodium sulfide (Na₂S) and sodium hydroxide (NaOH) are the most widely used precipitants when recovering metals. Although NaOH is considerably cheaper than the sulfide (40.6 € kg⁻¹ vs. 1016 € kg⁻¹), its dosage is limited by the possible resolubilization of many common metals present in WPCB leaching solutions, such as Cu, Ni or Zn, unless the pH is maintained within a narrow range [20,21]. This phenomenon can be

avoided with Na_2S , which forms metal sulfides precipitating at lower concentrations and generates a smaller volume of sludge [21,22]. The quantity of Na_2S to be added must, likewise, be controlled in order to prevent sulfide ion accumulation and the need for subsequent removal.

The aim of this work was to leach metals from mobile phone PCBs using two different solutions for comparison purposes. One of them contained ferric iron as the main oxidant and the bacteria *A. ferrooxidans* for regenerating the oxidant. The other one only contained sulfuric acid for studying the contribution of the acid medium. A previous decision about using the PCBs after grinding (powder sample) or after the removal of the epoxy layer without grinding (PCB pieces) was made. Once the metals were extracted, two alternatives for metal precipitation were selected: the individual or consecutive addition of NaOH and N_2S . This step was designed with a double objective: to precipitate iron and other metal compounds and to “clean” the solution for its ulterior discharge.

2. Materials and Methods

2.1. PCB Samples

A total amount of 29 obsolete Nokia mobile phones manufactured between 2000 and 2011 were collected from the local scrap market. A specific trademark was selected to delimit the commercialized models and seek to ensure similar PCB composition in all samples. Mobile phones were manually dismantled to separate PCBs (Figure 1).

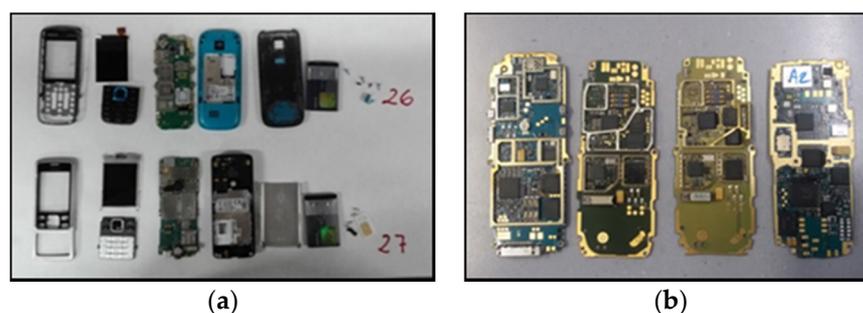


Figure 1. (a) Manual dismantling of mobile phones and (b) recovered PCBs.

The average weight of the PCBs was $16.0 (\pm 5.7)$ g, which represented approximately 19% of the total average weight of the complete mobile phone (82.6 ± 10.2 g). Among the wide variety of metals contained in the PCBs from mobile phones (Table 1), Al, Fe, Ni, Cu, Zn, Pd, Sn and Pb were selected to be quantified in this study.

Table 1. Average metal content (mg g^{-1} PCB) and market price (€ kg^{-1}) in mobile’s PCBs. (nm = not measured).

Metal	[7]	[23]	[24]	[25]	[26]	[27]	This Study	Price ^{a,b}
Cu	345	378	389	360	408	230	435 ± 54	7.7
Sn	nm	25.5	24.9	nm	16.0	nm	32.9 ± 3.7	26.6
Al	nm	6.1	9.6	6.6	nm	10.3	19.6 ± 0.9	2.0
Fe	105.7	48.5	107.9	10.5	2.8	38.3	12.6 ± 0.2	0.2 ^c
Ni	26.3	25.4	17.3	8.5	3.9	11.5	11.4 ± 1.1	14.5
Pb	18.7	nm	16.7	12.1	13.6	1.2	5.9 ± 1.4	1.8
Zn	nm	18.2	3.3	7.9	4.1	3.0	4.4 ± 1.1	2.4
Pd	nm	12.3	0.14	0.6	<0.1	nm	0.6 ± 0.1	69,090.7
Au	<0.01	0.9	1.6	0.1	<0.1	0.32	nm	46,977.8
Ag	2.1	0.5	4.0	0.3	1.1	nm	nm	698.9

^a Convert currency: 1 USD = 0.84 EUR; ^b Cash seller and settlement metal price (except for Fe) according to the London Metal Exchange (LME) (June 2021) [28]; ^c Price of iron ore (62% Fe), CFR China (TSI) (June 2021) [29].

The major element was copper, with an average content of $435.0 (\pm 54.0)$ mg g^{-1} PCB; an amount that is even higher than the pure copper amount contained in ores, such as chal-

copyrite [30]. The second metal was tin ($32.9 \pm 3.7 \text{ mg g}^{-1} \text{ PCB}$), which is conventionally used in welding processes.

2.2. Microorganisms and Culture Media

A. ferrooxidans DSM 14882 was acquired from the German collection Leibniz Institute DSMZ-German Collection of Microorganisms and Cell Cultures. Cells were cultured in the 9 K medium ($9 \text{ g Fe}^{2+} \text{ L}^{-1}$) [31]. The pH of the solution was adjusted to 1.8 with sulfuric acid (25% *v/v*).

2.3. PCB Sample Conditioning

Since most metals contained in PCB samples are immobilized under an epoxy cover, pre-treatment is mandatory for facilitating the access of leaching agents to the metals. Two different alternatives were tested: (1) mechanical grinding without any further treatment (powder PCB); and (2) chemical removal of the epoxy cover without grinding (entire PCB).

Regarding the sample grinding, PCB pieces were sliced into squares of $1 \text{ cm} \times 1 \text{ cm}$ and were consecutively crushed with three different mesh sizes (4 mm, 1.25 mm and 0.75 mm) using a RETSCH SM 2000 mill (RETSCH, Bilbao, Spain). Figure 2a shows the PCB particles according to their size. The particle-size distribution revealed that 60.7% of the crushed sample was in the smallest fraction (Supplementary data—Figure S1).

As far as the second alternative is concerned, the entire PCBs were immersed in a concentrated solution of sodium hydroxide (NaOH 10 M) under stirring for 72 h, with the objective of separating the protective layers of epoxy resin (Figure 2b) [32].



Figure 2. (a) Pulverized PCB sample according to particle size ($>1.25 \text{ mm}$, $1.25\text{--}0.75 \text{ mm}$ and $<0.75 \text{ mm}$) (1:30 magnification) and (b) entire PCB pieces ($3.5 \text{ cm} \pm 0.6 \text{ cm} \times 2.1 \text{ cm} \pm 0.1 \text{ cm}$) after treatment with a 10 M NaOH solution.

One-step bioleaching experiments (see Section 2.4.1) were conducted with both samples (powder PCB and entire PCB pieces) to analyze the effect of the pre-treatment method (Supplementary data—Figure S2). The rationale of selecting the Fe^{2+} containing medium was to let the microbes generate the oxidant for metal slow removal and to detect a possible inhibitory effect by the presence of the PCB.

2.4. Leaching Experiments

2.4.1. One-step Bioleaching Experiment

Biotic leaching experiments were carried out in 1 L Erlenmeyer flasks containing 350 mL of 9 K medium, where a 2% *v/v* of *A. ferrooxidans* in an exponential growth phase

was previously inoculated. An equivalent to the 3.5 g L^{-1} pulp density of the PCB powder sample or PCB piece was introduced into each Erlenmeyer. Both reactors were incubated at $31 \text{ }^\circ\text{C}$ and with 130 rpm orbital shaking. A pH threshold value of 1.8 was maintained by the continuous addition of sulfuric acid (25% *v/v*) (GLP 21+ pH-meter equipped with a sensION+ 5014T glass combination pH electrode, Crison, Spain). The removal efficiency for each metal was calculated as follows:

$$\text{Metal removal efficiency (\%)} = \left(\frac{C \cdot V}{C_{\text{in}} \cdot M} \right) \cdot 100 \quad (3)$$

where C is the metal concentration at the time of sampling (mg L^{-1}), V is the volume of the leaching solution (L), M is the amount of the solid sample (i.e., PCB powder or piece) involved in the leaching process (g) and C_{in} is the metal concentration in the original PCB sample.

2.4.2. Two-Step Bioleaching Experiment

The solubilization of the metals contained in the PCB pieces was carried out in a two-step procedure. First, 9 K medium was inoculated with a 2% *v/v* of *A. ferrooxidans* culture in the exponential growth phase until the complete oxidation of Fe^{2+} to Fe^{3+} was achieved (step 1), and, once Fe^{2+} was oxidized to Fe^{3+} , the bioleaching of the workpiece was then performed (step 2) at $31 \text{ }^\circ\text{C}$, 130 rpm orbital shaking and a pH of 1.8.

2.4.3. Leaching Experiments in Abiotic Medium

For comparison purposes, a blank experiment was conducted with biogenic Fe^{3+} but without the presence of bacteria. Thus, after the iron biooxidation, the solution was filtered with $0.45 \text{ }\mu\text{m}$ polyvinylidene fluoride filter while maintaining a constant pH at 1.8.

The treated PCB piece and detached electronic circuitry scraps were removed from both the biotic and abiotic two-step procedures once the experiments were finished, rinsed with deionized water and ethanol (96%), dried and characterized by X-ray fluorescence (XRF, Malvern Panalytical, Leioa, Spain). The precipitates formed during the leaching processes were also recovered and separated by filtration (Filter-Lab No. 1240 filter paper with a 7–9 μm pore diameter), then washed and dried. Elemental analysis and phase identification of the obtained powdery product was carried out by combining XRF and X-ray diffraction (XRD, Malvern Panalytical, Leioa, Spain) techniques.

Bearing in mind that sulfuric acid (H_2SO_4) is the other main reagent of biological origin responsible for metal leaching, another experiment was performed with the objective of assessing the contribution of this acid in the process performance. Thus, an abiotic leaching medium containing H_2SO_4 (2% *v/v*) was prepared and subsequently, the PCB workpiece was immersed into 350 mL of this acid solution. The same conditions ($31 \text{ }^\circ\text{C}$ and 130 rpm orbital shaking) were applied for the PCB pieces tested in the latter two experiments. In both cases, samples were collected from the medium on a regular basis to analyze their metal content (Cu, Fe, Ni, Zn and Pb) after filtration.

2.5. Chemical Precipitation Experiments for Metal Extraction

A leaching liquor residue containing Fe, Cu, Ni and Zn was synthesized in the laboratory, simulating the real solution obtained from the abiotic experiment with biogenic Fe^{3+} (see Section 2.4.3). Taking into account that Fe^{3+} selective precipitation over other metals, such as Cu and Zn, is more efficient in comparison with Fe^{2+} , all iron was present in its oxidized form [33]. In previous studies by the authors, the Cu solubilization rate was significantly reduced when the iron speciation ($\text{Fe}^{3+}/\text{Fe}^{2+}$ mass ratio) dropped below 2:1 in real bioleaches. In that case, sample pre-oxidation by means of H_2O_2 has been recommended for iron oxidation prior to chemical precipitation experiments [33,34]. Other minor metallic elements of the medium were not considered in this study. The pH was adjusted to 1.7 by adding H_2SO_4 (25% *v/v*).

Chemical precipitation experiments were performed with both sodium hydroxide (NaOH) and sodium sulfide (Na₂S) (individually or combined). Each experiment was conducted with a sample volume of 50 mL at room temperature under stirring conditions.

2.6. Analytical Methods

The metal content in the leaching solutions and the original PCB samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer, Bilbao, Spain) with a Perkin Elmer Optima 2000 OV equipment provided with a Scott spray chamber/nebulizer. In the latter case of the PCB samples, the finest fraction (<0.75 mm) was digested in aqua regia (HNO₃:HCl, 1:3 *v:v*) at 150 °C for 3 h (Ethos Advanced microwave).

The solids generated in the biotic (i.e., two-step bioleaching experiment) and abiotic (i.e., biogenic Fe³⁺ without bacteria) leaching solutions were identified by the XRD patterns that were obtained using a PANalytical Xpert PRO diffractometer (Malvern Panalytical, Leioa, Spain) with theta-theta configuration. This instrument was equipped with a secondary graphite monochromator adjusted to copper radiation and a PixCel solid-state fast detector, set to an active length of 2θ of 3.347°. Semi-quantitative chemical analysis of solid residues comprising remnants of PCB pieces, detached electronic circuitry scraps (e.g., integrated circuit components and submillimetric components) and precipitates was determined with a sequential fluorescence sequence X-ray Wavelength (XRF) spectrometer (PANalytical Axios mAX-Advanced), equipped with an automatic sample changer, vacuum measurement system, Rh tube and three detectors (gas flow, scintillation and sealing of Xe).

The redox potential was recorded with a Thermo-Orion 920+ instrument equipped with an Orion 9778BNWPO Sur-Flow[®] electrode with epoxy body (combination of a platinum redox and a silver/silver chloride reference electrode in one body (Ag/AgCl, 4 M KCl)). All potentials in this paper are given with respect to the reference electrode (+220 mV vs. Ag/AgCl).

3. Results and Discussion

3.1. Effect of the Pre-Treatment

PCB sample pulverization has been traditionally proposed as a prerequisite for improving the efficiency of metal bioleaching [27,35,36], and, only recently, several authors have incorporated the use of entire PCB pieces for this process [37,38].

The copper removal efficiency when using the PCB powder and the PCB piece in the bioleaching experiments is shown in Figure 3. The pulverized sample rendered a slightly higher removal efficiency in comparison with the non-pulverized one after 350 h of treatment (78.3% vs. 67.9%). This result revealed that the presence of the epoxy layer did not inhibit microbial activity by the end of the experiments. As expected, a smaller particle size allowed for a greater surface area and, consequently, closer contact between the powder and the leaching solution.

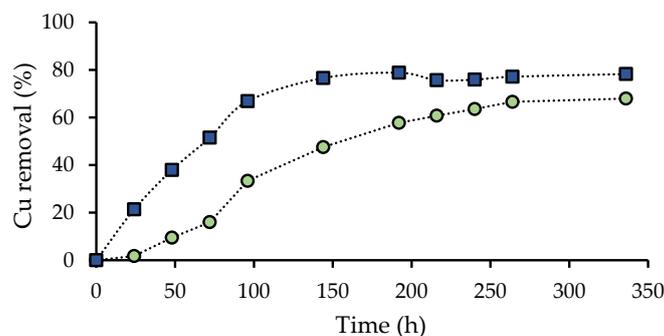


Figure 3. Cu removal efficiency during the bioleaching experiments for the PCB powder sample (blue square) and the PCB piece without epoxy layer (green circle).

In any case, previous studies attributed such removal efficiency differences to the operative variability of biological processes [39,40]. In addition, the crushing step to ensure the complete liberation (>99%) of copper and ferromagnetic metals contained in PCB samples [41] contributed to an important loss of material (about 15%). Taking into account that the pulverization pre-treatment entailed a high energy consumption and the additional complexity of separating the non-metallic materials from the precipitate formed during the bioleaching process, the use of epoxy-free PCB pieces was recommended for further bioleaching experiments.

In addition to copper, other minor metals were simultaneously bioleached, such as nickel, zinc or lead, among others. Comparative values obtained by the end of the experiment for Zn, Ni and Pb are shown in Table 2.

Table 2. Metal removal efficiency values obtained for Cu, Zn, Ni and Pb.

Metal	Removal Efficiency (%)	
	PCB Piece	Powder PCB
Cu	67.9	78.2
Ni	36.7	54.1
Zn	52.8	33.8
Pb	2.9	13.9

The bioleaching efficiencies obtained in this study were lower than those achieved by Shah et al. (2014) [25], who reported a Cu, Zn and Ni removal of 87.5%, 85.7% and 81.9%, respectively, by one-step bioleaching after 360 h (9 g Fe L⁻¹, 10 g powder L⁻¹, pH 1.8). This difference could be attributed to the use of an iron oxidizing and multi-metal resistant microbial culture adapted to PCB in their experiments.

3.2. Effect of the Presence of *A. Ferrooxidans* Activity and the Leaching Agent

One of the main drawbacks for continuous long-operation in bioleaching processes, even under optimum operating conditions, is the decrease in the amount of mobilized metal as a consequence of the relatively low bioregeneration rate of the oxidant in comparison with the fast chemical metal leaching option, which results in an inability to keep iron ions in the higher oxidized state and a significant reduction in the bacterial contribution to the corrosion process. Wu et al. (2018) [42] demonstrated that biooxidation of Fe²⁺ to Fe³⁺ was the rate-limited step in Cu bioleaching from PCBs. This technical pitfall is clearly observed in the evolution of the redox potential (Figure 4), which has been previously used as an indicator of the status of the Cu leaching progress by linking the redox potential (vs. Ag/AgCl) and the logarithm of Fe³⁺/Fe²⁺ ratio [34].

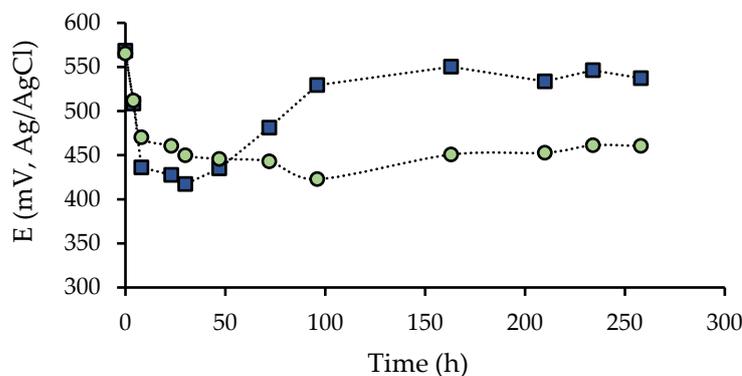


Figure 4. Evolution of the redox potential during the two-step leaching experiment in the biotic (blue square) and abiotic (green circle) media when using biogenic Fe³⁺ as the leaching agent.

In the biotic case, it took 96 h for the redox potential to reach the original value indicative of the complete conversion of Fe^{2+} into Fe^{3+} (550 ± 20 mV). It can be concluded that during this 96 h period the oxidant concentration was variable and metals such as Cu (74.6%) and Ni (90.1%) were extracted (Figure 5a,b), resulting in the microbial activity for regenerating the oxidant becoming irrelevant. Once the metal source progressively decreased and the oxidant consumption slowed down, the biooxidation of the Fe^{2+} into Fe^{3+} had an effect on the redox potential, rendering higher values. Similarly, the redox potential of the biogenic ferric iron control experiment decreased to its lowest value (422.8 mV vs. Ag/AgCl) in the same time period. The subsequent increase up to 460.4 mV (260 h) could be attributed to the spontaneous oxidation of Fe^{2+} to Fe^{3+} in the presence of the oxygen that was dissolved in the acid medium.

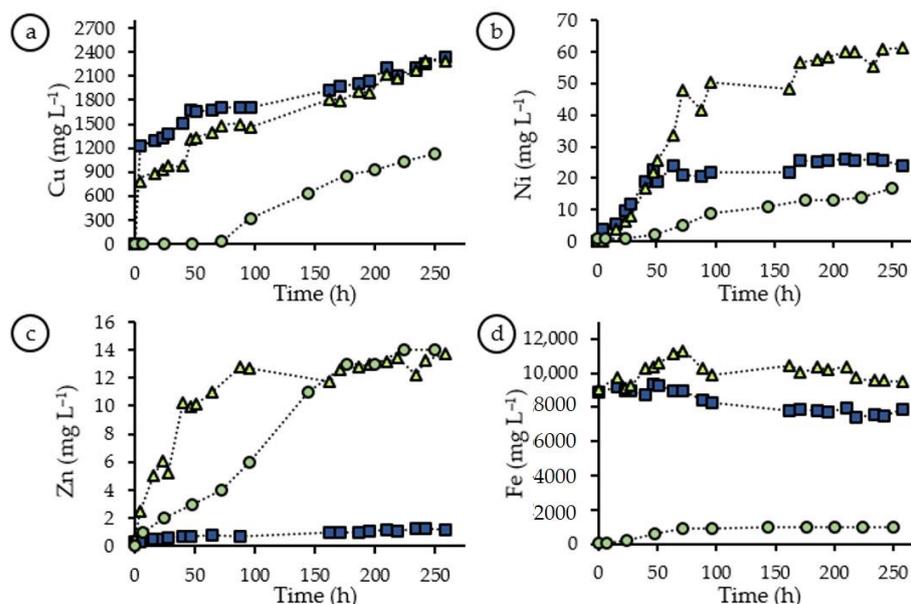


Figure 5. Extracted amount of (a) copper, (b) nickel and (c) zinc, and (d) total iron concentration during the two-step bioleaching experiment (blue square) and leaching experiments in abiotic medium employing biogenic Fe^{3+} (yellow triangle) or H_2SO_4 (green circle) as leaching agents.

In the case of copper dissolution in the presence of bacteria, the metal removal rate peaked during the first 4 h ($309 \text{ mg Cu L}^{-1} \text{ h}^{-1}$) and decreased significantly ($<6 \text{ mg Cu L}^{-1} \text{ h}^{-1}$) in the following 12 h (Figure 5a). After 218 h, the extracted amount of copper differed by less than 2% in Fe^{3+} biotic and abiotic medium, revealing the poor contribution of the suspended biomass to the copper solubilization rate [43].

Conversely, the nickel bioleaching rate remained constant throughout the whole experiment (in the range of $0.46\text{--}0.49 \text{ mg Ni L}^{-1} \text{ h}^{-1}$) (Figure 5b). A higher amount of Ni was obtained ($61.4 \text{ mg}\cdot\text{L}^{-1}$ vs. 26.2 mg L^{-1}) in the chemical leaching in comparison with the bioleaching solution, which was attributed to the inherent heterogeneity of the PCB pieces. In the same vein, no zinc was found in the sample introduced in the two-step bioleaching medium, while up to 5.3 mg were leached from the PCB piece attacked with biogenic Fe^{3+} without bacteria (Figure 5c).

Regarding the metal leaching efficiency by means of H_2SO_4 , the contribution of this acid to the solubilization process was almost negligible during the first 50 h in the case of Cu and Ni. The amount of Zn (61.6 mg) extracted in the abiotic ferric solution and in the acid solution only equaled after 130 h. These results are similar to those obtained by Jadhav and Hocheng (2015) [44], who studied the capacity of H_2SO_4 to remove metals from PCB pieces ($4 \text{ cm} \times 4 \text{ cm}$) previously treated with 10 M NaOH. These authors reported a Cu removal efficiency of 8.8% after 96 h. Likewise, Van Yken et al. (2020) [45] reported a low

leaching yield after 48 h for Cu (23.2%) and Ni (29.6%), using diluted H_2SO_4 at pH 1.4 (milled PCBs, 1% pulp density, 25 °C and 200 rpm).

As far as iron is concerned, the formation and precipitation of jarosite was observed in samples containing 9 K medium (with and without bacteria) at the end of both experiments, despite the continuous pH readjustment when its value was above the 1.8 threshold limit (Figure 6a,b) [43]. The pH increase during the first 88 h and its subsequent decline in the following hours was associated with the alkaline nature of the WPCBs and the hydrolysis of ferric ions, respectively [46,47]. In fact, Priya and Hait [46] described ferric hydroxide ($\text{Fe}(\text{OH})_3$) as precursor in the formation of jarosite.

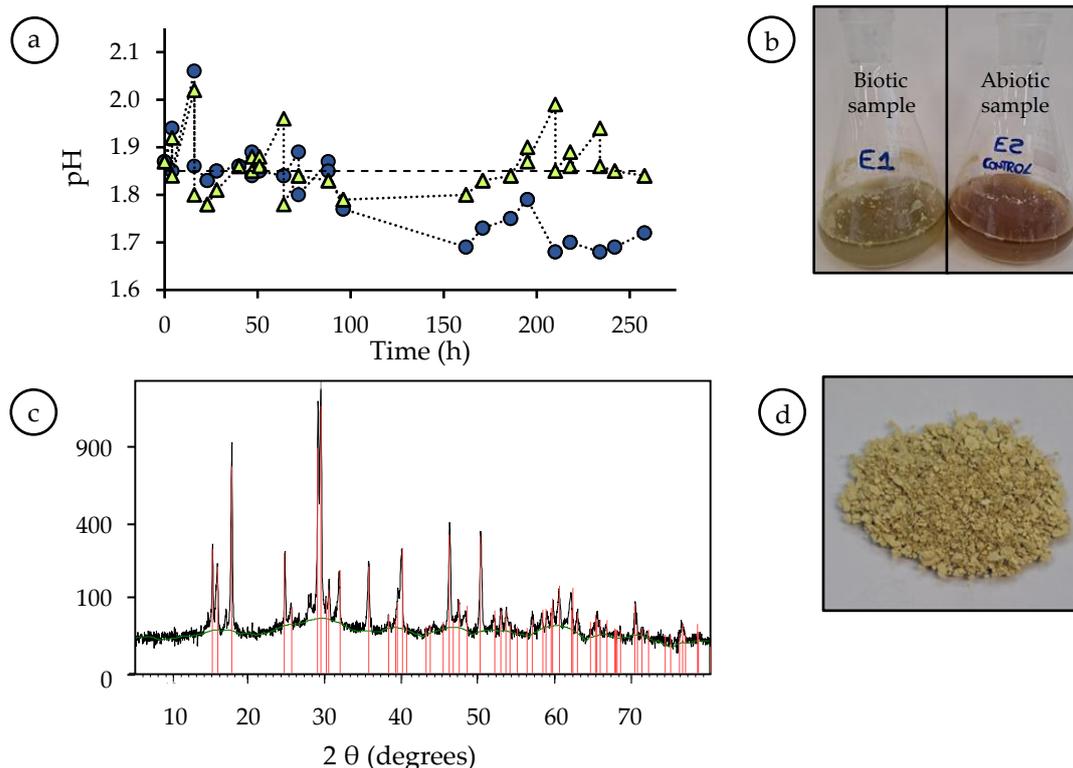


Figure 6. (a) pH evolution during the two-step leaching experiment in biotic (blue square) and abiotic (green circle) 9 K medium and (b) appearance of the leaching solutions when using Fe^{3+} as oxidant after 260 h. (c) XRD patterns for (d) solid precipitated at the end of the experiments (black line) and rhombohedral $\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$ jarosite (PDF: 36–427) (red line).

The mustard-colored solid precipitated in the Erlenmeyer flasks (Figure 6b) was identified by XRD as a compound related to the jarosite-group minerals with the chemical formula $\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$ (Figure 6c,d). The formation of Fe(III)-hydroxysulfate mineral precipitates is a common undesired phenomenon in numerous industrial processes involving bacterial cultures in acidic and sulfate-rich environments (e.g., biological gas desulfurization), irrespective of the absence of sulfur or reduced sulfur compounds in the bioleached sample [43,48].

The appearance of this solid reduced the content of dissolved iron in the biological 9 K medium below 7.9 g L^{-1} , which entailed a decrease in the oxidant availability of 17.2% in comparison with the abiotic experiment (Figure 5d). As Bao et al. (2018) [49] concluded, extracellular polymeric substances (EPS) secreted by microorganisms play a pivotal role in jarosite formation, shortening the induction phase of the mineral synthesis and consequently reducing the ferric iron amount in the leaching medium. The chemical composition of the jarosite-like residues determined by XRF spectroscopy in this study mainly contained Fe, S, K, Sn and Cu along with a negligible presence of other lixiviated metals (Ni, Zn and Pb) (Table 3).

Table 3. Elemental composition (wt%) of jarosite samples recovered from the two-step leaching experiments.

	Fe	S	K	Sn	Cu	Ba	Ni	Ag	Ti	Ta	Au	Si	Zn	Nb
Biologically promoted jarosite	39.8	10.1	4.23	0.63	0.61	0.34	0.10	0.09	bdl	bdl	0.04	0.05	0.02	bdl
Non-biologically promoted jarosite	39.0	10.8	4.06	0.67	0.53	bdl	bdl	0.08	0.05	0.07	bdl	0.03	bdl	0.02

bdl = below detection limit

As far as lead is concerned (Supplementary data—Figure S3), the content of soluble Pb was lower 2 mg L^{-1} in the experiments with Fe^{3+} as the leaching agent. The presence of this metal in the sulfuric acid leachate was not observed due to the formation of water insoluble species (i.e., PbSO_4 , $K_{ps} 1.8 \times 10^{-8}$) [50]. This whitish solid was not visually observed in the biogenic ferric leachate because it appeared together with the jarosite.

The complete detachment of the components integrated in the PCB pieces occurred after leaching (Figure 7a,b). Thus, electronic components, such as resistors and microchips were detached by a combination of the orbital shaking and the solubilization of the welding metals [36]. Considering the total mass of the eroded circuit board and the separated components, a weight loss of 0.73 g (37.1%) and 0.93 g (42.4%) was registered in biotic and abiotic 9 K medium, respectively, after 260 h.

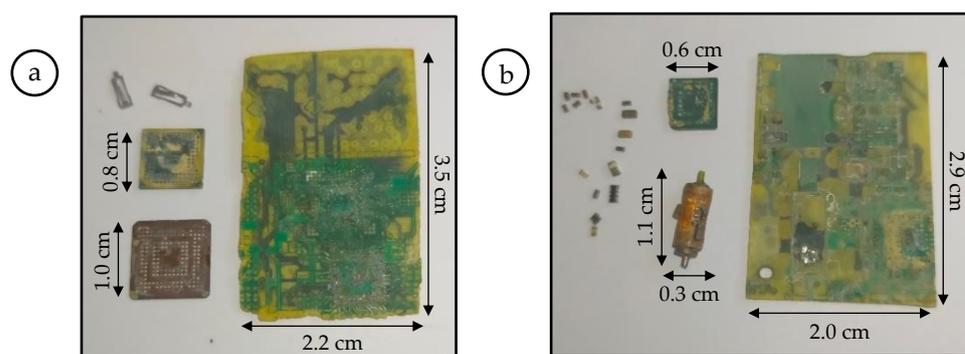


Figure 7. Eroded circuit board and detached pieces (e.g., attachment clips, microchips, capacitors and submillimetric components, such as resistors) after leaching with Fe^{3+} in (a) biotic and (b) abiotic medium.

The characterization of the circuit boards (Figure 8a,b) after the ferric leaching process showed that plastic was the main component, which suggested an effective lixiviation of the most abundant metals contained in the original samples (Table 1). Similarly, the relevant concentration of Ba and S (especially in detached pieces, such as microchips and submillimetric components (Supplementary data—Tables S1 and S2)) might indicate that the remaining quantities of metals (e.g., Cu and Sn) could still be embedded in the solder mask of the PCB, which is typically filled with barium sulfate (BaSO_4) as a fire retardant [51].

Regarding aluminum extraction, the absence of this metal in the treated PCB pieces (<0.1%, excluding plastic), despite being one of the most abundant metals in the original sample, was indicative of its priority oxidation in comparison with more electropositive metals, such as Cu [52]. These results are consistent with those reported by Van Yken et al. (2020) [45] who obtained relatively high leaching yields at 10 g L^{-1} of biogenic Fe^{3+} concentration (pH of 1.2) for Al (75.3%), Zn (78.1%) and Ni (60.5%).

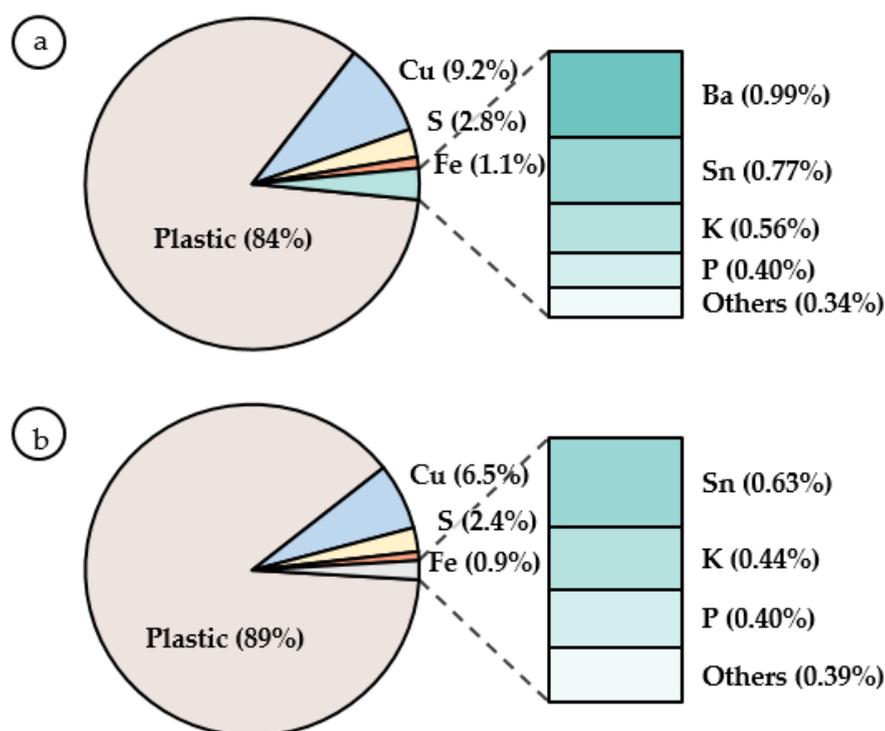


Figure 8. Elemental composition (wt%) of the treated circuit board after leaching with Fe^{3+} in (a) biotic and (b) abiotic medium.

3.3. Effect of the Precipitating Agent

Chemical precipitation in the form of poorly soluble metal hydroxides or sulfides is one of the most effective methods for treating heavy metal in wastewaters [33]. Lime ($\text{Ca}(\text{OH})_2$) and caustic soda (NaOH) are the most widely used hydroxide precipitants, while sodium sulfide (Na_2S), sodium hydrosulfide (NaHS) and sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) are typically applied in sulfide precipitation processes [53].

The removal efficiency of metals (Cu, Fe, Ni and Zn) by sulfide and hydroxide precipitation according to the precipitant concentration (Na_2S or NaOH) is presented in Figure 9a,b. Regardless of the low concentration of Ni and Zn concentrations in the ferric leaching system (Figure 5b,c), the precipitation of both elements remained relatively poor at Na_2S or NaOH concentrations below 10 g L^{-1} . Metal precipitation efficiency exceeded 90% in all cases at a concentration of 15 g NaOH L^{-1} , but only 59% of Fe precipitated with the same concentration of Na_2S . Nevertheless, when a higher amount of NaOH was added to the leachate (30 g L^{-1}), 19.2% of Zn was solubilized again in the medium.

According to the results of the sulfide precipitation experiment, a high amount of Cu (92.6%) and Zn (78.3%) was recovered when the pH was above 5.0 (5.05). Ye et al. (2017) [54] investigated the selective recovery of Fe (9.16 g L^{-1}), Zn (0.55 g L^{-1}), Cu (13.10 mg L^{-1}) and Pb (5.18 mg L^{-1}) in a bioleachate by the addition of Na_2S . The metals Zn, Cu and Pb quantitatively precipitated at an approximate pH of 4.50 and $12.5 \text{ g Na}_2\text{S L}^{-1}$. On the other hand, Wang and Cheng (2019) [33] reported that Zn started to precipitate only after the pH was raised above 6.0 in a 4.63 g Zn L^{-1} solution (338 times higher than Zn concentration in this study).

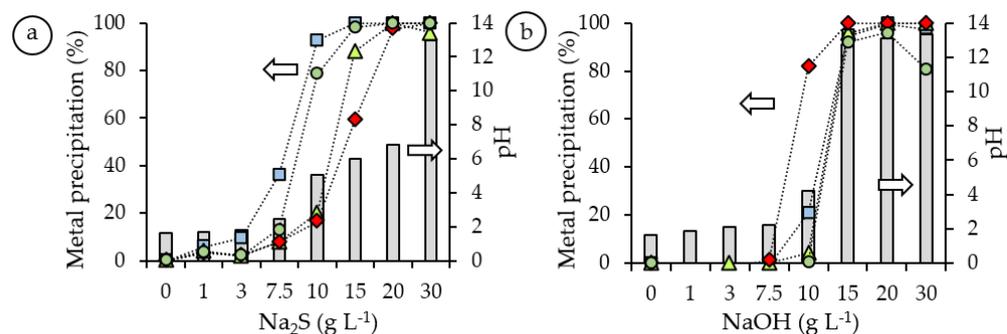


Figure 9. Effect of (a) Na_2S and (b) NaOH dosage on metal precipitation yield (circles (Cu (blue square), Fe (red diamond), Ni (yellow triangle) and Zn (green circle))) and pH evolution (columns).

On the basis of these results, an additional experiment was performed combining both precipitants. Thus, the experimental process involved, first, the addition of NaOH until a constant pH value of 4.0 was reached with the objective of precipitating all the iron and avoiding the simultaneous precipitation of other metals [55]. As a result, 85.7% of the Fe contained in the solution was precipitated (Figure 10). However, as demonstrated by Wang and Chen [33], the higher the initial concentration of the metal ion, the lower the pH when it starts to precipitate. Thus, Cu (20.7%) and Ni (9.2%) partially coprecipitated during this first step.

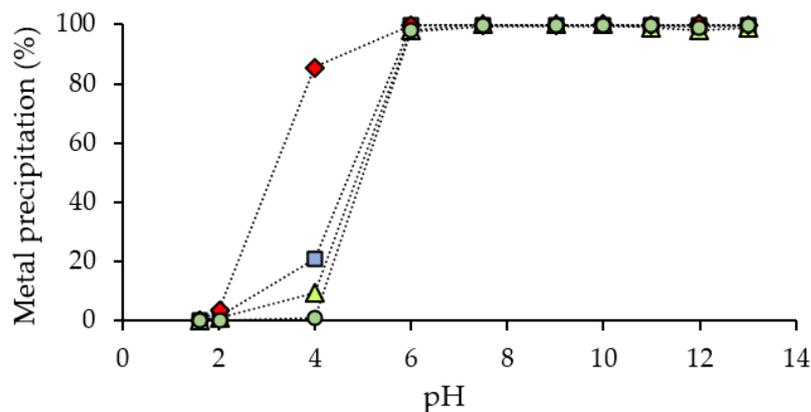


Figure 10. Metal precipitation efficiency (Cu (blue square), Fe (red diamond), Ni (yellow triangle) and Zn (green circle)) when combining NaOH and Na_2S as precipitant agents.

Subsequently, Na_2S was added to the solution with the objective of precipitating the other metals at pH 6.0. The precipitation efficiency recorded for Cu, Zn and Ni sulfides was 99.9%, 99.4% and 99.0%, respectively. An additional advantage of increasing the pH with NaOH before the sulfide precipitation was avoiding the generation of gaseous H_2S , widely known as a flammable, corrosive and highly toxic compound [56].

4. Conclusions

Metal recovery from obsolete printed circuit boards (PCBs) can significantly contribute to avoiding the depletion of natural sources and the hazardous disposal of this electronic waste. The bioleaching (or biohydrometallurgical) strategy for the PCB recycling is gaining relevance for its benefits in the environmental, human health protection and economic spheres. Nevertheless, the heterogeneity of the waste to be treated, in terms of size, shape and composition, together with the limitation of treating low quantities hinder the further scale-up.

In this study, several PCBs from disused mobile phones were grinded for homogenization. After acid digestion of the powder sample, the major element was found to be Cu

with an average content of $435 (\pm 54) \text{ mg g}^{-1}$, which was within the range published in the literature.

In addition to the powder sample, PCB pieces without the epoxy layer were also tested for the bioleaching experiments. The grinded sample rendered a higher Cu removal efficiency than the PCB pieces (78.3% vs. 67.9%), being that the difference was more noticeable during the first 150 h. Despite these results, the removal of the epoxy layer and the use of the pieces without grinding were selected for the ulterior extraction processes because it facilitated the management and separation of the pieces from the leaching medium and it also provided a “cleaner” medium for the microbial activity.

The bacteria *A. ferrooxidans* boosted the solubilization of Cu during the first hours in the two-step bioleaching experiments. Nevertheless, the total amount of Cu dissolved after 260 h differed by less than 2% in the biotic and abiotic ferric medium. The concentration of iron in the biotic medium (containing *A. ferrooxidans* and Fe^{3+}) decreased below 7.9 g L^{-1} due to the jarosite precipitation which was favored by the microbial presence. This phenomenon entailed a reduction in the Fe availability of 17.2% in comparison with the abiotic experiment.

Once the metals were leached, the partial separation of metal compounds was performed by adding NaOH and Na_2S as precipitating reagents in two pH dependent steps. About 85.7% Fe was precipitated after the NaOH addition at pH 4.0. When Na_2S was added subsequently, the precipitation efficiency for Cu, Zn and Ni sulfides was 99.9%, 99.4% and 99.0%, respectively. The main drawback of this process is the unavoidable coprecipitation, although it contributed to “cleaning” the solution for its proper discharge.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11091004/s1>, Figure S1: Particle-size distribution of pulverized PCB. Figure S2: A schematic flowchart illustrating the experimental design. Figure S3: (a) Lead concentration during the two-step bioleaching experiment (blue square) and leaching experiments in abiotic medium, employing biogenic Fe^{3+} (yellow triangle) or H_2SO_4 (green circle) as leaching agents. (b) PbSO_4 precipitate formed in the leaching medium containing H_2SO_4 . Table S1: Elemental composition (wt%) of microchip pieces detached from PCBs after leaching with Fe^{3+} , Table S2: Elemental composition (wt%) of submillimetric components detached from PCBs after leaching with Fe^{3+} .

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References

1. European Parliament, Council of the European Union. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on Waste Electrical and Electronic Equipment (WEEE). Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0019> (accessed on 28 July 2021).
2. Eurostat. Waste Electrical and Electronic Equipment (WEEE) by Waste Management Operations. Available online: https://ec.europa.eu/eurostat/databrowser/view/ENV_WASELEE__custom_174344/default/table?lang=en (accessed on 28 July 2021).
3. Ghosh, B.; Ghosh, M.K.; Parhi, P.; Mukherjee, P.S.; Mishra, B.K. Waste Printed Circuit Boards recycling: An extensive assessment of current status. *J. Clean Prod.* **2015**, *94*, 5–19. [[CrossRef](#)]
4. Evangelopoulos, P.; Persson, H.; Kantarelis, E.; Yang, W. Performance analysis and fate of bromine in a single screw reactor for pyrolysis of waste electrical and electronic equipment (WEEE). *Process Saf. Environ.* **2020**, *143*, 313–321. [[CrossRef](#)]

5. Hao, J.; Wang, Y.; Wu, Y.; Guo, F. Metal recovery from waste printed circuit boards: A review for current status and perspectives. *Resour. Conserv. Recy.* **2020**, *157*, 104787. [CrossRef]
6. Palmieri, R.; Bonifazi, G.; Serranti, S. Recycling-oriented characterization of plastic frames and printed circuit boards from mobile phones by electronic and chemical imaging. *Waste Manag.* **2014**, *34*, 2120–2130. [CrossRef] [PubMed]
7. Yamane, L.H.; de Moraes, V.T.; Espinosa, D.C.R.; Tenório, J.A.S. Recycling of WEEE: Characterization of spent printed circuit boards from mobile phones and computers. *Waste Manag.* **2011**, *31*, 2553–2558. [CrossRef] [PubMed]
8. European Parliament and the Council of the European Union. Directive 2002/95/EC of the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32002L0095&from=SV> (accessed on 28 July 2021).
9. Birloaga, I.; Veglio, F. Study of multi-step hydrometallurgical methods to extract the valuable content of gold, silver and copper from waste printed circuit boards. *J. Environ. Chem. Eng.* **2016**, *4*, 20–29. [CrossRef]
10. Diaz-Tena, E.; Barona, A.; Gallastegui, G.; Rodriguez, A.; Lopez de Lacalle, L.N.; Elias, A. Biomachining: Metal etching via microorganisms. *Crit. Rev. Biotechnol.* **2017**, *37*, 323–332. [CrossRef]
11. Díaz-Martínez, M.E.; Argumedo-Delira, R.; Sánchez-Viveros, G.; Alarcón, A.; Mendoza-López, M.R. Microbial bioleaching of Ag, Au and Cu from printed circuit boards of mobile Phones. *Curr. Microbiol.* **2019**, *76*, 536–544. [CrossRef]
12. Priya, A.; Hait, S. Comparative assessment of metallurgical recovery of metals from electronic waste with special emphasis on bioleaching. *Environ. Sci. Pollut. Res. Int.* **2017**, *24*, 6989–7008. [CrossRef] [PubMed]
13. Annamalai, M.; Gurumurthy, K. Enhanced bioleaching of copper from circuit boards of computer waste by *Acidithiobacillus ferrooxidans*. *Environ. Chem. Lett.* **2019**, *17*, 1873–1879. [CrossRef]
14. NASA. Technology Readiness Level. Available online: https://www.nasa.gov/directorates/heo/scan/engineering/technology/txt_accordion1.html (accessed on 28 July 2021).
15. Kaksonen, A.H.; Lavonen, L.; Kuusenaho, M.; Kolli, A.; Närhi, H.; Vestola, E.; Puhakka, J.A.; Tuovinen, O.H. Bioleaching and recovery of metals from final slag waste of the copper smelting industry. *Min. Eng.* **2011**, *24*, 1113–1121. [CrossRef]
16. Ye, M.; Yan, P.; Sun, S.; Han, D.; Xiao, X.; Zheng, L.; Huang, S.; Chen, Y.; Zhuang, S. Bioleaching combined brine leaching of heavy metals from lead-zinc mine tailings: Transformations during the leaching process. *Chemosphere* **2017**, *168*, 1115–1125. [CrossRef]
17. Santaolalla, A.; Rojo, N.; Gutierrez, J.; Barona, A. Immobilization of *Acidithiobacillus ferrooxidans* on two hydrogels. *Chem. Eng. Trans.* **2020**, *79*, 7–12.
18. Tabak, H.H.; Scharp, R.; Burckle, J.; Kawahara, F.K.; Govind, R. Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle. *Biodegradation* **2003**, *14*, 423–436. [CrossRef] [PubMed]
19. Yang, T.; Fu, X.; Liu, W.; Chen, L.; Zhang, D. Hydrometallurgical treatment of copper smelting dust by oxidation leaching and fractional precipitation technology. *JOM* **2017**, *69*, 1982–1986. [CrossRef]
20. Bilgin, A.; Jaffé, P.R. Precipitation of copper (II) in a two-stage continuous treatment system using sulfate reducing bacteria. *Waste Biomass Valorization* **2019**, *10*, 2907–2914. [CrossRef]
21. Wang, L.K.; Vaccari, D.A.; Li, Y.; Shammass, N.K. Chemical precipitation. In *Physicochemical Treatment Processes*; Wang, L.K., Hung, Y.T., Shammass, N.K., Eds.; Humana Press: Totowa, NJ, USA, 2004; Volume 3, pp. 141–198.
22. Zainuddin, N.A.; Mamat, T.A.R.; Maarof, H.I.; Puasa, S.W.; Yatim, S.R.M. Removal of nickel, zinc and copper from plating process industrial raw effluent via hydroxide precipitation versus sulphide precipitation. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *551*, 12122. [CrossRef]
23. Kasper, A.C.; Berselli, G.B.T.; Freitas, B.D.; Tenorio, J.A.S.; Bernardes, A.M.; Veit, H.M. Printed wiring boards for mobile phones: Characterization and recycling of copper. *Waste Manag.* **2011**, *31*, 2536–2545. [CrossRef] [PubMed]
24. Le, H.-L.; Okumura, H.; Ishihara, K.N. MEMRECS—A sustainable view for metal recycling from waste printed circuit boards. *J. Environ. Prot. Sci.* **2013**, *4*, 803–810. [CrossRef]
25. Shah, M.B.; Tipre, D.R.; Dave, S.R. Chemical and biological processes for multi-metal extraction from waste printed circuit boards of computers and mobile phones. *Waste Manag. Res.* **2014**, *32*, 1134–1141. [CrossRef]
26. Xiu, F.R.; Qi, Y.; Zhang, F.S. Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pre-treatment. *Waste Manag.* **2015**, *41*, 134–141. [CrossRef]
27. Isildar, A.; van de Vossenbergh, J.; Rene, E.R.; van Hullebusch, E.D.; Lens, P.N.L. Two-step bioleaching of copper and gold from discarded printed circuit boards (PCB). *Waste Manag.* **2016**, *57*, 149–157. [CrossRef]
28. LME (London Metal Exchange). LME COPPER. 2021. Available online: <https://www.lme.com/en-GB/Metals/Non-ferrous/Copper#tabIndex=0> (accessed on 28 July 2021).
29. Financial Times. Available online: <https://www.ft.com/> (accessed on 28 July 2021).
30. Hernández, P.C.; Taboada, M.E.; Herreros, O.O.; Graber, T.A.; Ghorbani, Y. Leaching of chalcopyrite in acidified nitrate using seawater-based media. *Minerals* **2018**, *8*, 238. [CrossRef]
31. Silverman, M.P.; Lundgren, D.G. Studies on the chemoautotrophic iron bacterium *Ferroplasma ferrooxidans*: I. An improved medium and a harvesting procedure for securing high cell yields. *J. Bacteriol.* **1959**, *77*, 642–647. [CrossRef] [PubMed]
32. Adhasure, N.N.; Dhakephalkar, P.K.; Dhakephalkar, A.P.; Tembhurkar, V.R.; Rajgure, A.V.; Deshmukh, A.M. Use of large pieces of printed circuit boards for bioleaching to avoid ‘precipitate contamination problem’ and to simplify overall metal recovery. *MethodsX* **2014**, *1*, 181–186. [CrossRef]

33. Wang, L.P.; Chen, Y.J. Sequential precipitation of iron, copper, and zinc from wastewater for metal recovery. *J. Environ. Eng.* **2019**, *145*, 1–11. [[CrossRef](#)]
34. Díaz-Tena, E.; Gallastegui, G.; Hipperdinger, M.; Donati, E.R.; Ramírez, M.; Rodríguez, A.; López de Lacalle, L.N.; Elías, A. New advances in copper biomachining by iron-oxidizing bacteria. *Corros. Sci.* **2016**, *112*, 385–392. [[CrossRef](#)]
35. Zhu, N.; Xiang, Y.; Zhang, T.; Wu, P.; Dang, Z.; Li, P.; Wu, J. Bioleaching of metal concentrates of waste printed circuit boards by mixed culture of acidophilic bacteria. *J. Hazard. Mater.* **2011**, *192*, 614–619. [[CrossRef](#)]
36. Priya, A.; Hait, S. Extraction of metals from high grade waste printed circuit board by conventional and hybrid bioleaching using *Acidithiobacillus ferrooxidans*. *Hydrometallurgy* **2018**, *177*, 132–139. [[CrossRef](#)]
37. Monneron-Enaud, B.; Wiche, O.; Schlömann, M. Biodismantling, a novel application of bioleaching in recycling of electronic wastes. *Recycling* **2020**, *5*, 22. [[CrossRef](#)]
38. Sodha, A.B.; Tipre, D.R.; Dave, S.R. Optimisation of biohydrometallurgical batch reactor process for copper extraction and recovery from non-pulverized waste printed circuit boards. *Hydrometallurgy* **2020**, *191*, 105170. [[CrossRef](#)]
39. Joshi, V.; Shah, N.; Wakte, P.; Dhakephalkar, P.; Dhakephalkar, A.; Khobragade, R.; Naphade, B.; Shaikh, S.; Deshmukh, A.; Adhapure, N. Comparative bioleaching of metals from pulverized and non-pulverized PCBs of cell phone charger: Advantages of non-pulverized PCBs. *Environ. Sci. Pollut. Res.* **2017**, *24*, 28277–28286. [[CrossRef](#)]
40. Jiménez, L.; Arriaga, S.; Aizpuru, A. Assessing biofiltration repeatability: Statistical comparison of two identical toluene removal systems. *Environ. Technol.* **2015**, *37*, 681–693. [[CrossRef](#)]
41. Zhang, S.; Forssberg, E. Mechanical separation-oriented characterization of electronic scrap. *Resour. Conserv. Recycl.* **1997**, *21*, 247–269. [[CrossRef](#)]
42. Wu, W.; Liu, X.; Zhang, X.; Zhu, M.; Tan, W. Bioleaching of copper from waste printed circuit boards by bacteria-free cultural supernatant of iron–sulfur-oxidizing bacteria. *Bioresour. Bioprocess.* **2018**, *5*, 10. [[CrossRef](#)]
43. Díaz-Tena, E.; Gallastegui, G.; Hipperdinger, M.; Donati, E.R.; Rojo, N.; Santaolalla, A.; Ramirez, M.; Barona, A.; Elías, A. Simultaneous Culture and Biomachining of Copper in MAC Medium: A Comparison between *Acidithiobacillus ferrooxidans* and *Sulfobacillus thermosulfidooxidans*. *ACS Sustain. Chem. Eng.* **2018**, *6*, 17026–17034. [[CrossRef](#)]
44. Jadhav, U.; Hocheng, H. Hydrometallurgical recovery of metals from large printed circuit board pieces. *Sci. Rep.* **2015**, *5*, 14574. [[CrossRef](#)] [[PubMed](#)]
45. Van Yken, J.; Cheng, K.Y.; Boxall, N.J.; Nikoloski, A.N.; Moheimani, N.; Valix, M.; Sahajwalla, V.; Kaksonen, A.H. Potential of metals leaching from printed circuit boards with biological and chemical lixivants. *Hydrometallurgy* **2020**, *196*, 105433. [[CrossRef](#)]
46. Priya, A.; Hait, S. Biometallurgical recovery of metals from waste printed circuit boards using pure and mixed strains of *Acidithiobacillus ferrooxidans* and *Acidiphilium acidophilum*. *Process Saf. Environ. Prot.* **2020**, *143*, 262–272. [[CrossRef](#)]
47. Daoud, J.; Karamanev, D. Formation of jarosite during Fe²⁺ oxidation by *Acidithiobacillus ferrooxidans*. *Miner. Eng.* **2006**, *19*, 960–967. [[CrossRef](#)]
48. Gramp, J.P.; Jones, F.S.; Bigham, J.M.; Tuovinen, O.H. Monovalent cation concentrations determine the types of Fe (III) hydroxy-sulfateprecipitates formed in bioleach solutions. *Hydrometallurgy* **2008**, *94*, 29–33. [[CrossRef](#)]
49. Bao, P.; Xia, M.; Liu, A.; Wang, M.; Shen, L.; Yu, R.; Liu, Y.; Li, J.; Wu, X.; Fang, C.; et al. Extracellular polymeric substances (EPS) secreted by *Purpureocillium lilacinum* strain Y3 promote biosynthesis of jarosite. *RSC Adv.* **2018**, *8*, 22635–22642. [[CrossRef](#)]
50. Kail, H.; Inoue, K.; Harada, H.; Kawakita, H.; Ohto, K. Leaching behavior of heavy metals with hydrochloric acid from fly ash generated in municipal waste incineration plants. *Trans. Nonferrous Met. Soc. China* **2011**, *21*, 1422–1427.
51. Hu, C.; Zhou, L. Failure analysis for micro-short circuit between two pins in printed circuit board assembly. In Proceedings of the 11th International Conference on Reliability, Maintainability and Safety (ICRMS), Hangzhou, China, 26–28 October 2016; pp. 1–4.
52. Hong, Y.; Valix, M. Bioleaching of electronic waste using acidophilic sulfur oxidising bacteria. *J. Clean. Prod.* **2014**, *65*, 465–472. [[CrossRef](#)]
53. Pohl, A. Removal of heavy metal ions from water and wastewaters by sulfur-containing precipitation agents. *Water Air Soil Pollut.* **2020**, *231*, 503. [[CrossRef](#)]
54. Ye, M.; Li, G.; Yan, P.; Ren, J.; Zheng, L.; Han, D.; Sun, S.; Huang, S.; Zhong, Y. Removal of metals from lead-zinc mine tailings using bioleaching and followed by sulfide precipitation. *Chemosphere* **2017**, *185*, 1189–1196. [[CrossRef](#)]
55. Wei, X.; Viadero, R.C. Synthesis of magnetite nanoparticles with ferric iron recovered from acid mine drainage: Implications for environmental engineering. *Colloids Surf. A Physicochem. Eng. Asp.* **2007**, *294*, 280–286. [[CrossRef](#)]
56. Prokkola, H.; Nurmesniemi, E.-T.; Lassi, U. Removal of Metals by Sulphide Precipitation Using Na₂S and HS⁻-Solution. *ChemEngineering* **2020**, *4*, 51. [[CrossRef](#)]