

Microbial extraction of critical raw materials and gold recovery from outdated printed circuit boards

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Abstract

The European Union's Parliament has recently passed the Critical Raw Materials Act (CRMA) to address the global energy transition and the growth in demand for critical raw materials. This law aims to make the EU more self-sufficient, get its critical raw materials from more places, and encourage recycling. This study as a part of the INN4MIN project has tested a new approach to get valuable elements such as Au, Cu, Zn, among others, from spent printed circuit boards (PCBs) in an environmentally friendly way. To reduce the size of PCBs, instead of using incineration or comminution, which are highly energy intensive methods, a concentrated ferric sulfate solution was utilized to de-solder the components and solubilize metals. This solution was then regenerated through utilization of iron oxidizing bacteria in an aerated bioreactor. The gold was then processed in a solution containing thiourea and ferric sulfate. The results in the end showed a very promising recovery rate as follows: Fe (99%), Au (96%), Cu (86%), Ni (40%), Ag (99%) and Zn (90%). The best result was achieved by using 43g/l ferric iron. The iron reduction took 5 days, from 42 to 5 g/l and the bio-regeneration of ferric iron was achieved in 25 days. For optimization, the pH was kept below 2 by adding concentrated sulphuric acid, to minimize the generation of Jarosite or any other iron hydroxides and their subsequent interfere on reaction progress of ferric sulfate with metals, which happens when they cover the surface of components.

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Introduction

According to the [European Commission report \(2013\)](#) considering the dearth of certain elements on Earth, coupled with the environmental consequences of exploration activities, and the rapid expansion of the battery industry, there is a pressing need to develop novel, optimised and environmentally friendly approaches to the circular economy. This necessitates a closer examination of viable substitutes to ensure the provision of safe, reliable and resilient critical raw materials ([European Commission report 2020](#)).

According to [European Commission \[online\] 09.08.2024](#), as the EU is highly dependent on imports of raw materials from third countries ([Figure 1](#)), for example China, which is the main supplier of raw materials to the EU, the European Council, following a series of communications from 2008 on the 'Raw Materials Initiative', has decided to develop further the concept of 'substitution, recycling and domestic extraction' ([European Commission report 2020](#); [European](#)

Commission report 2023; European Commission proposal 2023).

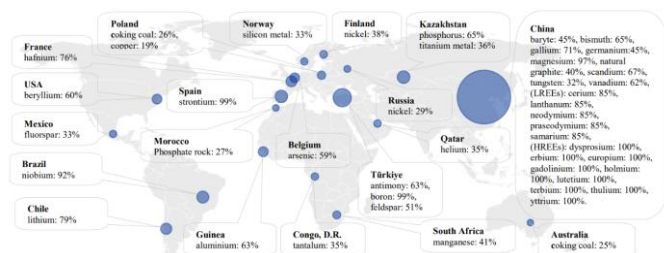


Figure 1. Major EU suppliers of critical raw materials including percentage of specific elements supplied by each country (European Commission [online] 09.08.2024).

Regarding the composition of Waste Electrical and Electronic Equipment (WEEE), a considerable body of research has been conducted, yielding comparable findings (Hubau *et al.* 2019; Hagelueken 2006). Figure 2 represents a comparative analysis of four studies examining the composition of WEEE, as referenced by Ghosh *et al.* (2016).

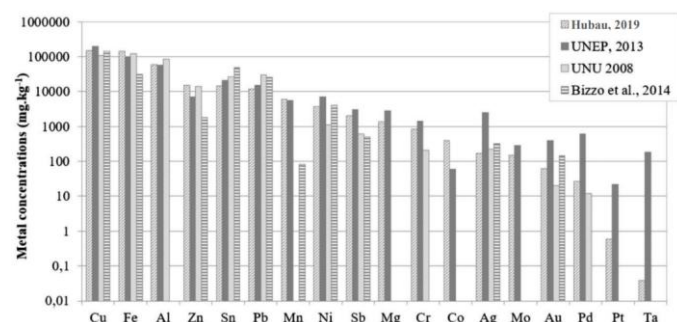


Figure 2. Comparison of metal concentrations in waste printed circuit boards from different studies (edited according to Hubau *et al.* 2019).

To gain access to the entirety of PCBs, it is first necessary to undertake a disassembly process or mechanical pre-treatment (Hubau *et al.* 2019; Hagelueken 2006). This process may entail crushing, grinding, magnetic separation, electrostatic separation or gravimetric separation, as outlined by Ghosh *et al.* (2016).

On the other hand, Pyrometallurgy, as a general approach to the recovery of metals from PCB, has both advantages and disadvantages. As Cui *et al.* (2008) provided an exhaustive review of this method, the recovery of copper as the primary metal will result in a significant loss of other metals in the slag. Additionally, the process requires a considerable amount of energy, and the use of

molten salts (Flandinet *et al.* 2012) to dissolve and destroy parts made from plastic without oxidising the metals eliminates the necessity for mechanical treatment, due to the published report from Ghosh *et al.* (2016).

Nevertheless, the utilisation of ferric sulphate as an oxidising reagent obviates the necessity for this step, as ferric sulphate would oxidise the tin/lead solder and dismantle the components from the PCB. However, in order to oxidise the copper traces in PCBs, the conformal coating (lacquer) must first be removed (Karthikeyan *et al.*, 2014).

In a patented approach proposed by Monneron-Enaud *et al.* (2020), ferric sulphate is used to oxidise and remove the solders, thereby separating the components from the PCB. In this method, the ferric form of iron was employed as a potent reagent to oxidise the metals in solder.

Subsequently, the ferric iron would have been reduced to ferrous, which would then be oxidised once more by means of iron-oxidising bacteria, namely *Leptospirillum ferriphilum* or *Acidithiobacillus ferrooxidans*. An optimal environment, as outlined by Hedrich *et al.* (2020), should be established based on the provided information, including the appropriate temperature, the necessity of agitation, and the relevant medium for specific types of bacteria.

A mixture solution comprising thiourea, thiocyanate and ferric sulphate was employed to analyse gold leaching under a range of conditions, including varying pH values, temperatures and lixiviant concentrations (Yang *et al.* 2011).

In another study (Li *et al.* 2006), thiourea was mixed with ferric sulphate to process the gold, as well as using sulphuric acid to adjust the pH value. The use of this mixed solution resulted in the formation of formamidine disulphide, which played a crucial role in gold leaching, as reported by Li *et al.* (2006).

In this study, the methodology described by Monneron-Enaud *et al.* (2020) was used, further developed and optimised to facilitate the dissolution of almost all precious metals from PCBs and integrated by using the lixiviant introduced by Li *et al.* (2006) to process and extract the gold and silver.

Table 1. The general characterization of three randomly selected PCBs.

	Mainboard [g]	Pins + CPU [g]	Electrolytic capacitors [g]	Adapters & ports [g]	Plastic [g]	Total mass [g]
LP1	264.2	66.3	43.7	129.9	125	629.1
LP2	264.7	78.4	46.4	139.4	142	670.9
LP3	280.7	69.4	52.2	132.7	117.8	652.8
[g]	269.9	71.4	47.4	134.0	128.3	650.9
[%]	41.5	11.0	7.3	20.6	19.7	100.0

Experimental

Sample preparation

In this study, to determine the plausibility of lixiviants, which are described in coming section, a couple of experiments with a number of PCBs were conducted in different quality and quantity of material.

First, three PCBs (LP1, LP2 and LP3, different in brand and colour) out of tens of outdated printed circuit boards from TDE-recycling GmbH and ARG - Recuperação de Metais were selected in order to get the basic composition and characterisation of PCBs.

Then a hot air device was employed to melt the solder and set the component free from the board, thus facilitating the categorisation of the parts of the PCB into different groups (Table 1):

- Mainboard (Cu)
- Pins and CPU (Au, Ag, Cu, Pb, Ni, Zn and Sn)
- Electrolytic capacitors (Al and Ta)
- Adapters and connectors (same as Pins and CPU but lower concentration)
- Plastic

Subsequently, the disparate groups were initially subjected to hydrochloric acid and nitric acid digestion, followed by aqua regia, which facilitated the dissolution of the gold content and other valuable metals that were not dissolved, as reported by Hubau (2019).

As Figure 3 illustrates the results after acid leaching, a random PCB in general consists of plastic (glass fibre, epoxy resin) (75.06%), Cu

(21.3%), Zn (2.5%), Ni (0.22%), Sn (0.92%), Pd (0.0003%), Au (0.0077%) and Ag (0.0073%).

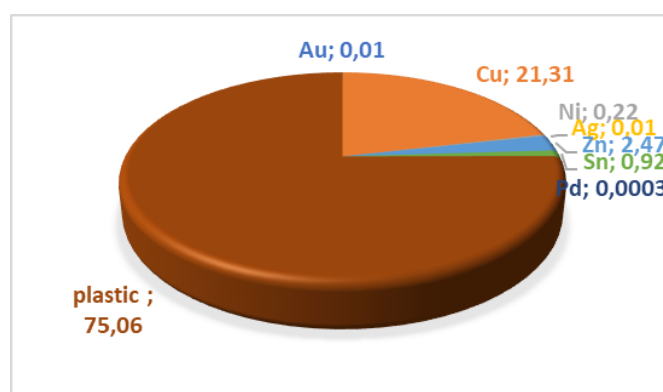


Figure 3. Calculated share (in W%) of each analysed element in a random PCB after acid leaching.

Also, one of the printed circuit boards was heated to 800°C for two hours, milled with a mortar and pestle to homogenise the particles, and dissolved in nitric acid for analysis using ICP-AES.

This result was then considered as a reference data to be compared with the recovery rate by using environmentally friendly solutions.

Leaching Solutions

A leaching solution containing ferric sulphate (containing 43 g/l ferric iron) was utilised. Which was then regenerated using iron oxidizing bacteria, i. e. *Acidithiobacillus ferrooxidans* and *Leptospirillum ferriphilum*, after reduction of ferric iron to ferrous iron during the leaching process.

The bacteria were fed according to the reference data from so called “HBS medium” consist of Na₂SO₄·10H₂O 7.5 g/l, (NH₄)₂SO₄ 22.5 g/l, KCl

2.5 g/l, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 25 g/l, KH_2PO_4 2.5g/l and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ 0.7 g/l, and the trace elements ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 10 g/l, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1 g/l, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ 1 g/l, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 1 g/l, $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ 0.5 g/l, H_3BO_3 0.6 g/l, $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ 0.5 g/l, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 1 g/l, $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$ 1 g/l, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ 0.1 g/l and NaVO_3 0.1g/l) by factor of 1ml/l of complete medium.

An air compressor was also used to provide the oxygen required by the micro-organisms and parameters such as pH, redox potential and electrical conductivity, iron/iron ratio and bacterial cell counts in the leachate were monitored.

The sedimented material from previous stage was then processed using two different leaching solutions to solubilize the gold and silver content, described by Table 2.

Table 2. Solutions for solubilizing of gold and silver.

	Lixiviant 01	Lixiviant 02
	Yang <i>et al.</i> 2011	Li <i>et al.</i> 2006
SCN	0.005 M	42 g/L
Thiourea	10 mM	9 g/L
Sulphuric acid	-	0.1 M
Ferric sulphate	0.055 M	
pH	1.5	
Temp	35 °C	20 °C

Results and discussion

Bio-dismantling and leaching

As it is shown in Figure 4, in a lab-scale experiment, the solder part of PCB has been solubilized in ferric sulphate (at pH 0.9 and room temperature 18-20°C). During this process the redox potential changed from 847mV at the beginning to 600mV. The pH was increased to 1.3 in the end, keeping the acidic condition.

The dismantling performance varies by different iron concentrations, and the redox potential and the pH value in the solution, as the higher redox potential leads to a competition between solder

leaching and copper leaching from copper traces on PCB (Monneron-Enaud *et al.* 2020), which explains the shorter time taken for dismantling in this study (higher iron concentration, lower copper content in PCB, even with high redox potential, i. e. 950 mV).

The dismantling process described by Monneron-Enaud *et al.* (2020) using 20 mM ferrous iron sulphate (pH 1.8 and 30°C) and 15 mM of Fe^{+3} took 20 days.

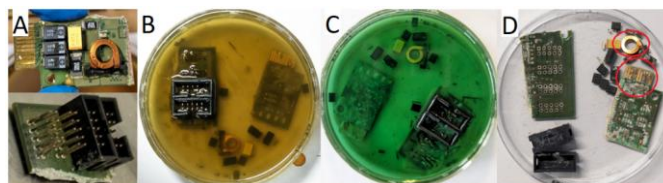


Figure 4. Running preliminary experiment using ferric sulphate as an active reagent. A) small cut of PCBs, B) PCBs merged into the ferric sulphate solution (brown colour), C) iron is reduced to ferrous sulphate, D) complete dissolution of metals in the solution (just the circuit boards with lacquered copper traces are left).

Therefore, to prepare the same condition in line with the approach by Monneron-Enaud *et al.* (2020), the copper content in the solution was extracted by using electrolysis cells. This was an effective approach as the use of electrolytic cells and the application of such a low voltage (1.5 V, 0.5 A) would not disturb any bacterial activity.

Then to conduct the test in a larger scale, four PCBs were placed in a bio-reactor containing ferric iron sulphate and iron oxidizing bacteria, whereby the iron concentration varied between 15 - 25 g/l and the cell number between $6.0\text{E}+08$ and $1.5\text{E}+09$ cells/l, depending on the activity of the bacteria.

The pH was kept between 1.5 - 2.0, and the temperature at 35°C. However, unlike the approach by Monneron-Enaud *et al.* (2020), the cultivation of bacteria was carried out in the same reactor, in which an ongoing bio-leaching process was kept running.

The redox potential was 930mV at the beginning and fluctuating during the experiment between 924 and 810mV at the lowest point which was indicating the oxidation and reduction of iron happening at the same time in different places.

Gold hidden in the sedimented material

Technically, the dissolution of metallic copper and zinc by Fe^{3+} resulted in the formation of divalent ions in solution. Metallic tin and lead were also dissolved, but precipitated as sparingly soluble phases, namely amorphous tin oxide and lead sulphate (anglesite).

The composition of this powder was determined prior to the test (Table 3) by dissolving it in aqua regia solution. In this way it was possible to compare the kinetics of gold leaching by taking the piece of gold and monitoring its behaviour next to tin oxide.

Table 3. Chemical composition [mg/kg] of sedimented yellow-brownish powder.

Fe	Au	Cu	Ni	Ag	Zn	Sn
151000	469	8420	1300	81	1200	101000

Tin extraction using hydrochloric acid is investigated by Soewarno *et al.* (2014), which was conducted on tin containing slags or by-product of smelting process.

Accordingly, the yellow-brownish powder conditioned in concentrated hydrochloric acid (35%) heating up to 85°C, aiming to dissolve the tin containing part in the solution, and letting the gold content free of other impurities (Figure 5).

The use of concentrated hydrochloric acid at high temperature (85°C) led to obtain a better (still mixed) product containing gold, but it is not plausible in terms of energy consumption.

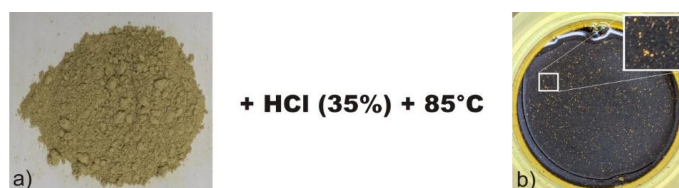
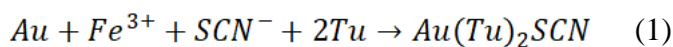


Figure 5. Using heated hydrochloric acid to remove the impurities from the sedimented material; (a) before using acid, (b) after using heated hydrochloric acid (gold particles can be recognised).

Gold recovery

From chemical point of view, the ferric sulphate in Lixiviant 01 provides the oxidation properties, where the thiocyanate leads the complexation

properties, which in parallel with thiourea generates a synergistic effect, also thiourea itself can improve the half reaction in the gold oxidation process (Yang *et al.* 2011):



Whereby in the second lixiviant (02) for gold leaching the ferric iron oxidizes thiourea and produces a transient and unstable by-product called formamidine disulphide, which acts as a gold oxidant, which is unstable, and the sulphur would precipitate and cover the sample surface, which could partially hinder the reaction (Li *et al.* 2006).

The efficacy of the two gold dissolution techniques was evaluated using pure gold powder (0.5 g, particle size < 100 μm) and solid gold wire (1 × 0.5 × 4 mm).

Due to larger effective surface area, the gold powder was fully dissolved in lixiviant 02 within two hours, while the gold wire required 72 hours (Figure 6).

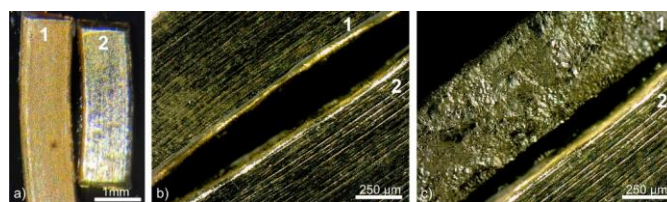


Figure 6. Leaching of gold pieces in thiourea; a&b) original pieces before leaching, c) after leaching (1), not leached (blank sample) (2).

After using both lixiviants to dissolve the gold content from the sedimented material, lixiviant 02 provided a better performance, i. e. 96% gold recovery by lixiviant 02 whereas 78% obtained by lixiviant 01 (Figure 7).

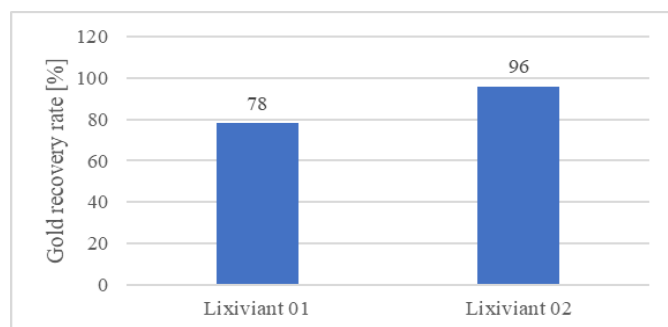


Figure 7. Comparison of gold recovery by using lixiviant 01 and 02.

The lower recovery rate obtained by using lixiviant 01 can be explained by considering the presence of other dissolved metals in the sediments along with their different reactivity potential, as well as the seemingly low iron concentration prescribed in the leaching solution (0.055 M).

The recovery rate of other metals in the sediments obtained by using lixiviant 02 is showed in [Figure 8](#). In this figure, the first column shows the initial concentration of each element in the sediments and next 5 columns illustrate the concentration of respective components in the solution after one hour, two hours, one day, two days and three days.

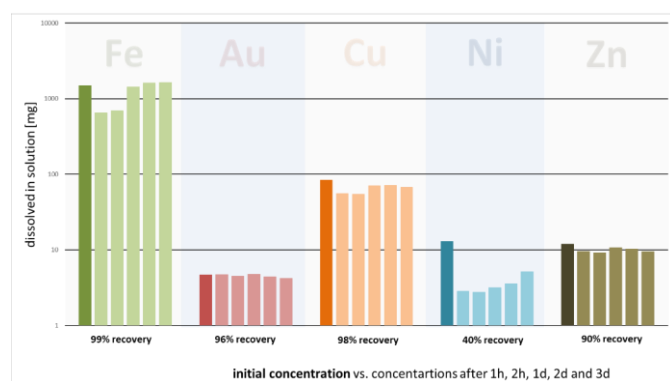


Figure 8. The recovery rate of metals from sediments by using the lixiviant 02.

Conclusions

In this study it was of utmost importance to use the most environmentally friendly approach possible to process and dissolve the gold content from primary (gold minerals) and secondary (e-waste recycling) resources. The main material used as an oxidant in this experiment was ferric iron sulphate, which was completely regenerated using iron oxidising bacteria. The ferric iron sulphate dismantled the components from PCB via solubilizing the solder metals (Sn, Pb). Then other metals from components and pins were solubilized in this leaching solution. The solubilized copper was extracted by using electrolysis. During this procedure, the gold and silver, which were liberated from respective components after having other metals solubilized in the solution, settled down, that was mixed with sedimented material consisting mostly of jarosite. This sedimented material was then processed by using lixiviants containing thiourea to recover the gold and silver.

In this study, the gold was the target element, whereby the recovery rate was 96%. In conclusion, in this study a rather complete recovery procedure has been initiated by applying and purposely improving and optimizing different approaches, which in the end led to a promising result. The objective of this study was to establish a foundation for further research aimed at enhancing and advancing the transition towards a circular economy. Consequently, all recommendations, suggestions, and critiques are encouraged to be proposed and deliberated.

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References

- Bizzo, W.A., Figueiredo, R.A., de Andrade, V.F. (2014) Characterization of printed circuit boards for metal and energy recovery after milling and mechanical separation. *Materials* 7: 4555–4566.
- Cui J., Zhang L. (2008) Metallurgical recovery of metals from electronic waste: a review. *J Hazard Mater* 158: 228-256.
- European Commission Report from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the implementation of the Raw Materials Initiative, 24 (6) (2013), 19 p.
- European Commission Report from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on making the recovery circular and green (2020) ST-13852-2020-INIT_en, 2020, 32 p.
- European Commission Report from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on a green deal industrial plan for the net zero age (2023) CELEX_52023DC0062_EN, 21 p.
- European Commission Proposal for REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on establishing a framework of measures for strengthening Europe's net-zero technology products manufacturing ecosystem (Net Zero Industry Act) (2023), 87 p.
- European Parliament and Council REGULATION (EU) 2024/1252 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL establishing a framework for ensuring a secure and sustainable supply of critical raw materials and amending Regulations (EU) No 168/2013

- (2013), (EU) 2018/858 (2018), (EU) 2018/1724 (2018) and (EU) 2019/1020 (2019), (2024), 67 p.
- European Commission [online]. (2024) [ct. 09.08.2024]. WWW: <<https://www.consilium.europa.eu/>>
- Flandinet L., Tedjar F., Ghetta V., Fouletier J. (2012) Metals recovering from waste printed circuit boards (WPCBs) using molten salts. *J Hazard Mater* 213-214: 485-490.
- Ghosh S. K., Lee J., Godwin A. C., Oke, Al-Rawi R., El-Hoz M. (2016) Waste management in USA through case studies: E-waste recycling and waste to energy plant. 31st international conference on solid waste technology and management, 3-6 April 2016, Philadelphia, USA.
- Hagelueken C. (2006) Recycling of electronic scrap at umicore's integrated metals smelter and refinery. *World Metall* 59: 152-161.
- Hedrich S., Schippers A. (2020) Distribution of acidophilic microorganisms in natural and man-made acidic environments. *Curr Issues Mol Biol* 40: 25-48.
- Hubau, A., Chagnes, A., Minier, M., Touze, S., Chapron, S., Guezennec, A. G. (2019) Recycling-oriented methodology to sample and characterize the metal composition of waste printed circuit boards. *Waste Manag* 91: 62-71.
- Karthikeyan A., Balamurugan K., Kalpana A. (2014) The effect of sodium hydroxide treatment and fiber length on the tensile property of coir fiber-reinforced epoxy composites. *Sci Eng Compos Mater* 21: 315-321.
- Li J., Miller J. D. (2006) A review of gold leaching in acid thiourea solutions. *Miner Process Extr Metall Review* 27: 177-214.
- Monneron-Enaud B., Wiche O, Schlömann M. (2020) Biodismantling, a novel application of bioleaching in recycling of electronic wastes. *Recycl* 5: 22.
- Reuter, M. A., Hudson, C., van Schaik, A., Heiskanen, K., Meskers, C., Hagelüken, C. (2013) Metal recycling: opportunities, limits, infrastructure. UNEP, International Resource Panel, 316 p.
- Soewarno N., Altway A., Susianto, Taufany F., Nurkhamidah S. (2014) Tin extraction from slags used hydrochloric acid. *J Eng* 1: 19-21.
- United Nations University Final Report on the Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE) (2008) Study No. 07010401/2006/442493/ETU/G4.
- Yang X., Moats M. S., Miller J. D., Wang X., Shi X., Xu H. (2011) Thiourea–thiocyanate leaching system for gold. *Hydrometallurgy* 106: 58-63.