University of Jordan

Chemical Engineering Department

Selected Topics in Chemical Engineering

Instructor Arwa Sandouqa

The Use of Electrolysis for the Recovery of Valuable Material from Waste Printed Circuit Boards

Tareq Khalil 0175595

Yazan Amer 0172754

Abstract

As recycling and sustainable development become more important, so too does electrolysis—a technique that is equal parts energy-efficient and non-polluting. In this paper we introduce the relevant concept of the circular economy, then describe three processes, all involving electrolysis, that could be used for the recovery of multiple sorts of metals, including copper and gold. In the last section we discuss the importance and environmental impact of these processes as well as others that belong to the same general category.

Table of Contents

Introduction

Humanity has yet to transition from a linear economy to a circular economy [1][2]. That is a problem. A linear economy entails greater waste production and is based upon the short-sighted assumption that Earth's resources might as well be infinite [1], while a circular economy is more realistic and takes into account issues such as anthropogenic climate change [3]. The following figure [1] illustrates the differences quite well.

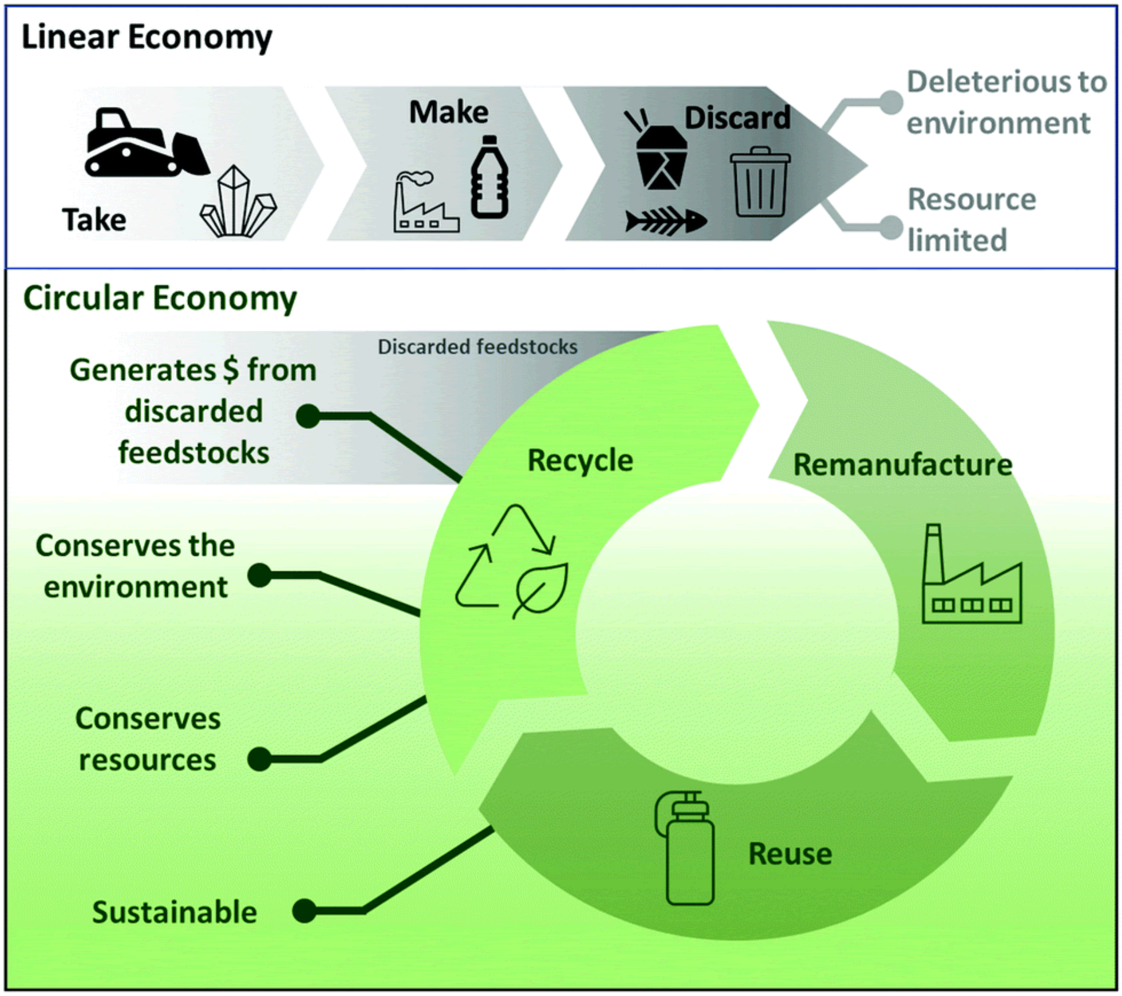


Figure 1: Circular vs Linear Economy

One of the issues that stand in the way of the establishment of a circular economy is that not everything is recyclable—not yet, at least [1].

This is where electrolysis comes in.

Electrochemical recycling enables us to recover raw materials that would otherwise end up in landfills [1]. Due to the limited scope of this paper, we will focus our attention on one particular type of process: that of the recycling of valuable metals from waste printed circuit boards (often abbreviated WPCBs).

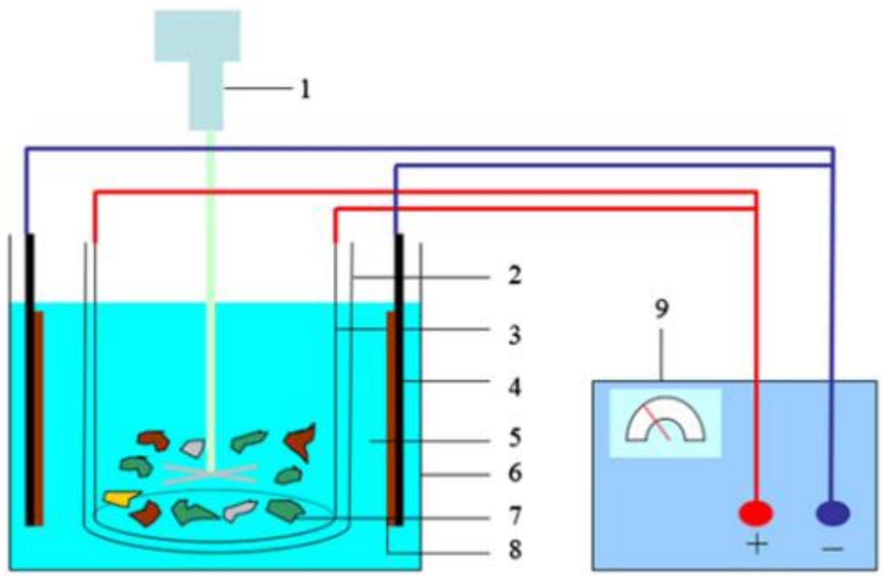
The recycling of WPCBs is important both environmentally and economically [1][4]. The first because WPCBs contain several hazardous materials (such as lead, mercury, cadmium, and brominated flame retardants), and the second because of the valuable substances they contain, such as gold, silver, and copper [4].

In the upcoming sections we will discuss the use of suspension electrolysis for the recovery of copper from WPCBs as described by Zeng et al. [4], the recovery of gold from scrap mobile phones by electro-generated chlorine as described by Kim et al. [7], and finally the electrochemical recovery of lead and tin as described by Mecucci and Scott [6].

Working Principles & Descriptions of Processes

Recovery of Copper from WPCBs

The process of copper recovery as described by Zeng et al. [4] starts with a pretreatment step. The circuit boards are first shredded into a 7.4 – 11.1 micron powder, which is then dissolved in a diluted aqua regia solution. It is at this point that the copper content of the powder should be analyzed if one wishes to carry out yield or efficiency calculations later on. The powder is then suspended in an electrolytic cell much like the one shown in the figure below.



Experimental setup of suspension electrolysis: (1) stirrer; (2) anode jacket; (3) titanium anode baskets; (4) graphite electrode; (5) electrolyte; (6) electrolytic bath; (7) waste printed circuit board; (8) copper powder; (9) electrical source

Figure 2: Suspension Electrolysis

The electrolyte cell solution had three constituents: sulfuric acid, copper sulfate, and sodium chloride. The stirrer operated at a speed of 400 revolutions per minute. In order to find out which operating conditions are best, Zeng and co carried out this process at various concentrations of sulfuric acid and copper sulfate and various current densities, but always for 5h and with 500 mL of solution.

The following model was obtained:

$$\text{Cu recovery} = 86.46 + 0.039x_1 - 5.34x_2 + 1.89x_3 + 4.47x_1x_2 - 12.17x_1x_3 - 7.28x_2x_3 - 7.87x_1^2 - 2.00x_2^2 - 0.12x_3^2$$

The R^2 value obtained was 0.9863, meaning the model could explain 98.63% of the variation in copper recovery based on the parameters x_1, x_2, x_3, which correspond to the concentration of copper sulfate, the concentration of sulfuric acid, and the current density, respectively. In the conclusion of the paper it is stated that concentrations of 30 g/L and 110 g/L of copper sulfate and sulfuric acid, respectively, coupled with a current density of 3 A/dm2 are 'suitable for the copper recovery process', and yielded a recovery fraction of 86.46%.

Recovery of Gold from Scrap Mobile Phones

This process, as described by Kim et al., uses electrolysis indirectly.

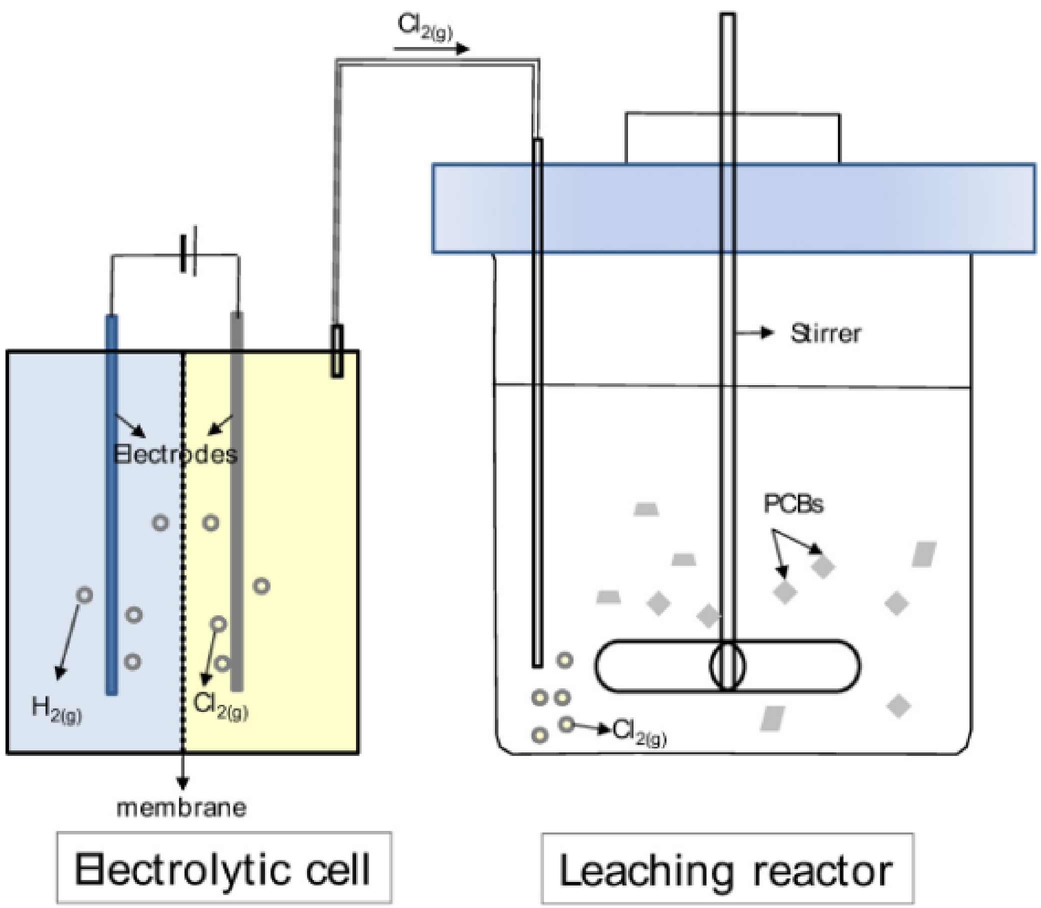


Figure 3: Recovery of Gold A

As shown in the figure, an electrolytic cell is used to generate chlorine gas. The electrolytic cell is divided into two compartments with an anion exchange membrane '(Neosepta AMX, Tokuyama Co.)'. Two cathodes and anodes are used, all made of high purity graphite. The chlorine gas generated is pumped into the leaching reactor. In the presence of chloride, the copper and gold in the WPCBs dissolve and form *chloride complexes*—such as $AuCl_4^-$ and $CuCl^+$. The leaching process is influenced by numerous variables. For the sake of example we will only discuss the concentration of acid in the leaching reactor. Since chlorine chemistry is pH dependent, the concentration of acid is of utmost importance. There are subtle details we are glossing over here, but they are beyond the scope of this paper. The following figure is sufficient.

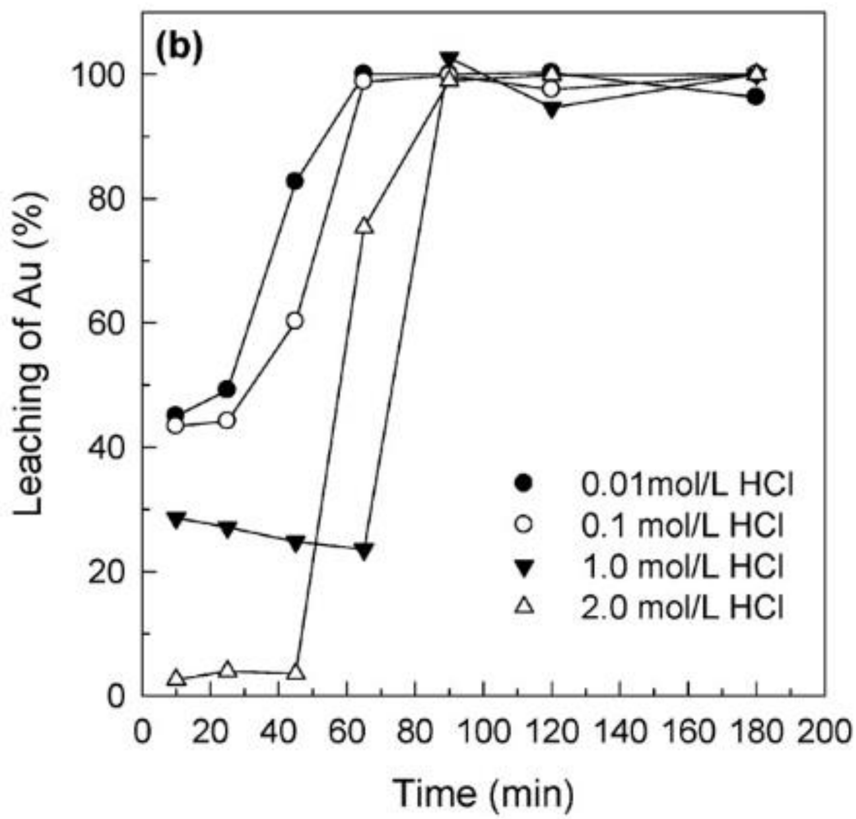


Figure 4: Effect of pH on %Au Leached

The remainder of the process is, as can be seen in the figure, rather unrelated to electrolysis. We've decided to include the figure, however, so our discussion of the process is complete.

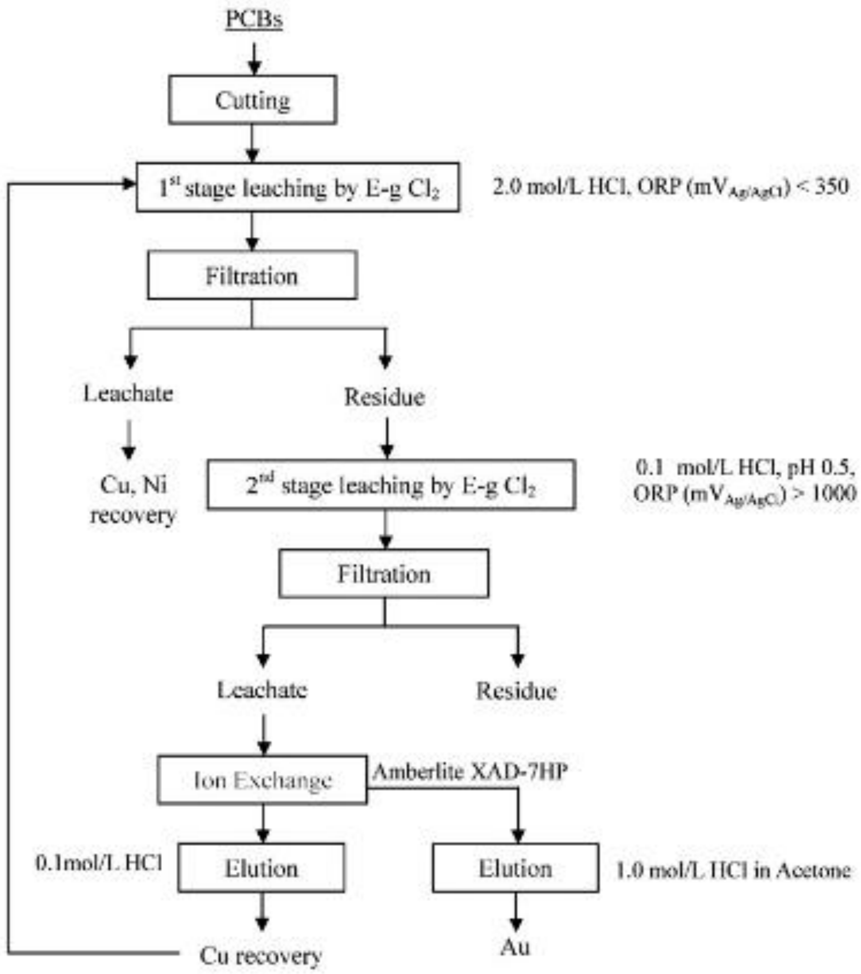


Figure 5: Recovery of Gold B

Recovery of Lead and Tin

Prior to leaching size reduction of the PCB boards by a granulator to approximately 2.52 is essential because the increasing use of multi-layer boards restricts access to the internal layers of the board by the stripping solution which therefore prevents complete extraction of the metals.

After reducing the size f the PCB boards to the appropriate size, leaching was carried out With (1-6M HNO3) at 80°C to increase the dissolution rate (to minimize the exothermic reaction and prevent excessive frothing due to release of nitrous oxide fumed and hydrogen evolution crushed boards were added to the solution in small increments).

Tin precipitation as metastannic acid occurs following the equation demonstrated below:

$$3Sn + 4HNO_3 + H_2O \rightarrow 3H_2SnO_3 + 4NO$$

Filtration of the obtained solution takes place to separate the Tin precipitate from the solution and the H_2SnO_3 is to be dissolved in 1.5M hydrochloric acid:

$$H_2SnO_3 + 6HCl \rightarrow H_2SnCl_6 + 3H_2O$$

Tin (IV) is moved to electrolytic cell to be deposited according to the following equation:

$$Sn(IV) + 4e^- \rightarrow Sn$$

Finally, HCl is recovered for H_2SnO_3 dissolution repeating all the steps above.

The other part of the filtered solution (HNO_3) is neutralized by the addition of sodium hydroxide (NaOH).

To produce $NaNO_3$ which is the supporting electrolyte for lead and copper:

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

And it all comes together to form the electrochemical cell below:

Cathode: Electrodeposition of Cu:

$$Cu(II) + 2e^- \rightarrow Cu$$

Anode: Electrodeposition of PbO_2:

$$Pb(II) + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^-$$

After the deposition of both cathode and anode HNO_3 is regenerated for reuse.

Importance & Applications

There are, according to Qiu et al. [8], numerous economic benefits to the recycling of WPCBs, and huge environmental stresses that have necessitated the development of new technologies. In 2011, Hundreds of millions of mobile phones were being taken out of use each year [7]. The amount of e-waste generated annually has only grown, going from, according to UN data, 14 million tons in 1992, to 24 million in 2002, to 47.7 million in 2016—and WPCBs are considered the most valuable of all waste electronic equipment [9]. Some have suggested that the recovery of metals from WPCBs is not only a more environmentally friendly approach as compared with extraction from natural minerals, but also more energy-efficient [10]. Work by Cucchiella et al. has revealed that the recycling of e-waste is 'essential', and likely to create 'huge' benefit [11].

Many critical raw materials (materials that are important for the economy but can be difficult to procure) successfully undergo *industrial-scale* electrochemical recycling [1].

Harkening back to Qiu and co, in their paper they state that a common problem standing in the way of the recycling of WPCBs is the lack of systematicness and the difficulty of recovering all the constituents of the boards. In fact, this problem can be seen in this very paper—three methods are described, and they are, in ways, at odds with each other. Qiu and co have found the answer, though, and developed a process that can be used to recover the 'full metallic resources' that a circuit board contains. The process is a combination of many sub-processes, including, of course, electrolysis, heating, crushing, and bioleaching. The advantages of that process, which can be considered a sort of spiritual successor to the processes we have discussed, are numerous, as it is *green*, economic, energy-saving, and can promote the rapid development of metals supply chains.

We conclude on this note: it is possible that the work of Qiu et al., which puts together and homogenizes the work of previous researchers, will prove to be the last piece of the puzzle that is the recycling of WPCBs, and will lead to the establishment of a circular economy in the relevant industries, and perhaps to wider application of recycling methods that utilize electrolysis.

Summary

The development of new technologies for the purpose of recycling waste that cannot be recycled as of yet is absolutely essential for the establishment of a circular economy, which, in turn, is essential for the preservation of the environment and Earth's resources. In this paper we have described three novel processes that could be used for the recycling of an increasingly prevalent type of waste—e-waste. The three processes show that electrolysis can be used both directly and indirectly for the recovery of all sorts of metals from circuit boards. In the last section, we cite select statistics and facts to show just how important it is that WPBCs are not simply discarded.

References

1. Petersen, Haley A., Tessa H. T. Myren, Shea J. O'Sullivan, and Oana R. Luca. Rep. Electrochemical Methods for Materials Recycling, January 2, 2021.

   https://pubs.rsc.org/en/content/articlehtml/2021/ma/d0ma00689k#cit1.

2. Van Ewijk, Stijn; Stegemann, Julia, Why we'll still need waste in a circular economy, 2020. https://theconversation.com/why-well-still-need-waste-in-a-circular-economy-136470
3. United Nations Framework Convention on Climate Change. Circular Economy Crucial for Paris Climate Goals, 2019.

   https://unfccc.int/news/circular-economy-crucial-for-paris-climate-goals

4. Guisheng Zeng; Xingzhen Sui; Xiang Zhao; Zhongjun Li; and Qian Guan, Efficient Recycling of Copper from Waste-Printed Circuit Boards via Suspension Electrolysis Using Response Surface Methodology, 2018.

https://ascelibrary.org/doi/10.1061/%28ASCE%29EE.1943-7870.0001350

5. Szabolcs Fogarasi, Florica Imre-Lucaci, Árpád Imre-Lucaci, Petru Ilea, Copper recovery and gold enrichment from waste printed circuit boards by mediated electrochemical oxidation, Journal of Hazardous Materials, Volume 273, 2014, Pages 215-221.

https://www.sciencedirect.com/science/article/abs/pii/S0304389414002295

6. Mecucci, A. and Scott, K., Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. J. Chem. Technol. Biotechnol., 2002

   https://doi.org/10.1002/jctb.575

7. Eun-young Kim, Min-seuk Kim, Jae-chun Lee, B.D. Pandey, Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process, Journal of Hazardous Materials, Volume 198, 2011, Pages 206-215, ISSN 0304-3894.

https://www.sciencedirect.com/science/article/abs/pii/S030438941101274X

8. Ruijun Qiu, Mi Lin, Jujun Ruan, Yonggao Fu, Jiaqi Hu, Meiling Deng, Yetao Tang, Rongliang Qiu, Recovering full metallic resources from waste printed circuit boards: A refined review, Journal of Cleaner Production, Volume 244,2020,118690, ISSN 0959-6526

   https://doi.org/10.1016/j.jclepro.2019.118690

9. Juanjuan Hao, Yishu Wang, Yufeng Wu, Fu Guo, Metal recovery from waste printed circuit boards: A review for current status and perspectives, Resources, Conservation and Recycling, Volume 157,2020,104787, ISSN 0921-3449

   https://www.sciencedirect.com/science/article/abs/pii/S0921344920301087

10. Congren Yang, Jinhui Li, Quanyin Tan, Lili Liu, and Qingyin Dong, ACS Sustainable Chemistry & Engineering, Green Process of Metal Recycling: Coprocessing Waste Printed Circuit Boards and Spent Tin Stripping Solution, 2017

    https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.7b00245

11. Cucchiella, F., D Adamo, I., Lenny Koh, S.C., Rosa, P., 2015. Recycling of WEEEs: an economic assessment of present and future e-waste streams. Renew. Sustain. Energy Rev. 51, 263–272. https://doi.org/10.1016/j.rser.2015.06.010