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ADVANCED RECOVERY OF VALUABLE MATERIALS FROM E-WASTE

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Abstract

Due to rising customer demand, the manufacturing of electrical and electronic equipment has expanded dramatically in recent years; nevertheless, because technology is advancing so quickly, the equipment's lifespan has decreased. Consequently, an enormous volume of electronic waste (also known as "e-waste") is produced each day.
The majority of these wastes consist of materials that, in the wrong hands, can have an adverse effect on the habitats they are placed in and, indirectly, the species that live there. Metals, polymers, and refractory oxides are frequently found in these wastes. These materials can be highly valuable economically if they are correctly collected and separated. The main strategies for isolating and recovering valuable components from electrical and electronic waste were examined in this study, along with how successful these approaches were at disposing of waste.

Key words: *electronic, metals, pollution, recycle, waste.*

INTRODUCTION

In the last decades, a large amount of waste has been generated at an alarming rate, thus electrical and electronic waste has been attracting the attention of scientific communities in recent years, this fact being mainly due to the composition of this waste and the abundant presence of metals in this waste, such as copper (Cu), cobalt (Co), nickel (Ni) or silver (Ag) (Russo et al., 2022). The main component of electrical and electronic waste is represented by printed circuit boards (Fariborz et al., 2022).
It is estimated that the composition of printed circuit boards is composed of 40% metals, 30% plastics and 30% ceramics (Gamez et al., 2019). The printed circuit boards represent a high percentage of all electronic waste, accounting for approximately 3-5% of the total mass (Fariborz et al., 2018). This type of waste metals can exist in different forms, elemental form, various oxides and various alloys (Touze et al., 2020).
The complications in the processing of this type of waste come from the fact that it has a multi-metallic composition, and this aspect makes the development of a universal and at the same time efficient recovery process quite difficult (Fariborz et al., 2022).
The concentration of metals depends on the nature of the waste; for example, devices that require better (faster) connections have higher concentrations of precious metals and devices that contain larger amounts of connections and wiring have higher amounts of elemental copper (Mesquita et al., 2018). Many of these materials are incorporated into printed circuit boards to provide good high temperature insulation properties and high thermal stability of the boards (Qiu et al., 2020).
Fariborz et al. (2022) shows that the composition of printed circuit boards can be different, depending on the nature of the waste. Table 1 (adapted from Fariborz et al., 2022) highlights the composition of printed circuit boards from mobile phones, laptops, televisions and others.

Table 1. PCB elemental metal composition

Types of PCBs	Types of materials					
	Al	Cu	Pb	Ni	Fe	Ag
Mobile phones	0.26	35.50	1.87	3.41	12.49	2100
Laptops	1.47	39.20	1.54	0.64	1.98	165
Television	0.30	11.2	-	0.02	-	48
Old computers	-	34.26	1.11	0.43	2.45	-
Copper-rich PCBs	5.2	34	0.75	-	2.80	-
Mixed PCBs	-	26.82	-	0.20	5.36	530

For an efficient recovery of these metals, several methods have been developed, such as: solvent extraction, ion exchange, membrane separation, compaction, retention on porous polymers, coprecipitation, sequential distillation, precipitation and adsorption, the last one being presented in the literature as the method showing the highest degree of recovery of metals from aqueous solutions (Mokhodoeva et al., 2020).

Metal recovery methods from electrical and electronic waste are chemical precipitation, coagulation and flocculation, ion exchange, membrane filtration, adsorption, electrochemical treatment and photocatalysis (Azmi et al., 2018). These are also the most common methods of metal recovery from electrical and electronic waste (Fan et al., 2018; Martinas-Ionita et al., 2023).

Chemical precipitation is a process of forming insoluble metal precipitates by the reaction of the precipitating agent of hydroxides or sulfides with dissolved metal ions. This technique is the most used treatment method in today's industries by adjusting the pH to basic conditions to reduce the solubility of metal ions in wastewater. The metal precipitates formed are recovered using a solids separation process. The advantages of the method are simple operation and low cost due to their availability and low-cost precipitating agents. The disadvantages are generation of excessive amount of sludge, with negative impact over environment (Azmi et al., 2018).

Coagulation and flocculation are common methods of treating process waters where coagulation is the destabilization of the surface charge of colloids to make flocs and flocculation is the aggregation of these flocs into larger particles. The two methods can significantly improve separation in subsequent treatments such as sedimentation or filtration (Hubert et al., 2024).

In the ion exchange process, the ion exchanger (resin) exchanges its cations with metal ions from the wastewater without any structural modification of the resin. The metal is then recovered by elution with a suitable product after separating the charged resin from the wastewater.

Common cation exchangers are strongly acidic resins with sulfonic acid ($-SO_3H$) groups and weakly acidic carboxylic acid (-COOH) resins where the hydrogen ions in the groups serve as exchange ions with the metal cations in the wastewater (Azmi et al., 2018).

Membrane filtration is an emerging technology for the separation of ions or molecules (Shuaifei et al., 2024). It exhibits high efficiency and low cost, but also has disadvantages such as unsatisfactory selectivity for small ions and short membrane lifetime (Zhao et al., 2021).

Recently, several absorption methods have been developed for the recovery of metals from the leachate in the final stage of the process. These methods include adsorption by various adsorbents, such as chitin, chitosan and activated carbon (Zazycki et al., 2017), membrane-based separation with polymer inclusion, and adsorbent based on biomass derived from agriculture (Rizki et al., 2023).

Electrodeposition precipitates one or more metal ions in leaching solution to achieve ion separation by controlling voltage, current and other influencing factors (Xiaohui et al., 2024).

Photocatalysis is a method that couples low-energy ultraviolet light with semiconductor catalyst particles to reduce the metal ions they contain in an electrolyte by photogenerated electrons. Photocatalysis has emerged as a promising alternative approach to conventional pollutant degradation methods. In this method, organic compounds are degraded by the generation and subsequent reaction of hydroxyl radicals and other compounds. The most widely used semiconductor photocatalysts are TiO_2, ZnO, CeO_2, CdS and ZnS which are derived from chalcogen compounds (Fernandes et al., 2024).

In addition to these classic methods, in recent years more advanced bio processes have appeared that can lead to the extraction of metals from electrical and electronic waste without polluting the environment. They can also be integrated into classic recovery processes to achieve a higher and faster recovery rate. An example of such an integrated process is the integrated bio- and hydrometallurgical process developed for the extraction of base metals from electronic waste. It is composed of three operation units: biogenic generation of H_2SO_4, biogenic ferric (Fe^{3+}) generation and non-contact indirect bioleaching of base metals from ground waste with biogenic leaching (Yken et al., 2023).

Investigations into the nature and structure of chemical compounds of copper in electrical and electronic waste were carried out by the method of X-ray diffraction analysis.

Since no two chemicals are in the crystalline state where the distance between the reflection planes is identical in all directions, placing a crystal at all possible angles to the X-ray beam produces a characteristic image.

The qualitative analysis is based on the calculation of the d-spacings (lattice constants) for all diffraction lines in the spectrum and their comparison with the d-values given in the literature. A general use in this regard is the ASTM card, with tabular sheets, in which the d values for substances, the relative intensity of the lines (%, relative to the most intense line) and h, k, l are entered indices of the lines. To identify a crystalline phase, the presence of the first 3 intense lines in the spectrum is sufficient.

The identification of copper chemical compounds from the obtained spectra is done with the help of A.S.T.M.

Considering that in the electrical and electronic waste analyzed, copper is found in the form of metallic copper and the fact that the other components do not react with the ammonium sulfate solution, the stoichiometric equation of the copper extraction process from the electrical circuit, the electronic waste, in the form of cuproammonia complex can be written as follows:

$$Cu + (NH_4)_2SO_4 + 2NH_4OH + 1/2O_2 \rightarrow [Cu(NH_3)_4]SO_4 + 3H_2O$$

MATERIALS AND METHODS

In this study, two laptops and two mobile phones presented in Figure 1 were recycled.

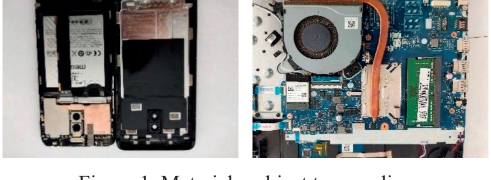

Figure 1. Materials subject to recycling

The first step of this process was to manually disassemble the waste and separate it into components (case, screen, parts attached to the printed circuit board and printed circuit boards) using different techniques (Kaya, 2016). During disassembly, various components that could be removed were also separated, such as batteries, capacitors and wiring.

RESULTS AND DISCUSSIONS

The main objective of this work is to recycle copper and silver from electrical and electronic waste by passing them into solutions and introducing them into non-polluting chemical processes.

After performing the manual disassembly and separation, a manual mechanical shredding of the printed circuit boards shown in Figure 2 was performed.

Figure 2. Printed circuit boards subjected to the shredding process

The separation of the ferrous metal fraction from the non-ferrous one was achieved by highlighting the magnetic properties of the ferrous metal fraction with the help of magnets, this fact being highlighted in Figure 3.

Figure 3. Separation of the ferrous metal fraction from the non-ferrous metal fraction

In order to reach the smallest possible diameter of the printed circuit boards, grinding was carried out in a rotating drum mill (Figure 4). A quantity of 200 g of manually shredded waste was prepared for the grinding process. Balls of different sizes (40 g, 50 g, 140 g and 300 g) were added to the mill, their total weight being 3 kg. The grinding time was 2 hours.

Figure 4. Rotary drum mill used in the printed circuit board grinding process

After the grinding process, the metals can be separated by several methods, not before the metals are put into solution. After mechanical processing, the waste is subjected to various metallurgical processes for metal recovery (Ding et al., 2019).
In order to achieve the non-catalytic process that takes place in heterogeneous systems, several preceding steps were carried out. After the grinding process, in the rotary mill, the material was subjected to separation using sieves and a vibrating table. The distribution of the material on the sieves is shown in Table 2.

Table 2. Distribution of the material on the site

Sieve size (mm)	Waste particle obtained (g)
< 2	158.88
< 1 >2	7.76
< 0.315 >1	16.1
< 0.250 >0.315	1.2
< 0.05 >0.250	12.7
>0.05	2.58

From the granulometric curve (Figure 5) it can be seen that almost 80% of the amount of waste subjected to the grinding process had dimensions greater than 2 mm, which shows that the grinding in the rotary drum mill did not have a very good yield.

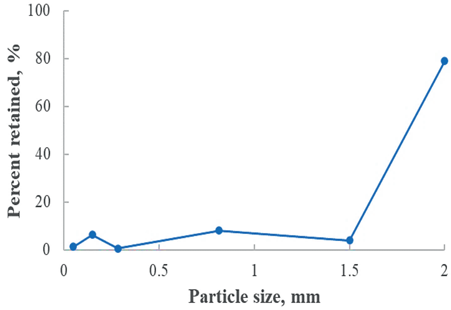

Figure 5. Granulometric curve before pyrometallurgical process

For the process of passing the copper into the solution to be effective, the size of the waste particles must be as smaller. Thus, for this process, a pyrometallurgical separation of copper was achieved. This process was carried out in an electric furnace of the type "*S.Y. electric melting furnace Italy*" and as a support was used a graphite crucible (Figure 6), so that the adhesion of the melt to the walls of the crucible is as low as possible, and the losses are minimum.

Figure 6. Pyrometallurgy process installation

In this melting process, 30 g of waste was used, previously sorted and shredded by hand. After burning, it was observed that 20.15% of the waste mass considered were volatile substances. In this processing mode, the distribution of particles on the sieve was more uniform (Table 3) and the granulometric curve is represented in Figure 7

Table 3. Distribution of the material on the sieve

Sieve size (mm)	Mass retained (g)
< 1.25	4.278
< 0.5>1.25	4.689
< 0.2 >0.5	3.872
> 0.2	10.877

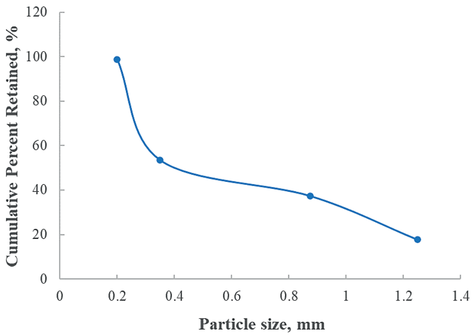

Figure 7. Granulometric curve after the pyrometallurgical process

It is worth noting that following the pyrometallurgical process, metal agglomerates can be observed (Figure 8).

Figure 8. Printed circuit boards after melting

CONCLUSIONS

Different methods can be used for recovery of valuable metals from e-waste. From these, the most common are: chemical precipitation, electrochemical, coagulation, flocculation, ion exchange, membrane filtration, adsorption, pyrometallurgical, etc.
Although have been noticeable advancements in precious metals recovery technologies, there are still certain obstacles to overcome.

There are different factors in order to attain the high recovery rate and environmentally friendly recycling of precious metals. The new technologies have in consideration low emissions, "zero waste", decrease investment and costs. Recovery technologies should be varied and integrated, based on the physical and chemical properties of different materials. Other purpose is higher leaching efficiency, that determine a less pollution. For increase recovery efficiency, different assisted methods or pretreatments are important (ultrasound, microwave, etc.).
As preliminary procedures, reducing particle size is crucial. The particle size of printed circuit boards directly influences the degree of recovery of metals from e-wastes. On the other hand, the environmental pollution is a very important aspect to take into consideration for choosing the better methods for valuable metals recovery, for example in pyrometallurgical processes, volatile materials must not be released into the atmosphere, while in chemical precipitation, flocculation or coagulation processes, no sludge or other waste should result. In this study was demonstrated that for a better yield it is necessary to increase the time of the pyrometallurgical process, the resulting materials being easy to process by grinding.
On the base of this study, upcoming technologies for metals recovering can be improved, with higher efficiency, less environmental impact, inferior cost, and advanced recovery rate.

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