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Characterisation of Printed Circuit Boards of Mobile Phones Discarded in Brazil

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The characterisation of printed circuit boards (PCB) removed from discarded mobile phones in Brazil and an inventory of data of the components in PCB were accomplished in this paper. Data of chemical composition of PCB were obtained from the physicochemical characterisation of their components through the analysis of granulometry, scanning electron microscopy with energy dispersive x-ray detector (SEM/EDS), infrared spectroscopy (FT-IR) and inductively coupled plasma optical emission spectrometry (ICP-OES). The analysis allowed a broad view and a highlight for the wide variety of elements and heterogeneity of the material. It can be also highlighted the high amount of copper, lead and other high-value metals in the PCB. This study is relevant for the development of new recycling technologies, once this material has been discarded incorrectly in Brazil. Based on the percentage of mobile phones recycled and disposed in Brazil, it is possible to quantify financial loss resulting from incorrect disposal.

1. Introduction

One of the industrial sectors that have grown the most presently is the electronics equipment industry. The lifetime of these devices is relatively short, and in a short period, this material becomes a residue, known as e-waste (Robinson, 2009). Aiming the recovery of raw materials for reuse in other production chains, evaluation of the life cycle, from the extraction of raw materials to the final destination, allows an improvement in the treatment of waste generated at every stage of the product life.

Due to the high demand in the market of mobile phones and other electronic equipment, once access to these products has grown significantly to a greater portion of the population, the industry that manufactures these products requires a greater amount of precious metals and other specific materials in its production chain, and this increases consumption of natural resources (Ayres, 1997). Although the mobile phone is among the smallest electronic equipment, it has the highest concentration of precious metals in its constitution (Moraes, 2010). The mobile phone consists of several components, such as liquid crystal display (LCD), rechargeable battery and printed circuit board (PCB). The PCB is the equipment that controls all the functions of the phone, and in its composition, there are almost all elements of the periodic table (Robinson, 2009). PCB contributes in 59 % of the environmental impacts caused by incorrect discarded mobile phones; the liquid crystal display is responsible for 39 % of the impacts, which are caused due to toxicity of the components that are leached into groundwater (Boks et al., 2000). Many waste mobile phone (WMP) components, particularly batteries and PCB, contain heavy metals, such as Cd, Cu, Ni, Sb, and Pb, and other persistent biologically accumulative toxic substances (Vieira et al., 2014) that can pollute the air, soil, and water if the WMP is arbitrarily discarded, incinerated, buried, or otherwise disposed of improperly (Bian et al., 2016).

Besides the increase of accessibility to the mobile phone, the technological advances in this area occur at a steady pace, leading consumers to feel the need to always have the newest and most modern equipment (Parson, 2006). Moreover, there is the intentional practice of the industry to limit the useful life of electronic products and do not provide a wide assistance for repairs, so consumers are always getting new products and

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sustaining this market, a practice known as planned obsolescence, which goes completely against sustainable actions (Paiano et al., 2013). The combination of these factors justify that the amount of electronic waste is increasing worldwide.
The problem of electronic waste is a reality for developed countries, such as German and USA that export obsolete products to other countries, and for developing countries, where productivity and imports of these products grows on a large scale (Sthiannopkao and Ming, 2013). Developed countries export their e-waste to poor countries to solve the problem of waste in its territory, once there is little space available for waste disposal, and poor countries import these products in order to sell the components as raw material, which represents a source of income for a contingent of the population (Kahhat and Williams, 2012).
The handling of e-waste is an important step in its recovery. Disassembly is a difficult and delicate task, but it must be done with caution to not damage the next steps of recycling (Jolly and Rhin, 1994). There is also the complication due to the presence of heavy metals such as lead, cadmium and mercury, which have high potential for environmental impacts and health of animals and humans, and therefore its handling and treatment require the right treatment (Wu, 2008). The preprocessing gathers components that contain fractions richest in one or more types of precious metals and are sent for recycling. The recovery is done by mechanical process or fusion, as pyrolysis (Goosey and Kellner, 2003). The recycling of waste cell phones not only bring large benefits, but also reduce environmental problems (Li et al., 2016), and for this purpose, the characterisation of this kind of waste in an important step in the recycling process.
This work aimed at the characterisation of printed circuit boards taken from discarded mobile phones in Brazil and will provide important information for future life cycle assessment of this product in the country.

2. Methodology

2.1 Characterisation of printed circuit boards

One kilogram of printed circuit boards removed from various models of mobile phones, kindly provided by University of São Paulo (USP/CEDIR/Brazil), were ground in a knife mill. Various particle sizes of the material were separated gravimetrically, by means of vibrating screens (brand Produtest, Brazil).
Six vibrating screens and background with meshes of 1 mm, 0.71 mm, 0.60 mm, 0.425 mm, 0.18 mm, 0.075 mm were used for granulometric classification. The Sauter mean diameter was calculated and this value was chosen to represent the average diameter of the particles. The ground material was characterised by Scanning Electron Microscopy with energy dispersive x-ray detector (SEM/EDS), infrared spectroscopy (FT-IR) and inductively coupled plasma optical emission spectrometry (ICP-OES). In all these analysis, it was used the particle size more suitable for each technique.
The technique of Scanning Electron Microscopy (SEM) was used in order to obtain images of high magnification and detail of the material surface with the equipment LEO Electron Microscopy / Oxford model 440i. It was not necessary to perform the metal plating surface, once the sample already had metallic material sufficient for the analysis to be performed. The EDS, a tool of SEM, model 6070, was used to identify the composition of the sample, in a semi-quantitative way, at specific points in the images produced by SEM.
The infrared spectrum by the Fourier Transform Infrared (FT-IR), manufactured by Thermo Scientific Model 6700 Nicolet, was obtained using KBr pellets. The measurement was done in transmittance in the range 4,000 - 400 cm^{-1}. Thus, it was possible to identify organic functional groups present in the sample, from the polymeric material.
For analysis by ICP-OES with Perkin Elmer - 3000 DV, samples were previously subjected to magnetic separation, by means of magnetic blankets, to remove the high iron concentration that might interfere in this analysis. The samples were digested in aqua regia (HNO_3 : HCl 1 : 3) in the ratio 1 g of solid residue in 20 mL of solution for 24 h at room temperature. The material not dissolved in the leaching corresponded to the polymer and ceramic fraction, and leached contains the metals soluble in aqua regia. The leach liquor separated from undissolved solids (by simple filtration using filter paper quantity porosity of 7.5 mM) was analysed for metals. This allowed identifying, using a radiation detection system, a large number of elements in the sample. It was also carried out an acid leaching in sulfuric acid with solid: liquid ratio 1 : 10 at 75 °C and pH = 0.5. An aliquot of leached liquor was collected after 4 h and analysed by ICP-OES. The resulting undissolved material was washed with deionised water and dried at 60 °C +/- 5 °C for 24 h and passed through acid leaching in oxidising environment, with sulfuric acid and hydrogen peroxide under the same temperature and same solid: liquid ratio used in the acid leaching. It was added 10 mL of hydrogen peroxide every 30 min, totaling 80 mL after 4 h. The leach liquor was analysed by ICP-OES for cations identification/quantification (Moraes, 2010).

3. Results and Discussion

The ground material, about 400 g, was separated by vibrating screens that remained in agitation for about an hour. The Sauter mean diameter calculated for the entire sample was 0.2158 mm. According to a specific size diameter, aliquots part of particles distributed in the screens were used for morphological analysis and other analyses.

3.1 Morphological analysis of surface

Figure 1 shows the analysis of images obtained by Scanning Electron Microscopy. There are several patterns of particles with different qualitative compositions. Figure 1(a) refers to the material with an average particle size 0.125 mm, the image is magnified 50 times. It is possible to see the heterogeneity and variety of species of particles in the sample, as expected. In Figures 1(b) and 1(d) with a particle size smaller than 0.075 mm and magnification 500 times and 1,000 times, respectively, is also visible the range of the material and becomes sharper the size difference between them. The micrograph in Figure 1(d) is referred to a particle consisting essentially of copper, which often coats by a layer of other materials such as gold, copper, zinc and nickel (Robinson, 2009). Figure 1(c) has the same granulometry of Figure 1(a) and focuses on specific parts of the sample that illustrates further details with magnification of 150 times.

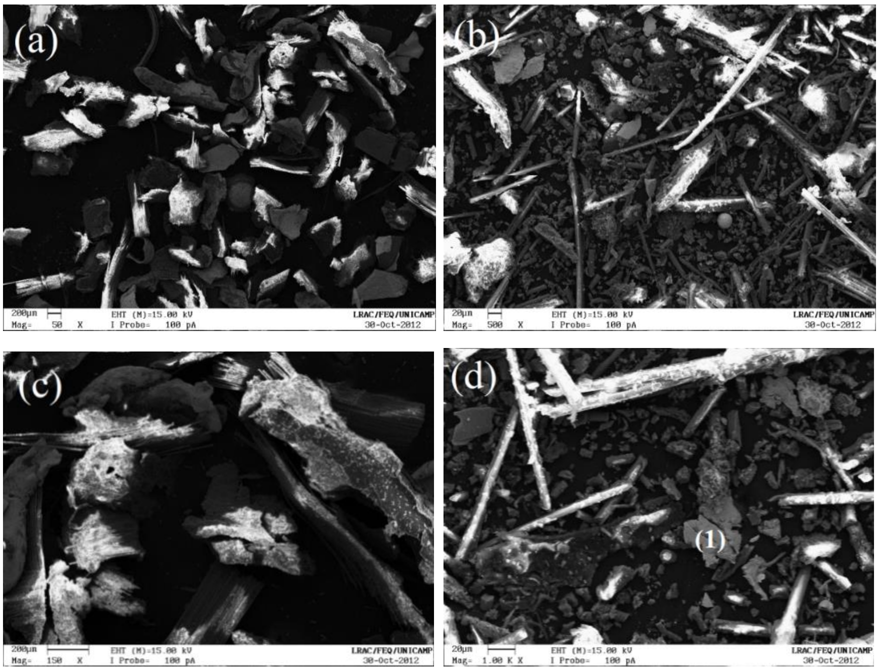

Figure 1: Scanning Electron Microscopy of the ground sample of printed circuit boards of mobile phones

Table 1: Average percentage of elements present in the sample analysed by EDS

Element	O	Mg	Si	Ca	Ti	Fe	Ni	Cu
Average (%)	28.492	0.118	9.573	4.750	0.565	0.842	0.612	24.178
Element	Br	Mo	Ba	Al	C	S	Zr	Total
Average (%)	4.383	0.722	1.168	1.260	23.225	0.013	0.098	100

3.2 Chemical composition by EDS

EDS analyses were performed with the material with a particle size less than 0.075 mm. The readings were made focusing on different parts of the sample for the analysis provides a result as close as possible to the real amounts of the elements. Table 1 refers to the average of the elements found in the six measurements. Through this analysis, it can note that there is a high amount of oxygen, copper, carbon and silicon in the samples analysed. It is noteworthy the high amount of copper, the metal present in the greatest amount according to the analysis, which is a metal with considerable monetary value.

3.3 Identification of functional groups

Figure 2 shows the infrared spectrum obtained for the sample of particles of comminuted PCB. From the spectrum it was possible to determine functional groups and chemical bonds in the sample, identified in Table 2.

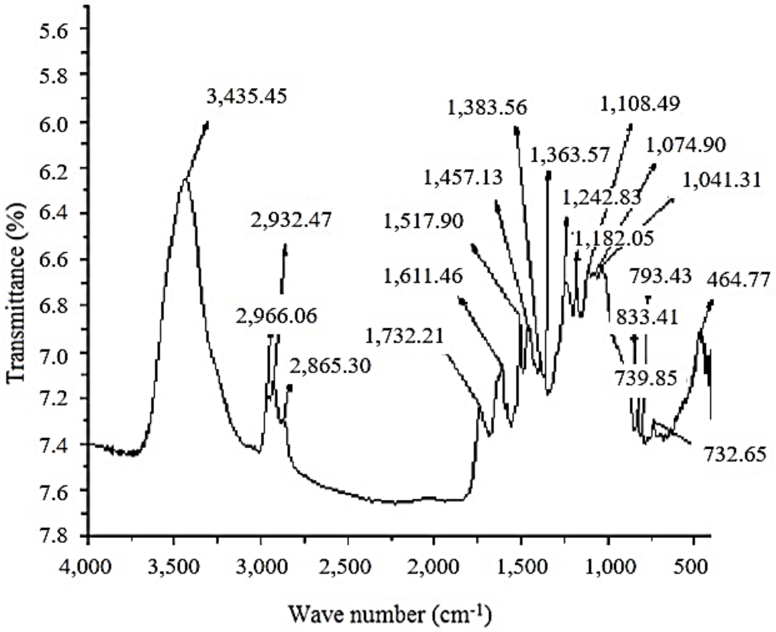

Figure 2: Infrared spectrum of the ground sample from printed circuit boards of mobile phones

The absorption bands in the infrared spectrum refer to polymer and paper materials present in PCB, particularly to the components fixed on the baseboard. Through observation of the characteristic peaks, we found that the PCB is composed primarily of epoxy resins (peaks at 833 cm^{-1}, 1,242 cm^{-1}) and polyester (peaks in 1,242 cm^{-1}, 1,108 cm^{-1}, 1,732 cm^{-1}). The peak at 1,242 cm^{-1} due to CO bond and the peak at 1,732 cm^{-1} corresponding to the C = O stretch, indicated the presence of ester grouping. Since these resins are thermoset materials, the impossibility of melting complicates the recycling of polymers. The presence of crosslink in the structure of these polymers further complicates their recover. In addition to the polymeric material, glass fibers are present, which are used together with the epoxy resin in composition of the material of the base of PCB and also ceramic material (Paiano et al., 2013).

Table 2: Functional groups of the polymer printed circuit boards of mobile phones

Peak (cm^{-1})	Functional Group
3,435.45	Group OH
2,932.47	C-H Stretch
1,732.21	C=O
1,611.46	Stretch double bond: C = C, C = N, C = O
1,517.90	
1457.13	Carboxylic acid salts
1242.83	C-O Stretch
1182.05	C-N Aliphatic
1041.31	S=O
793.43	C-H Out of plane
739.85	Aromatic ring

3.4 Chemical composition by ICP-OES

Acid leachings of PCB particles (aqua regia, acidic and oxidising environment) were carried out for ICP-OES analysis and it was determined the contents of aluminum, arsenic, barium, cadmium, lead, copper, chromium, manganese, silver, selenium, sodium, iron, zinc, mercury and palladium from the leaching extracts, shown in Table 3.

Table 3: Chemical composition of the PCB obtained by ICP-OES

	Extract obtained from the leaching		
Parameters	Aqua regia	Sulfuric acid	Oxidising medium
Aluminum, % m/m	0.382 +/- (0.004)	0.79 +/- 0.01	17.7 +/- (0.4)
Arsenic, mg/kg	114 +/- (4)	< 10	< 10
Barium, % m/m	1.36+/- (0.03)	< 9	< 9
Cadmium, mg/kg	< 13	< 13	< 13
Lead, % m/m	1.57 +/- (0.02)	43.6 +/- (0.4)	42.4 +/- (0.4)
Copper, % m/m	7.4 +/- (0.3)	1000 +/- (30)	3.11 +/- (0.04)
Chromium, mg/kg	660 +/- (20)	46.0 +/- (0.2)	< 9
Iron, % m/m	1.21 +/- (0.02)	1.05 +/- (0.01)	< 2
Manganese, mg/kg	470 +/- (20)	313 +/- (1)	32 +/- (2)
Mercury, mg/kg	< 0.15	< 0.15	< 0.15
Palladium, mg/kg	215 +/- (9)	< 2	< 2
Silver, mg/kg	620 +/- (40)	< 4	< 4
Selenium, mg/kg	< 2	< 2	< 2
Sodium, mg/kg	320 +/- (10)	532 +/- (3)	310 +/- (2)
Zinc, % m/m	0.219 +/- (0.006)	0.106 +/- (0.001)	0.161 +/- (0.001)

From this analysis, we can identify the metals that are present in higher concentrations in each leached extract in order to follow the recovery process according to the metal to be recovered. Copper is the metal present in greater quantity in accordance with the EDS analysis, and it has a considerable great value (Da Silva et al., 2016). Besides, in accordance with the ICP-OES analysis, it is found in higher concentrations in solution of sulfuric acid and also in sulfuric acid oxidising environment. Therefore, these would be the most appropriate leaching to recover this metal, which upon leaching must be made through the electrowinning process (Moraes, 2010).

It can also be identified the high concentration of lead leaching in acidic and oxidising environment, which is a metal that is considered highly dangerous and, currently in Brazil, its ores are practically exhausted (Lima et al., 2014). Recovery of this metal through electro hydrometallurgical process is an alternative economical and environmentally appropriate (Scott, 1997). Lead is a metal widely used in the electronics industry. The largest amount of this metal is in the welds of PCB. However, there are laws limiting the amount of this metal thus enforcing replacement by more environmentally friendly alloys. Despite this limitation that has been imposed, in some cases there are no materials which replace that with the same level of performance and reliability (Vasconcelos et al., 2012).

Silver, although present in small quantities compared to other metals, is one of the materials of electronic equipment with higher environmental impact because it is easily leached from wastes and can contaminate groundwater (Cantuaria et al., 2016).

4. Conclusions

In spite of low concentration in PCBs, the precious metals have an economic value and environmental significance well above other substances present in much greater quantities, such as iron, plastics. Precious metals represent over 80% of the economic value of the PCB of computers, phones and calculators.

The characterisation of PCB from discarded mobile phones exposed a very large variety of elements present in the PCB. This factor hinders the recovery of separated elements, because each element has a technique more suitable and efficient for its recovery. The fact that PCB is the most expensive part of mobile phone is explained by the presence of precious elements with high benefit. This, in addition to a large amount of copper present, justifies the financial benefits of recycling.

The concentration of precious metals in printed circuit boards of mobile phones is higher than in the mines where ores are extracted. The importance of the recovery of precious metals from electric and electronic equipment is shown obvious and with great importance, when faced with the impacts that the primary extraction causes in environment. The environmental and economic impacts of secondary production are much lower than primary production. Thus, it should also consider the environmental risks associated with the generation of waste from mining steps to obtain the raw materials that support the electronics industry.

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