

Leaching of gold and silver from printed circuit board of mobile phones

Lixiviação de ouro e prata de placas de circuito impresso de celulares

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Abstract

Nowadays there is a wide variety of models, sizes and configurations of mobile phones available for consumption. After the life cycle of this equipment, the recycling and reuse of the precious metals found in the printed circuit boards (PCB) of the mobile phones are principal objectives. Thus, the objective of this work was to characterize the gold and silver present in a PCB and develop a recycling route using alternative reagents for cyanide, such as sodium and ammonium thiosulfate. These reagents are less harmful to the environment and worker health. The first characterization of gold and silver was performed with aqua regia. The results show 86.26g Au/ton of PCBs and 123.85g Ag/ton of PCBs. The second characterization was performed with a commercial cyanide-based reagent and 112.02g Au/ton of PCBs and 26.13g Ag/ton of PCBs were obtained. A leaching study with solutions based on thiosulfate was performed and an extraction of 9.02g Au/ton of PCBs and 33.88g Ag/ton of PCBs was obtained, compared to characterization results using a cyanide-based reagent.

Keywords: printed circuit boards; leaching; thiosulfate solutions.

Resumo

Nos dias atuais, há uma infinidade de modelos, tamanhos e configurações de equipamentos eletro-eletrônicos disponíveis para o consumo. Visando a realizar a reciclagem e o reaproveitamento dos metais preciosos encontrados nas placas de circuito impresso (PCI) dos celulares, esse trabalho tem o objetivo de caracterizar o ouro presente nas PCI dos aparelhos celulares e desenvolver uma rota de reciclagem para o ouro e a prata, utilizando reagentes alternativos ao cianeto, como o tiosulfato de sódio e tiosulfato de amônio. Esses reagentes agridem, numa menor intensidade, o meio ambiente e a saúde do trabalhador. Primeiramente realizou-se uma caracterização com água-régia. Os resultados mostraram 86.26g Au/tonPCI e 123.85g Ag/tonPCI. Na segunda caracterização, foi utilizado o reagente comercial a base de cianeto e o resultado foi de 112.02g Au/tonPCI e 26.13gAg/tonPCI. Para a lixiviação com tiosulfato de sódio, chegou-se ao resultado de 9.02g Au/tonPCI, na lixiviação do ouro, e de 33.88g Ag/tonPCI, na lixiviação da prata, comparando com os resultados da caracterização usando reagentes a base de cianeto.

Palavras-chave: placas de circuito impresso; lixiviação; soluções de tiosulfato.

1. Introduction

The consumption of electronic equipment has been increasing con-

stantly, since with the speed of technological advancement, it becomes obso-

lete in a relatively short period of time. Cell phones are part of this waste

and show a great potential for the recovery of metals that are present in its composition. The number of devices becoming obsolete every year is increasing, so proper disposal has become an environmental concern. The recycling or reuse of components, especially metals, is a good alternative for this waste.

According to Kasper *et al* (2011), a mobile phone consists of a polymeric fraction, a printed circuit board (PCB), a liquid crystal display (LCD), a battery, a keyboard and an antenna.

The printed circuit boards (PCB), units present in all types of electronic equipment, are present in the waste and have an extremely heterogeneous composition, generally containing plastic, ceramics, base metals and precious metals (Veit *et al*, 2008; Hall and Williams, 2007 and Yamane *et al*, 2011).

The metallic fraction contains various metals, such as copper (Cu), tin (Sn), zinc (Zn), nickel (Ni) and precious metals as gold (Au), silver (Ag) and palladium (Pd) (Yamane *et al*, 2011).

According to Wu *et al* (2008), in general, a printed circuit board from mobile phones has a composition of polymers (30 to 35%), oxides (30%),

and metals (30 to 40%). According to Huissman *et al* (2007), the fraction of greater economic interest is the metal, which comprises 20 to 30% of copper, 6 to 8% of iron, 5% of nickel, 2.5% of tin, 1.1% of lead, 1.1% of zinc, 250mg of silver, 24mg of gold, 9mg of palladium and others.

Evaluating the economic point of view, the recycling of mobile phones can be very attractive, because every ton of material contains on average 130kg of copper (Cu), 3.5 kg of silver (Ag), 340 g of gold (Au) and 140g palladium (Pd) (Schulep *et al*, 2009).

The hydrometallurgical process is one of the ways to extract these metals. This process consists in a leaching of the PCB's residues by dissolving the metals with an appropriate leaching solution, purifying the original leaching solution and recovering the metals (Syed, 2006).

Generally, the oxidative leaching process is required for an efficient extraction of base metals and precious metals of interest (Tuncuk *et al* 2012 and Syed, 2006). Currently, the most commonly employed method for the extraction of gold and silver in ores, is cyanidation (Syed, 2006 and Chu *et*

al, 2003). Therefore, this process could be used for the extraction of metal in printed circuit boards (Kasper *et al*, 2012 and Öncel *et al*, 2005). Cyanidation has some problems: it uses a highly toxic reagent, the process should be handled carefully and disposal of wastewater must be done with extreme rigor after the residue has its proper treatment (Trindade and Barbosa Filho, 2002).

In recent years, the leaching of precious metals with thiosulfate solutions has been presented as an alternative technology to cyanidation, due to growing environmental concerns regarding the use of cyanide (Feng and Deventer, 2010, Chandra and Jeffrey, 2004). According to Grosse *et al* (2003), Aylmore and Muir (2001) and Aylmore and Muir (2002), the thiosulfate solutions may be an adequate substitute for the use of cyanide as a leaching agent for precious metals, such as gold and silver, in the presence of ammonia and copper (II) to form compounds with metals.

Thus, this study investigated the possibilities of extracting gold and silver, present in PCB's from mobile phones, by leaching with thiosulfate solutions.

2. Materials and methods

The mobile phones used in this research, damaged or obsolete, were collected in multi technical assistance shops. However, only equipment of the same brand and model were used in this

study, enabling a better assessment of the real amount of metal leached.

After collecting this equipment's, a manual disassembling was performed and the batteries and polymer substrates

were separated.

In this work, the leaching tests were performed only with whole PCB's.

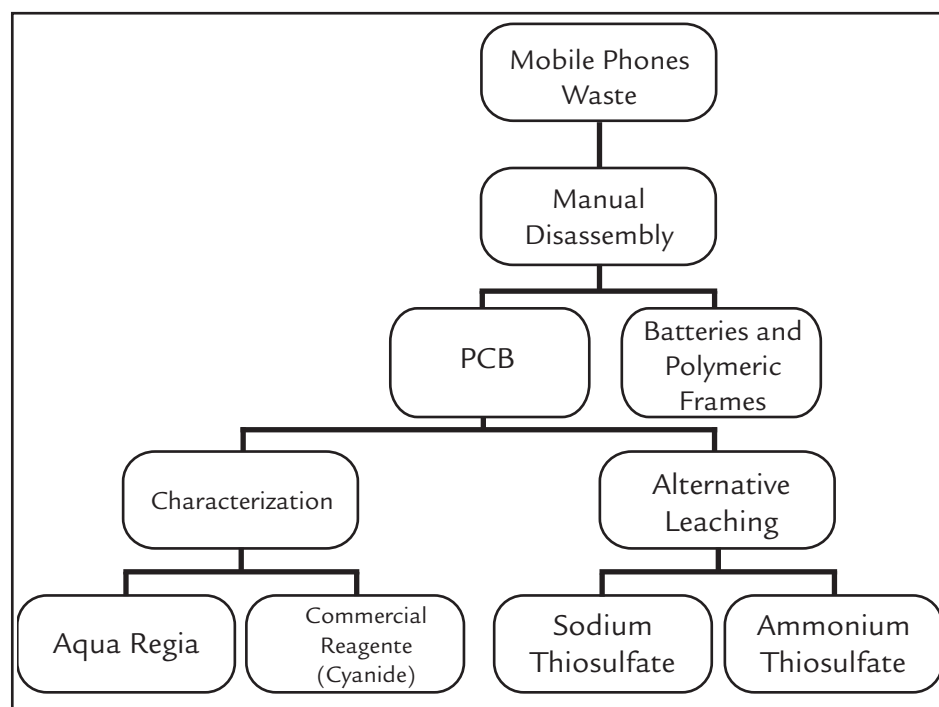


Figure 1
Flowchart with steps of the work..

Figure 1 shows a flowchart with all steps performed in this study. In the first test (Test 1), the PCB's were leached with aqua regia and the solutions obtained were diluted with acid solution (HNO₃) and afterwards were characterized by the Atomic Absorption Spectroscopy method. The leaching tests were performed in a solid/liquid ratio (S/L) 1/20, using approximately 30g of PCB, with magnetic stirring, in 2 hours and 60 ± 3 °C.

After, a characterization test (Test 2) with a commercial cyanide-based leachate was performed to obtain values similar to those usually obtained by industry.

The commercial leachate used for comparison purposes was a chemical leacher (Galvastrepper®) for gold and its alloys. This product is supplied as a liquid containing potassium cyanide in a concentration of 6 to 8%, slightly yellow, and removes up to 1 mm gold

per minute at room temperature by simple immersion. These leaching tests were performed in a solid/liquid ratio (S/L) 1/20, using a concentrate solution (pH=12.5), for 2 hours, at room temperature (25 °C).

In the next step, in possession of the results of the leaching with aqua regia and commercial cyanide-based leachate, leaching tests were performed with alternative reagents (thiosulfate) to evaluate efficiency and thus determine the reaction conditions for a possible currently-used cyanide replacement by thiosulfate solutions for leaching precious metals.

Sodium thiosulfate (Na₂S₂O₃) and ammonium thiosulfate ((NH₄)₂S₂O₃) were evaluated as to PCB leachers. Different concentrations of ammonium hydroxide (NH₄OH), copper (II) sulfate (CuSO₄) and hydrogen peroxide (H₂O₂) were added in the leaching tests with

thiosulfate. The order of addition was as follows: first sodium thiosulfate or ammonium thiosulfate, second ammonium hydroxide and finally the cupric ions or hydrogen peroxide.

The tests with sodium and ammonium thiosulfate were performed with whole printed circuit board, using one unit for each test, with mechanical agitation and temperature of 25°C ± 2°C. The pH of the system was controlled between 9.0 and 11.5 with sodium hydroxide (NaOH) or sulfuric acid (H₂SO₄). According to previous studies (Breuer and Jeffrey, 2003), this is the best pH range for the leaching of precious metals.

In the system with sodium thiosulfate, ammonium hydroxide (NH₄OH), copper (II) sulfate (CuSO₄) and hydrogen peroxide (H₂O₂) were evaluated at different molar concentrations of each reagent. Table 1 shows the parameters used in the leaching test with sodium thiosulfate.

Test	[S ₂ O ₃ ²⁻] (M)	[NH ₄ OH] (M)	[Cu ⁺²] (M)	[H ₂ O ₂] (M)	Tem- perature (°C)	Time (hours)	pH	Ratio S/L
3	0.1	0.2	-	-	25	4	11.2	1/20
4	0.1	0.2	0.015	-	24	4	10.7	1/20
5	0.1	0.2	0.03	-	24	4	10.4	1/20
6	0.1	0.2	0.05	-	26	4	10.4	1/20
7	0.1	0.2	-	0.01	26	4	11.0	1/20
8	0.1	0.2	-	0.05	26	4	11.0	1/20
9	0.1	0.2	-	0.1	26	4	11.0	1/20

Table 1
Parameters used for leaching PCB's with sodium thiosulfate and different concentrations of ammonium hydroxide, copper II sulfate and hydrogen peroxide.

In system with ammonium thiosulfate ((NH₄)₂S₂O₃), ammonium hydroxide (NH₄OH), copper (II) sulfate (CuSO₄) and hydrogen peroxide (H₂O₂) were also

evaluated at different molar concentrations for each reagent. The tests were prepared at a ratio liquid/solid of 1/20 keeping the final volume of the solution

constant. The tests were performed with mechanical agitation and temperature of 25°C ± 2°C. The parameters for these leaching tests are shown in Table 2.

Test	[S ₂ O ₃ ²⁻] (M)	[NH ₄ OH] (M)	[Cu ⁺²] (M)	[H ₂ O ₂] (M)	Temperature (°C)	Time (hours)	pH	Ratio S/L
10	0.1	0.2	-	-	27	4	9.2	1/20
11	0.1	0.2	0.015	-	26	4	9.2	1/20
12	0.1	0.2	0.03	-	25	4	9.1	1/20
13	0.1	0.2	0.05	-	25	4	9.0	1/20
14	0.1	0.2	-	0.01	26	4	9.2	1/20
15	0.1	0.2	-	0.05	25	4	9.0	1/20
16	0.1	0.2	-	0.1	26	4	9.0	1/20

Table 2
Parameters used for leaching of PCB with ammonium thiosulfate and different concentrations of ammonium hydroxide, copper (II) sulfate and hydrogen peroxide.

All samples obtained at different leaching tests, during this study, were analyzed by Flame Atomic Absorption Spectroscopy, in a Varian model FS240 device.

In Test 1 (with aqua regia) the solutions were diluted with acid solution to prevent the silver precipitation.

are shown in Table 3.

3. Results and discussion

Leaching of PCB's with aqua regia

The results obtained of leaching PCB's, after the aqua regia dissolution,

are shown in Table 3.

Test	Au (g/tonPCB)	Ag (g/tonPCB)
1	86.27	123.35

Table 3
Results of PCB leaching with aqua regia for the elements gold and silver.

According to Fray and Park (2009), Tenório et al. (1997) and Veit et al. (2006), the composition of printed circuit boards may vary, probably due to the different methodologies used in each study, and due to the composition changes with brand, model and year of manufacture. Ilyas et al. (2007) also suggest that the analytical methods and the origin of the material (equipment type, brand, model and year of manufacture) can also be attributed to these differences.

are shown in Table 3.

Leaching of PCB's with leachate commercial cyanide-based

The results of the leaching with the commercial reagent are shown in Table 4.

Table 4
Results to leaching of PCB's with commercial reagent (cyanide).

Test	Leaching	gAu/tonPCB	gAg/tonPCB
2	Commercial Reagent (Cyanide base)	112.02±22.03	26.13±1.9

The results demonstrate that the commercial reagent was efficient for leaching gold, but as expected, the results for silver were not significant. Anyway,

these results show the amount of precious metals that would be recovered in real conditions using a commercial reagent.

Thus, these values were used, as

a reference, to compare the amount of silver and gold leached using alternatives reagents, such as sodium and ammonium thiosulfate.

Leaching of PCB's with sodium thiosulfate and ammonium thiosulfate

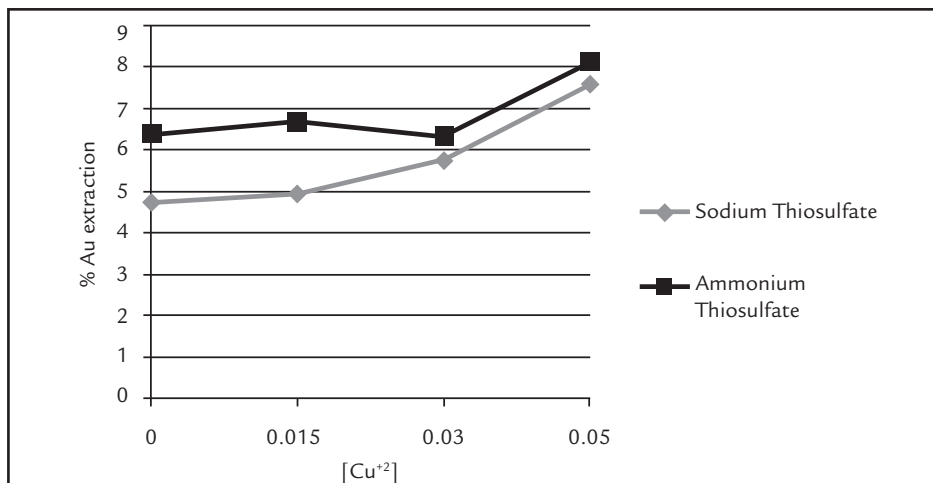
In this step, sodium and ammonium thiosulfate were used to extract gold and silver of whole PCBs. In both leachates, the effect of adding copper, as a catalyst agent, and hydrogen peroxide, as the oxidizing agent to the reaction were evaluated.

The extraction of gold in both sys-

tems: solutions containing 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.2M NH_4OH and solutions containing 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ and 0.2M NH_4OH , with different concentrations of copper are shown in Figure 2. The addition of cupric ions increases the leaching of gold for both systems, showing that the addition of this

agent catalyst increases the gold extraction. The addition of 0.05M of cupric ions obtained the best extraction reaching similar results for sodium and ammonium thiosulfate. In this case, further studies are needed to evaluate the addition of cupric ions above 0.05M.

Figure 2
Effect of copper concentration in the extraction of Au with 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH and 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH .



The effect of adding an oxidizing agent (H_2O_2) for gold extraction in solutions of sodium thiosulfate and ammonium thiosulfate are shown in Figure 3. It was observed that the addi-

tion of the oxidizing agent increases the gold extraction, reaching a percentage similar to that of the cupric ion addition. It can also be observed that the best efficiency with ammonium thiosulfate was

obtained at 0.05 M of peroxide. The best efficiency for sodium thiosulfate was achieved with 0.1 M of hydrogen peroxide in the system, extracting 11% of gold.

Figure 3
Effect of H_2O_2 concentration in the extraction of Au with 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH and 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH .

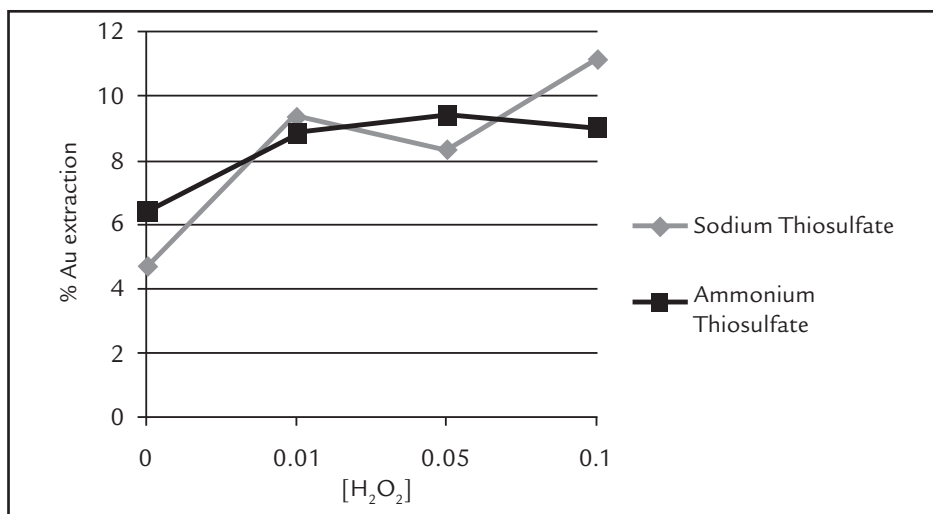


Figure 4 shows the extraction of silver in a solution containing 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.2M NH_4OH and a solution containing 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ and

0.2M NH_4OH with different concentrations of cupric ions.

It was observed that the addition of cupric ions is more efficient for a

$\text{Na}_2\text{S}_2\text{O}_3$ based leaching solution .

The best result was obtained with 0.03M of cupric ions, achieving a silver extraction of 21%.

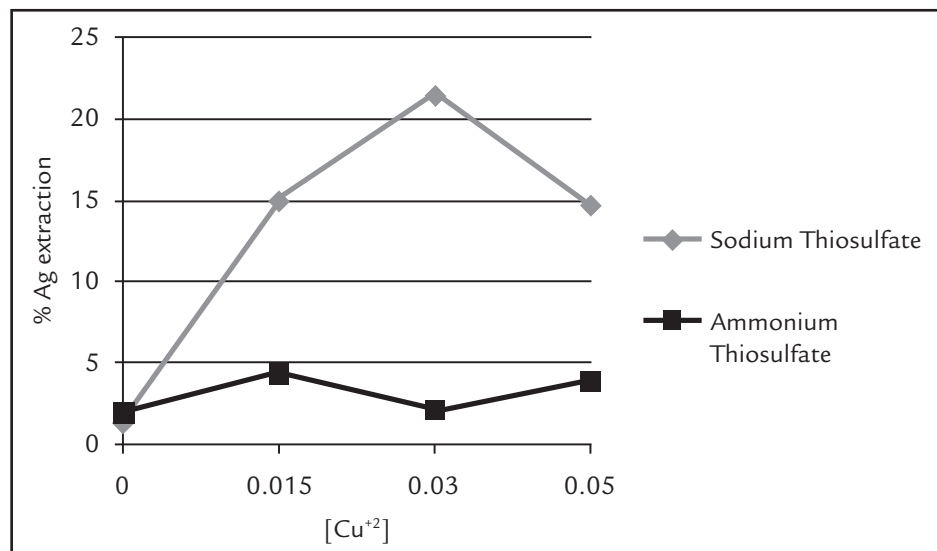


Figure 4
Effect of copper concentration in the extraction of Ag with 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH and 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH .

The effects of adding the oxidizing agent (H_2O_2), in the extraction of silver, for solutions of sodium and ammonium

thiosulfate are shown in Figure 5. The results show that the addition of hydrogen peroxide has a small influence on the

extraction levels of silver in both solutions, increasing slightly the efficiency of the process.

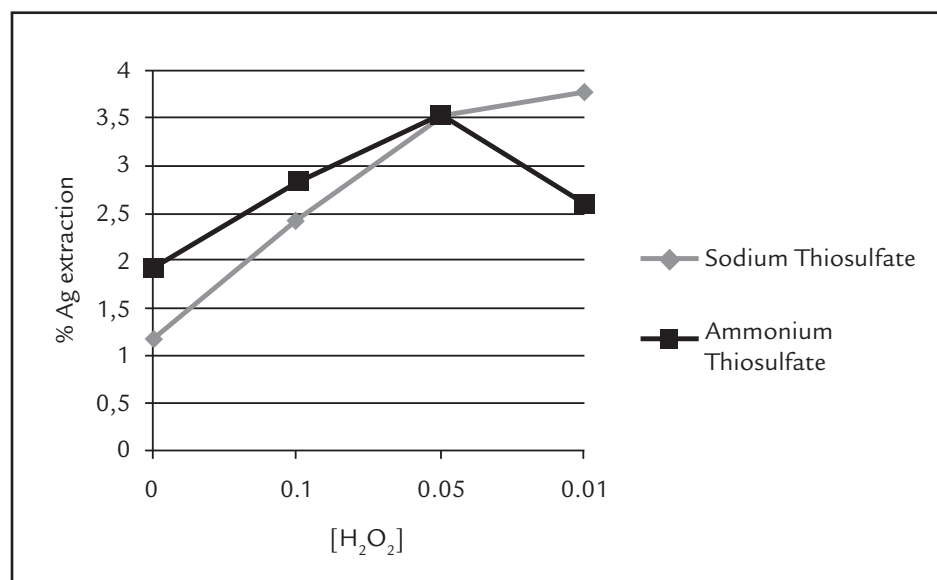


Figure 5
Effect of H_2O_2 concentration in the extraction of Ag with 0.1M $\text{Na}_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH and 0.1M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ - 0.2M NH_4OH .

4. Conclusions

The chemical leaching of whole PCB's extracted 86.23 g of Au/ton and 123.25 g of Ag/ton using aqua regia. The leaching with the commercial cyanide-based reagent obtained mean values of 112.02 g of Au/ton and 26.13 g of Ag/ton from whole PCB's.

The results for leaching gold with alternative reagents, sodium thiosulfate and ammonium hydroxide, show that the best extraction was achieved at 0.1M sodium thiosulfate and 0.2M ammonium hydroxide, when adding 0.1M of hy-

drogen peroxide as an oxidation agent, obtaining approximately 11% of gold. A similar result was obtained at 0.1M ammonium thiosulfate and 0.2M ammonium hydroxide, when adding 0.05M of peroxide, obtaining approximately 9% of gold.

The leaching of silver reached the best result with ammonium thiosulfate. It was possible to extract approximately 21% of silver by adding 0.03M of cupric ions. The addition of hydrogen peroxide did not obtain a significant increase in the

silver extraction.

In general, it can be concluded that for the gold and silver extraction from PCB waste, under the conditions tested, the use of solutions containing thiosulfate did not show favorable results when compared to the extraction levels achieved by a commercial cyanide-based reagent.

These results demonstrate that more studies are necessary, using other parameters and different solution concentrations to increase the efficiency of the leaching process.

5. Acknowledgements

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