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Synthesis of Gold Nanoparticles Using Recovered Gold from Electronic Waste

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Electronic waste contains considerable amounts of gold in its composition, especially some composting pieces like CPUs and memory cards. Recovered gold can have many uses, among those it can be an excellent alternative source for low-cost nanoparticles synthesis. Commercial chloroauric acid is the main precursor for nanoparticle synthesis, however its cost makes the process very expensive. Finding a lower cost alternative precursor is very important because it allows to economically enabling several gold nanoparticles applications. Through the hydrometallurgical method, it was possible to recover and to purify the appreciable amount of gold from old CPUs. This gold has been used to synthesize nanoparticles with a size of 198.5 nm and moderate stability.

Graphical abstract
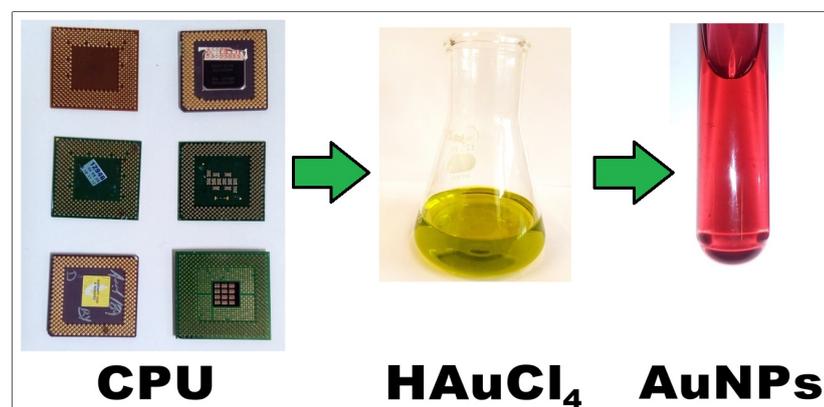
CPU → **HAuCl$_4$** → **AuNPs**

1. Introduction

In recent years, the disposal of electrical and electronic equipment has become a major environmental problem while generating interest for its great added economic value. The worldwide production of electronic equipment waste was approximately 44.7 million tons in 2016, and the production has grown by approximately 4% per year [1]. Electronic waste has considerable quantities of base metals (iron, copper, aluminum, nickel, and zinc), hazardous metals (lead, cadmium, and mercury), rare metals (tantalum and gallium) and small quantities of precious metals (silver, gold, platinum and palladium) [2, 3]. Gold is found in small quantities on printed circuit boards (PCBs) (150 ppm) however, this amount is 10 times higher than that found in gold-rich ores [4, 5]. Gold recovery from printed circuit boards is difficult due to the presence of large quantities of base metals that have lower nobility in the galvanic series and which are always leached before consuming large amounts of reagents [6].

In laboratory-scale it is possible to recover very small quantities of gold from electronic waste however, this amount is sufficient for the synthesis of nanoparticles, a product of great importance for several research areas. In recent years several applications for gold nanoparticles and other metals have been emerging as drug delivery [7-9], electrochemical and gas sensors [10–13], artificial photosynthesis [14], hydrogen production, [15], photovoltaic

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cells [16], photocatalysis [17-19] among others applications.

The synthesis of gold and other metal nanoparticles by reduction with white phosphorus and their interaction with light was first described by Michael Faraday in 1857 [20]. In 1951 John Turkevich described a method in which he used a sodium citrate solution to reduce Au^{3+} ions of a boiling-heated chloroauric acid solution, which was called the Turkevich Method [21]. In 1973 Frens improved the Turkevich method, which was then called the Turkevich-Frens Method [22].

The advantage of this method is that sodium citrate acts as both reducing and stabilizing agents and the synthesis procedure generally lasts a few minutes and allows to obtain a red-colored colloid with approximately 20nm nanoparticles [21].

The Turkevich Method is long standing, it is still widely used by many researchers, and many new methodologies for nanoparticle synthesis were created from the original procedure. Variations of the Turkevich-Frens method include initialization of nanoparticle formation in solution containing chloroauric acid and citrate or other reducing agents using ultraviolet radiation [23], gamma radiation [24] and micro-waves [25], being possible to modulate the particle size according to the time and intensity of irradiation on the solution. There is also the inverted Turkevich method used by the addition of a chloroauric acid solution over a sodium citrate solution, which is the most efficient method for modulating particle size and shape [26,27]. The nanoparticles obtained can have stability of some hours to years [28].

The high concentration of sodium citrate significantly improves AuNPs stabilization while gold concentration above 0.8 mM destabilizes and causes particle growth and precipitation, difficulty in reproducing the method due to the particle size range [23]. Many studies also report nanoparticle synthesis using other reducing agents such as sodium borohydride [29, 30], fructose [31], ascorbic acid [23], besides some natural extracts of plants such as palm oil (*Elaeis Guineans*) [32] or fungal extracts such as *Puccinia graminis f. sp* [33].

The main source of gold used as a precursor for AuNPS synthesis is chloroauric acid dihydrate $HAuCl_4.2H_2O$, however, this reagent is expensive and therefore large-scale AuNPS production is very expensive and should be limited to small quantities [34].

Electronic waste such as obsoletes computers can be used as such a secondary source of gold, mainly scraps with high concentration of gold such central processing units (CPU) pins, wires, memory RAM chips and contacts [35]. *Aqua regia* solution is the mixture of concentrate chroridric acid and concentrated nitric acid (3:1 respectively) is efficient for leaching metals presents in electronic waste, but is non-selective, highly corrosive and release chorine and nitrous oxide gases [36, 37].

$$Au_{(s)} + HNO_{3(aq)} + 4\ HCl_{(aq)} \rightarrow HAuCl_{4(aq)} + NO_{(g)} + 2\ H_2O_{(l)} \quad (1)$$
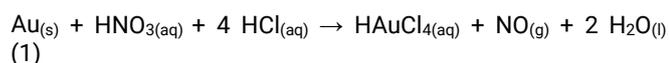
Sodium or potassium metabisulphite can be used such a selective reductant for precipitation gold in *aqua regia* solutions, after neutralization of excessive nitric acid with urea [35].

$$K_2O_5S_{2(aq)} + H_2O_{(l)} + HAuCl_{4(aq)} \rightarrow K_2SO_{4(aq)} + HCl_{(aq)} + SO_{2(g)} + Au_{(s)} \quad (2)$$
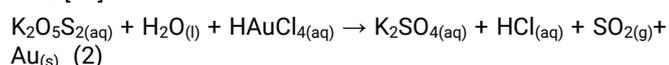
The purity of the gold obtained can be decreased due to the presence of precipitated such silver chloride and

metastannic acid (H_2O_3Sn), both originated when *aqua regia* reacts with silver and tin respectively present in electronic waste [36]. Silver chloride can be removed by complexation using ammonium hydroxide and metastannic acid can be removed using ethylenediaminetetraacetic acid [38, 39].

$$AgCl_{(s)} + 2\ NH_4OH_{(aq)} \rightarrow [Ag(NH_3)_2]^+_{(aq)} + Cl^-_{(aq)} + 2\ H_2O_{(l)} \quad (3)$$
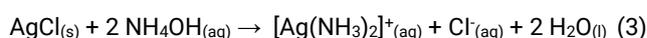
Few authors reported the use of gold obtained from an alternative source to replace commercial chloroauric acid in AuNPs synthesis. Park and Fray (2009) who recovered gold from PCB leach liquors using liquid-liquid extraction with toluene and tetraocylammoniun bromide followed by nanoparticle formation with sodium borohydride and dodecanethiol [40].

McDonagh, Massicot and King (2015) used chlorine gas to dissolve gold foil in water to obtain gold chloride solution stable for more than 12 months that can be directly used to produce nanoparticles [34].

Concerning the context presented above this paper describes the production of gold nanoparticles by Turkevich methodology using Au^{3+} ions solutions extracted from obsolete Central Processing Units (CPU). The main contribution of this work was the development of a methodology to purify the leached metallic mixture aiming to produce high purity gold nanoparticles.

2. Material and Methods

For the extraction of metals, eight models of obsolete Central Processing Units (CPU) (numbered from 1 to 8), of two different brands (A and B) were used, with 4 models for each brand, with different years of release. For duplicate determination, two identical pieces were used for each model, so 16 pieces were used.

Each CPU was leached using 30.0 mL of concentrated hydrochloric acid (Synth®) and 10.0 mL of concentrated nitric acid (Synth®) (*aqua regia* solution) heated to 80 °C for 30 minutes. The gases emitted by the decomposition of *aqua regia* were neutralized by bubbling them into sodium hydroxide solution using a trap by mounting the system shown in Figure 1. To minimize power consumption and to make the method simpler, no procedures such as milling or calcining CPUs were performed prior to leaching. The resulting solutions were diluted to 100.0 mL and the concentration of the metals present was determined using Varian® AA240FS flame atomic absorption spectrometer.
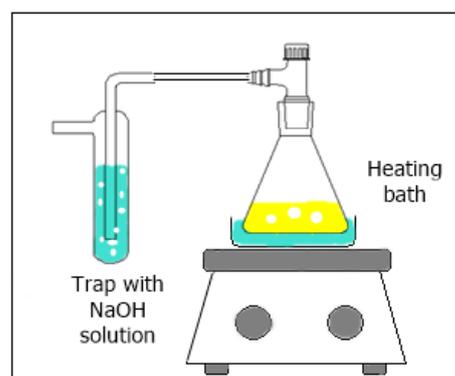
Fig. 1. System used to neutralize acidic vapors released by *aqua regia*.

For extraction of the metals present in solution, 50.0 mL of the leach liquor was neutralized with 25.0 mL of sodium hydroxide (Synth®) solution 2.0 mol L^{-1}, under magnetic stirring until pH 2.0. After that, sodium metabisulphite solution 2.0 mol L^{-1} was added to the mixture to selectively reduce the gold present in the solution converting it to a fine powder. The formed powder was vacuum filtered using a cellulose acetate membrane filter with porosity 200nm. The gold powder retained on the filter was then transferred to a Becker cup and washed with 2.0 mL of concentrated nitric acid for five hours to remove base metals ions. A second wash was performed with 2.0 mL of 1.0 mol L^{-1} EDTA solution for five hours at room temperature to remove metastannic acid. A third wash was performed with 2 mL NH$_4$OH 2.0 mol L^{-1} for five hours to remove silver chloride residue. Between these washes, Milli-Q® 18MΩ cm ultra-pure water washes were performed to remove residues of the previous process. After each cleaning process, the gold powder composition was determined using Tescan® Mira 3 Field Emission Electron Microscopy coupled with Dispersive Energy Spectrometry.

The gold powder was dissolved with 1.0 mL of *aqua regia* in a hot bath at 60 ºC for 15 minutes and then the solution was heated to boiling and total drying of the using the assembly shown in figure 1 for neutralization of vapors of *aqua regia* by bubbling with sodium hydroxide solution. The small amount of a green-yellow HAuCl$_4$ powder at the bottom of the container was subsequently dissolved with 50.0 mL of ultra-pure water for use as a gold stock solution with 2.44 mmol L^{-1}. The concentration of gold and other metals in stock solution was determined by flame atomic absorption spectroscopy.

For the production of nanoparticles, the Turkevich Method was used with small modifications, adding 0.5 mL of stock solution in 9.0 mL of Milli-Q® water and 0.5 mL of previously prepared 34 mmol L^{-1} sodium citrate solution. The solution was kept under magnetic stirring in a 95 °C bath for 8 minutes. The characteristic absorbance of the nanoparticles was determined using Varian® Cary 50 UV-Visible Spectrometer and the particle size and Zeta potential was determined using Malvern® Zetasizer Nano Zs90.

3. Results and Discussion

Table 1 shows the amount of gold obtained for the different obsoleted CPU related to the year of manufacturing. It was found that older CPUs have larger amounts of gold while newer models have smaller quantities.

Table 1. Amount of gold obtained for the different obsoleted CPU related to the year of manufacturing.

Model	Brand	Release year [41]	Weight of Gold mg/piece*	Standard deviation mg/piece*
1	A	1993	54.3	±2.21
2	A	1999	25.17	±1.24
3	A	2000	9.68	±1.47
4	A	2000	3.03	±0.42
5	B	1997	47.7	±1.12
6	B	1999	10.09	±0.65
7	B	2006	9.85	±1.32
8	B	2009	7.85	±1.06

obtained by flame atomic absorption spectroscopy

In addition to gold, the solutions produced by the CPU leaching present high concentrations of other metals such as iron, nickel, cobalt, copper, zinc, lead, aluminum as is showed in Table 2 and small quantities of precipitate of metastannic acid and silver chloride.

Table 2. Concentration of metals found in each CPU in percentage by weight.

	Metal concentration in each CPU %W/W *									
CPU	Al	Fe	Ni	Co	Cu	Zn	Sn	Pb	Ag	Au
1A	0.076	3.303	2.968	0.047	0.077	0.002	0.453	0.270	0.001	0.185
	±0.011	±0.060	±0.079	±0.011	±0.012	**	±0.032	±0.002	**	0.004
2A	0.352	0.132	11.053	0.175	1.442	0.030	0.235	0.033	**	0.108
	±0.040	±0.009	±0.047	±0.011	±0.097	±0.003	±0.024	±0.002	**	±0.005
3A	0.857	0.408	0.471	**	13.096	0.033	0.527	0.692	**	0.105
	±0.071	±0.028	±0.064	**	±0.045	±0.004	±0.009	±0.010	**	±0.016
4A	0.912	0.037	0.233	0.007	2.989	0.012	0.023	**	**	0.013
	±0.041	±0.009	±0.021	±0.002	±0.149	±0.003	±0.009	**	**	±0.002
5B	0.097	0.136	0.447	**	0.823	0.015	0.776	0.311	0.001	0.026
	±0.021	±0.007	±0.025	**	±0.094	±0.004	±0.003	±0.002	**	0.005
6B	0.065	1.104	2.282	**	42.368	0.094	0.968	1.828	0.001	0.078
	±0.008	±0.020	±0.039	**	±0.381	±0.008	±0.020	±0.002	**	±0.006
7B	1.076	4.153	3.237	0.073	0.295	0.003	0.365	0.075	0.001	0.216
	±0.009	±0.055	±0.039	±0.011	±0.013	±0.001	±0.020	±0.003	**	±0.010
8B	0.443	0.866	1.713	**	34.905	0.056	0.836	1.802	0.003	0.093
	±0.026	±0.082	±0.010	**	±0.733	±0.002	±0.015	±0.004	**	±0.003

*Obtained by flame atomic absorption spectroscopy. ** Value below than 0.001% our not detected.*

The solution obtained from processor 1A was the one that contained more gold than others, so it was chosen for the gold recovery process. After selective precipitation of gold with sodium metabisulphite, the gold powder was washed with nitric acid to remove possible contaminants. Figure 2 shows the SEM image for the gold powder and the EDS signal and the mapping showing the presence of gold, tin, probably in the form of metastannic acid, silver and chloride forming silver chloride. This observation shows that further purifying process is needed for producing solution appropriated to be used in nanoparticles preparation.
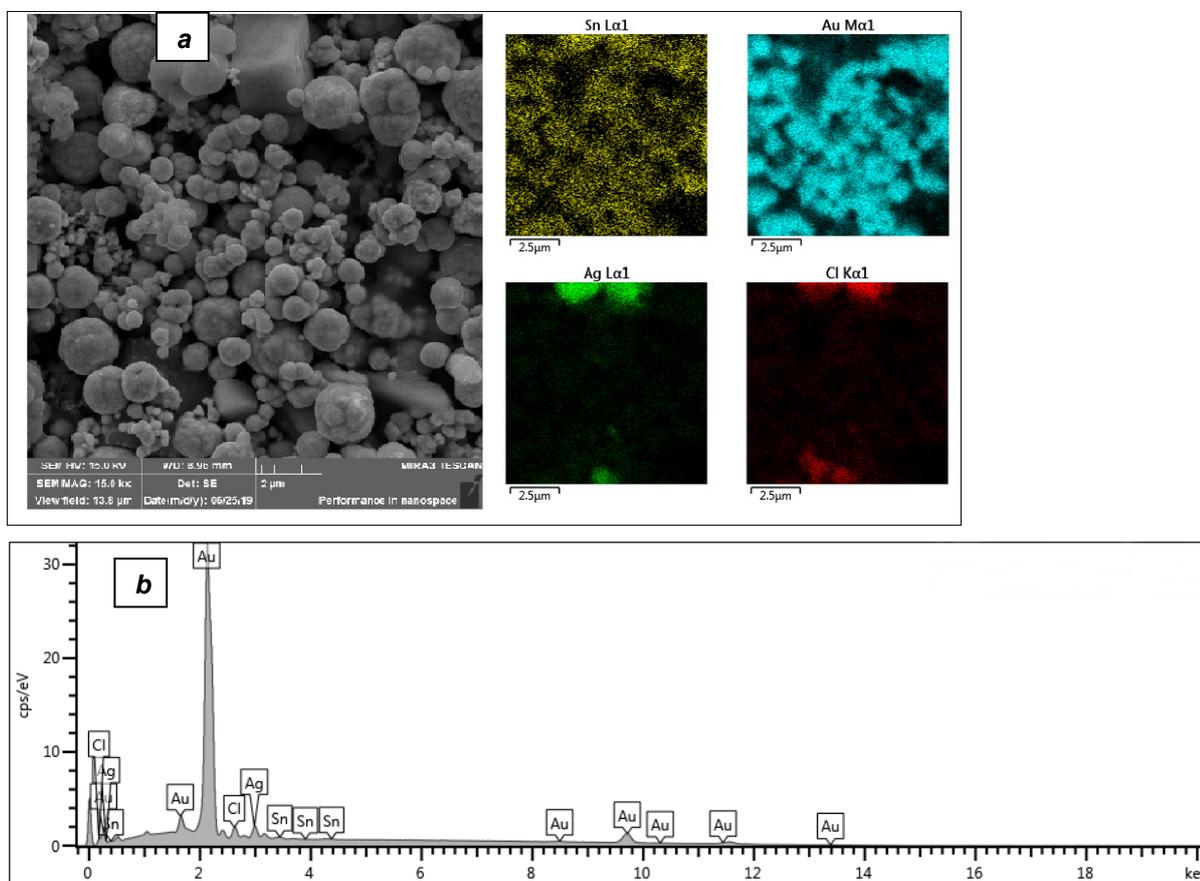
Fig. 2. *a)* SEM and elementary map and b) EDS signal for the gold powder after recovery with sodium metabisulphite and cleaning with concentrated nitric acid.

Therefore, the next step was to perform additional purifying process by EDTA and Ammonia solution cleaning. Figure 3 shows, by EDS signal, that cleaned with EDTA and ammonia was effective in obtaining an increase on the purity of the gold powder. The gold powder obtained does not present contaminants and the chloroauric acid stock solution obtained by the same gold powder, when analyzed by FAAS showed no other metal than gold. It is believed that EDTA solution is able to remove tin ions while ammonia solution is effective in removing silver chloride residues. The CPU 1A solution that initially contained 54.3 mg dL of gold, as half of the solution was used, it was expected to obtain 27.15 mg, however the powdered gold obtained had a mass of 24.1 mg, which corresponds to at a recovery rate of 88.7% of the gold contained in the solution.
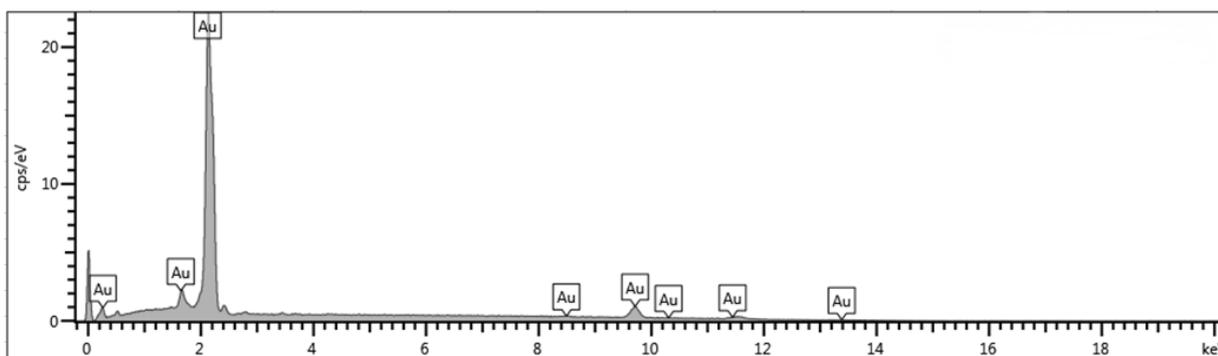
Fig. 3. EDS signal for the gold powder after further purification using, EDTA and NH_4OH solution.

Figure 4 shows a diagram produced to illustrate the efficiency of the purify process using EDTA and NH4OH solution and the efficacy of the EDTA in eliminate Sn ions and the efficacy of the NH4OH in remove AgCl impurity.
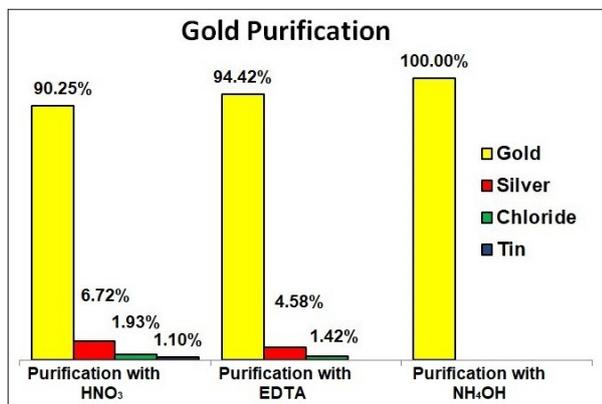
Fig. 4. EDS signal for the gold powder after further purification using, EDTA and NH4OH solution.

In the synthesis of nanoparticles by the Turkevch Method, it was possible to obtain a freshly colored red colloidal suspension with characteristic absorbance at 529 nm. On the first day, nanoparticles had an average size of 198.5 nm and Zeta potential of -13 mV, as showed on Figure 5 *a)* and *b)* respectively.

The suspension was kept at room temperature, protected from light. After one week the same suspension was analyzed again and it was possible to notice a decrease in the absorbance value, as showed in Figure 6, but without the presence of visible precipitates. After two weeks, the absorbance shifted to 548 nm with a visible change in color, the average size had shifted to 162.8 nm and Zeta potential to -20.5 mV. Those changes indicate a possible agregation of the formed particles with causes a decrease on the stabilization of the particles suspention. This destabilization causes precipitation of agglomerates particles, while smaller and more stable particles remained in suspension.
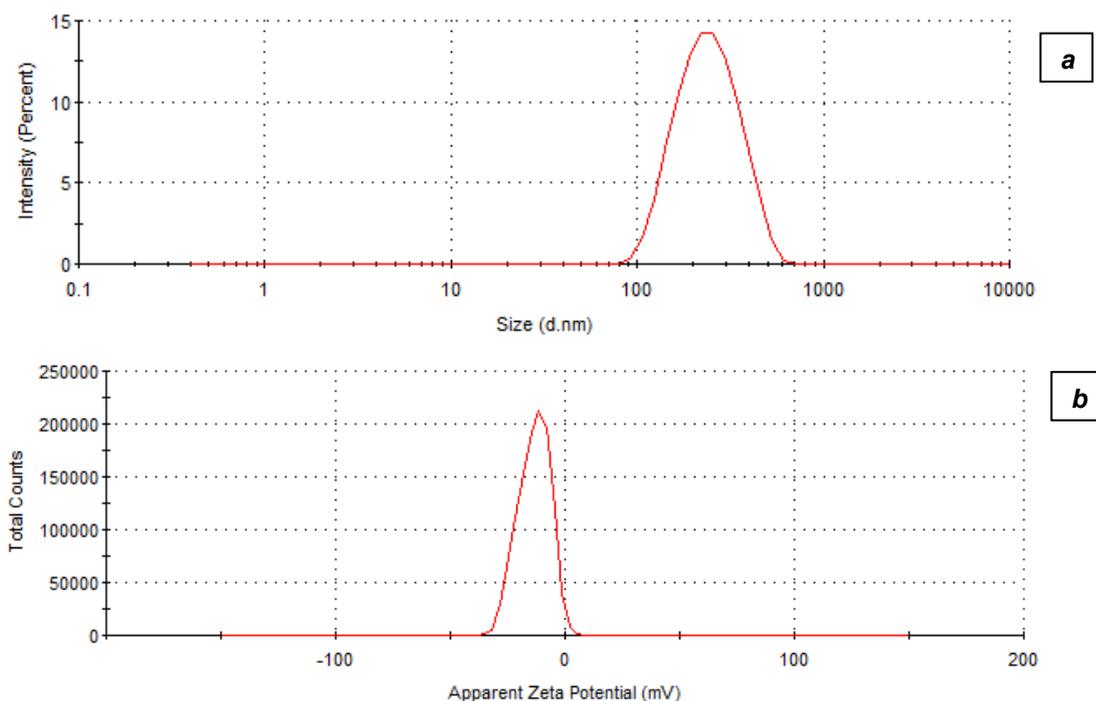
Fig. 5. *a)* Nanoparticle size distribution (DLS) and *b)* Zeta potential measured in recent Gold Nanoparticles suspension.
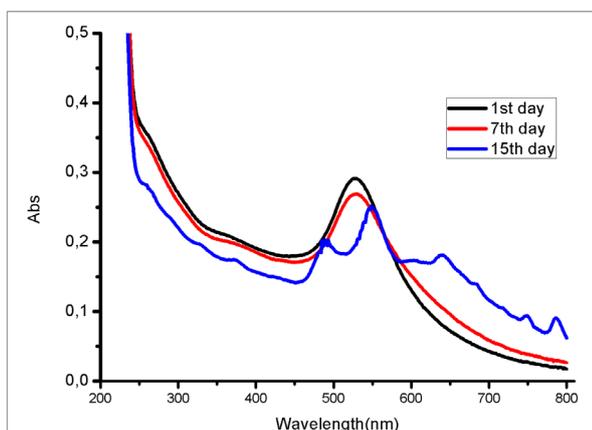
Fig. 6. UV-visible spectrum of gold nanoparticle suspension.

4. Conclusions

Electronic waste can be used as an alternative source of gold for the synthesis of AuNPs. The idea is to choose some specific parts of this waste, such as obsoletes CPUs due to a high concentration of this precious metal. *Aqua regia* is efficient for leaching gold and base metals present in electronic scraps. The initial amount of gold obtained by precipitation with sodium metabisulphite and washed with HNO3 showed impurity due to the presence of tin and silver chloride indicating a requirement of further purification. Additional refining with EDTA and NH4OH solutions have shown efficiency in purifying the gold produced with purity close to 100% of the recovery material.

Nanoparticles were obtained by the Turkevich method

with moderate size distribution and restrained stability. It is possible to obtain nanoparticles wit greater stability but for that it it would be necessary to optimize the synthesis process by varying temperature, concentration of reducing agent and addition of other reducing and stabilizing agents. The use of electronic waste has proved to be a valuable alternative source of gold for nanoparticle synthesis. It is important to mention that the lack of stability can be mostly solved by the improvement of the process of the nanoparticle production.

Acknowledgments

Author Contributions

Josias R.V. Nascimento contributed with conceptualization, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing-original draft, writing-review and editing; Karen Wohnrath contributed with conceptualization, funding acquisition, resources, writing review and editing and Jarem Raul Garcia contributed with supervision, conceptualization, funding acquisition, resources, writing review and editing.

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