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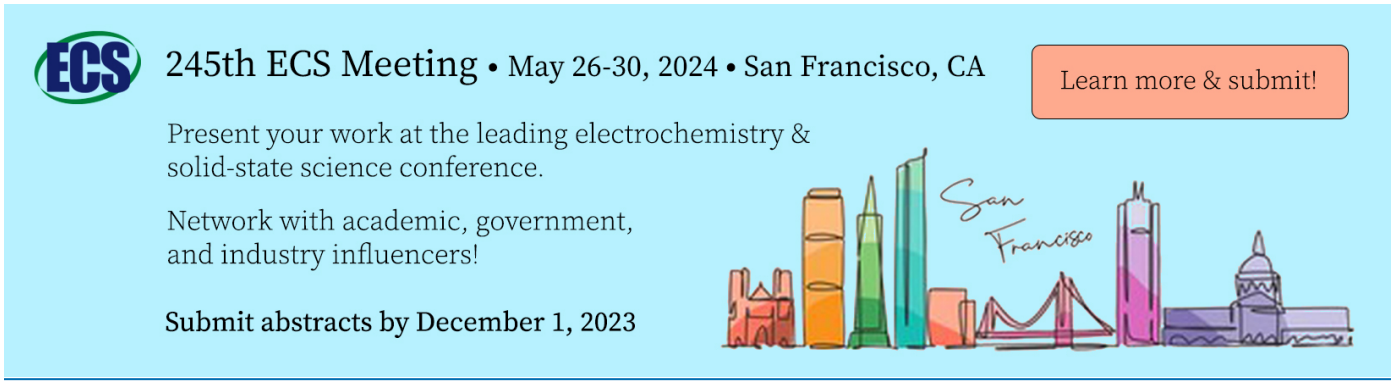

IOP Conf. Series: Earth and Environmental Science **897** (2021) 012010 doi:10.1088/1755-1315/897/1/012010

Influence of the volume of ascorbic acid in the synthesis of copper nanoparticles mediated by chemical pathway and its stability over time

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Abstract. In the present investigation, the effect of ascorbic acid volume in the synthesis of copper nanoparticles (Cu NPs) mediated by chemical route and their stability over time was evaluated. For the synthesis, copper sulfate pentahydrate $CuSO_4$ ($5H_2O$) was used as a precursor agent and ascorbic acid (AA) as a reducing agent. Cu NPs was characterized by the following techniques: UV-Visible spectrophotometry to evaluate structural changes that are evidenced in the absorbance peak and atomic absorption spectrophotometry to define nanoparticulate concentrations material in the precipitated and supernatant phases generated. On the methodology it was possible to observe a controlled formation based on the increase in the volume of ascorbic acid in the presence of sodium hydroxide, noticing a production of Cu nanostructures with a tendency to oxidation over time. The UV-visible results showed characteristic surface plasmon resonance peaks of metallic copper for the colloid containing 1.2 mL of A.A; as well as a specific copper concentration of 0.14 ppm in the supernatant and 1519.1 ppm in the precipitate. It is also evidenced that the solution exhibits a rapid reaction on exposure to air by shifting the absorbance peak to 386 nm. In addition, it does not present notable photosensitivity with respect to exposure to sunlight.

1. Introduction

There is currently a growing demand for nanomaterials due to the novel properties they exhibit and the wide field of application, among which optoelectronics, electronics, food industry, textile industry, biosensors, catalysts, and especially medical and biological applications [1–5]. Among these materials there is special interest in the metallic nanostructures of copper, silver and gold because they show a wide spectrum of antimicrobial activity against different species of microorganisms such as fungi, Gram positive and Gram negative bacteria. However, among these, copper turns out to be more attractive for some researchers since, in addition to its excellent physical and chemical properties, it has low cost and abundant availability [6–9].

Previous studies have confirmed that Cu NPs have antimicrobial activity against E. coli and Staphylococcus among other species, as well as antifungal properties. The ability of Cu NPs to interact with and neutralize microorganisms lies in their morphological characteristics of shape, size, and stability to form other compounds; however, its synthesis in an uncontrollable atmosphere continues to

be a challenge due to its electrical properties, which generate a rapid reaction on exposure to air [10–12]. It has been reported that copper oxidizes forming cuprous oxide (CuO) and cupric oxide (Cu2O) over time and its properties depend on a series of factors such as the type of reactants, concentrations, temperature, pH, among others. Nanostructures developed in aqueous medium or other fluids, for example, usually present a deposition phase which implies the existence of manometric material both in the precipitate and in the suspension. Under these conditions, the atomic absorption spectrophotometry test performed on the sediment and the supernatant can quantify the concentration of the analyte in a sample [13].

Copper oxide (CuO) is also an accessible material compared to noble metals and polymeric compounds can be made due to its stability [14]. A series of methods have been tested, the best known being the wet chemistry method, electrochemical synthesis, sonochemical synthesis, laser ablation and heat treatment, among others [15–17]. There are reports of copper nanoparticles obtained from a copper salt as a precursor and AA as a reducing agent, revealing an XRD pattern of a mixture of metallic Cu and copper (I) oxide of cubic shape and average size of 28.73 and 25.19 nm respectively, results that were corroborated with EDX spectroscopy and SEM analysis, the process was carried out at a temperature of 80 ° C and in aqueous solution, using a starch solution as dispersant without being able to avoid a later and slow oxidation process in which the role of AA plays an important role in slowing down oxidation and agglomeration, helping nanoparticles to obtain better stability. Different states of copper matrices have been identified by UV-vis spectroscopy: absorption bands at 250nm (Cu +), 320-370nm (cuprous peroxide), 400-440 (charge transfer bands of cuprous oxide), 510-580 (neutral Cu plasmon resonance) and 620-850 nm (dd transitions in Cu2 ions) [18–21].

One of the new areas that takes advantage of the antipathogenic properties of nanomaterials is agriculture. Copper and copper oxide ions have been reported as pesticides, fungicides, and fertilizers, being considered friendly control strategies because they require a low concentration of the metal [19]. This was proven in the effective inhibition of *Xanthomonas axonopodis pv. Punicae* (Xap), a bacterium that affects the cultivation of *Punica granatuma* in India, inducing great economic losses for the producers of the sector. Nanomaterials with a particle size less than 100 nm not only influence important events in plant life but could also reduce the dangerous effects of pesticides by improving the quality and yield of crops by delivering the macronutrients and micronutrients required with a reduction in the use of conventional chemical fertilizers and pesticides [22,23]. Alternative pesticides were also explored in the control of S. littoralis based on oxides derived from essential nutritive elements of the soil, for their evaluation, nanostructures of CuO and CaO synthesized by means of wet chemistry methods were elaborated, both showed very efficient pesticidal activity against S. littoralis, being those of CuO those of fast effect, compared to those of CaO. The efficiency shown by metal oxides poses a new role for nanomaterials in the generation and formulation of pesticides [24]. Copper and copper oxide also have optical properties, in a report made on CuO, which was exposed to ultraviolet radiation, it was concluded that there was no change in the structure, this is important if it is to perform optical testing or use these nanomaterials in capturing light for solar cells [25–27].

The objective of the present investigation is to determine the influence of the volume of A.A. in obtaining copper nanoparticles by chemical route and their stability over time, determining if there is an influence of exposure to air and light on the stability of the nanostructure under uncontrolled atmospheric conditions, evaluated by the changes that can be generated in the absorbance peak by UV-vis spectrophotometry. For future application purposes in pest control on agricultural crops.

2. Materials and methods

2.1. Materials

The chemicals used in the experiment are described below: Copper Sulfate II pentahydrate ($CuSO_4$ * 5 H_2O) p.a. EMSURE® ACS, ISO, Reag. PH Eur (CAS number 7758-99-8), ultrapure water with 0.2 µm final filtration (reverse osmosis water purification system / UV light / activated carbon / Thermo

Scientific brand), Sodium hydroxide (NaOH) supplied by Merck Millipore (CAS number 1310-73-2), and Ascorbic Acid (CAS number 50-81-7).

2.2. Synthesis of Copper Nanoparticles

The experimental scheme for the synthesis of copper nanoparticles by chemical route consisted of adding, dropwise, to a solution of 10 mL of copper sulfate [C] 0.05 M, 0.5 mL of sodium hydroxide [C] 7.5 M, by means of vigorous stirring until convert it into a mixture of intense blue color and viscous consistency and then add a series of variant volumes of AA [C] 1.13 M as in Figure 1, which are 0.3 mL, 0.6 mL, 1.2 mL, 1.8 mL and 2.4 mL. This was done at room temperature and under conditions of uncontrolled atmosphere and lighting. The stability of the synthesis product was then analyzed after 4 days by recording the absorbance by UV-Vis spectrophotometry during days 0 and 4.

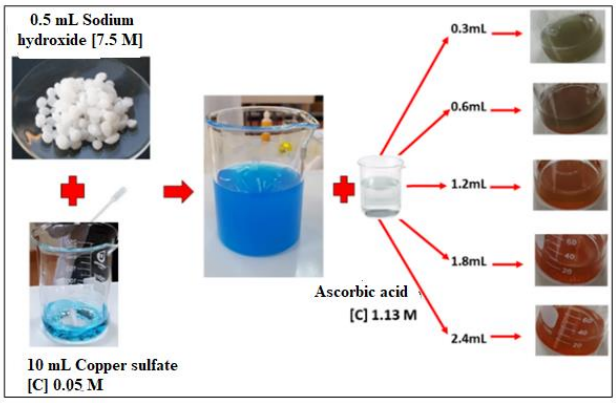

Figure 1. Process that shows color changes in the sample as an effect of varying the volume of A.A with values of 0.3 mL, 0.6 mL, 1.2 mL, 1.8 mL, and 2.4 mL from top to bottom in the extreme left of the image

2.3. Effect of light and air exposure on the absorbance peak

Due to the results reported on the influence of the atmosphere in the oxidation processes of Cu NPs, a follow-up was carried out to possible changes that the absorbance peak of a sample exposed to different light and air conditions may present, it was divided and stored in test tubes under the following conditions: one sample was left exposed to natural light and without a lid, a second sample remained with a lid and exposed to light, and the third sample was kept without exposure to light and with a lid; recording the ultraviolet absorption spectrum on days 0, 7 and 11 from the synthesis.

Also due to the presence of two phases of the mixture formed over time, precipitate and supernatant, an atomic absorption test was carried out to determine the concentrations of copper in the respective phases of the colloid.

2.4. Characterization of copper nanoparticles

The synthesis and experimental tests were carried out in the Physics Laboratory of the Department of Sciences of the Universidad Privada del Norte (UPN), Trujillo. Of the characterizations carried out by UV-vis spectrophotometry, the absorbance spectrum was monitored by means of a UV-Vis spectrophotometer (Shimadzu, UV 1900), in the range of 200 to 900 nm for all reactions. Thus, an analysis of the copper concentration in the precipitate and supernatant was also carried out with an Atomic Absorption Spectrophotometry test.

3. Results and Discussion

The obtained colloid has two defined absorption bands, one in the visible spectrum region and the other close to the ultraviolet. In the UV-Vis absorption spectrum that characterizes each sample according to the variation in the volume of A.A added to the base solution (Figure 2). The results are an indication that the colloid contains copper nanoparticles formed for the volumes of 0.6 and 1.2 mL

of A.A, since the peak close to the characteristic of metallic copper is observed in the visible range around 501nm. Thus, it can also be concluded that there is the presence of cuprous oxide nanoparticles, which are characterized by having an absorbance peak around 400 nm.

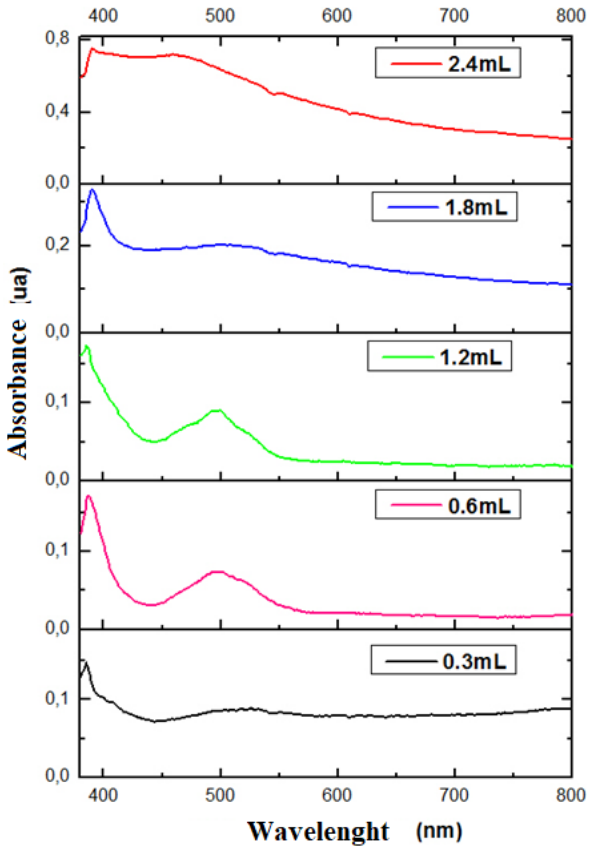

Figure 2. UV-vis spectrum of samples containing 0.3 mL, 0.6 mL, 1.2 mL, 1.8 mL and 2.4 mL of A.A

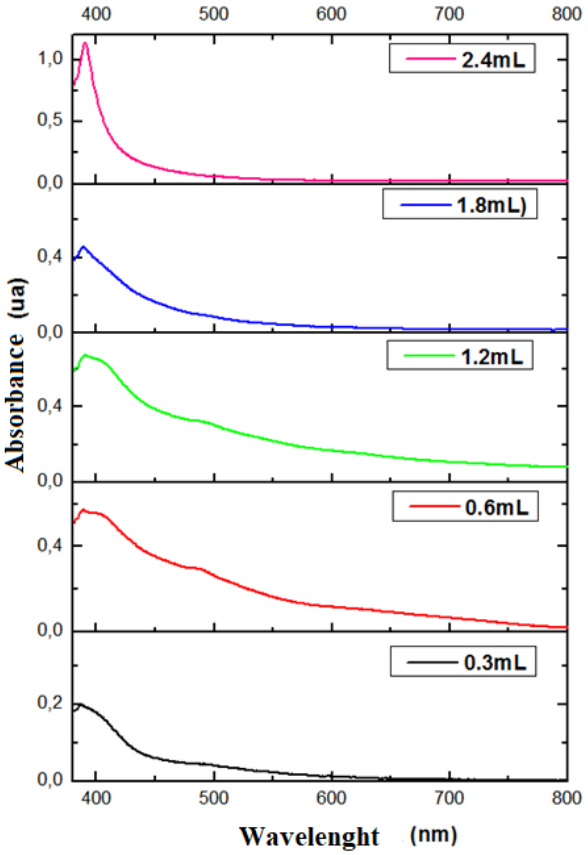

Figure 3. UV-vis spectrum of colloids containing 0.3 mL, 0.6 mL, 1.2 mL, 1.8 m and 2.4 mL of A.A after 4 days of synthesis.

However, volume additions above this value generate a shift towards the ultraviolet, evidence of a possible oxidation process in addition to a broadening of the peak indicating polydispersity in the size of the particles formed or agglomerations of them.

After four days, the spectrophotometry results obtained from the colloids stored in closed flasks, without exposure to air, show instability over time (Fig. 3), due to the shift of the 501 nm peak to the right for the samples with 0.3, 0.6 and 1.2 mL of AA, which register a shift to the left close to the ultraviolet range, which is an index of an oxidation process. A complete shift towards the 392 nm peak is also observed for the 1.8 and 2.4 mL volumes, indicating the possibility of the generation of cuprous oxide nanoparticles [15].

The spectrophotometric tests carried out to evaluate the stability to the exposure of air (Fig. 4) and light (Fig. 5) yielded the following results: After 7 days, the sample exposed to air (D-7-A) has a shift to the right at 385 nm unlike the unexposed sample (D-7-C) whose absorbance shows the existence of nanoparticles with a peak at 490 nm showing an incomplete oxidation process. In a similar way, the behavior is observed for the solution after 11 days (D-11-A and D-11-C) in which the sample open to air shows a greater tendency to shift the peak to the right side.

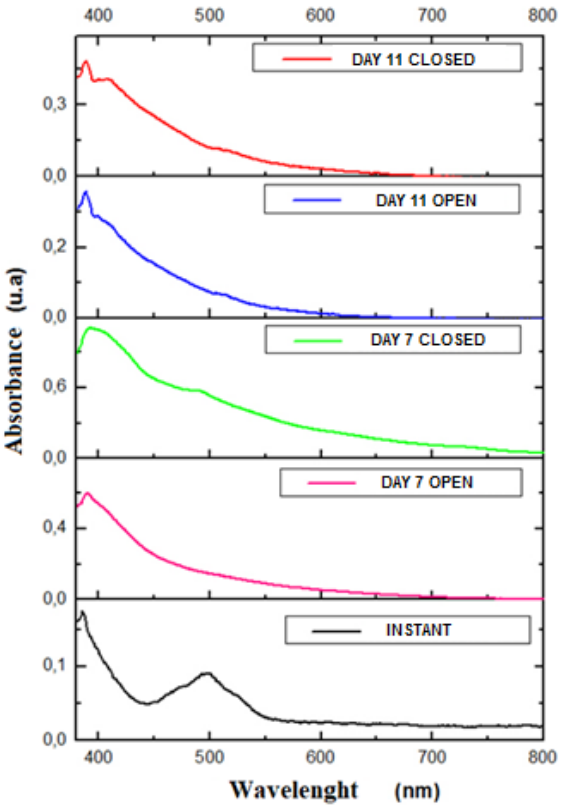

Figure 4. UV-vis spectrum of 1.2 mL AA samples at: 0 days (D-0), 7 days exposed to air (D-7-A), 7 days closed without air (D-7-C), 11 days exposed to air (D-11-A), 11 days closed without air (D-11-C).

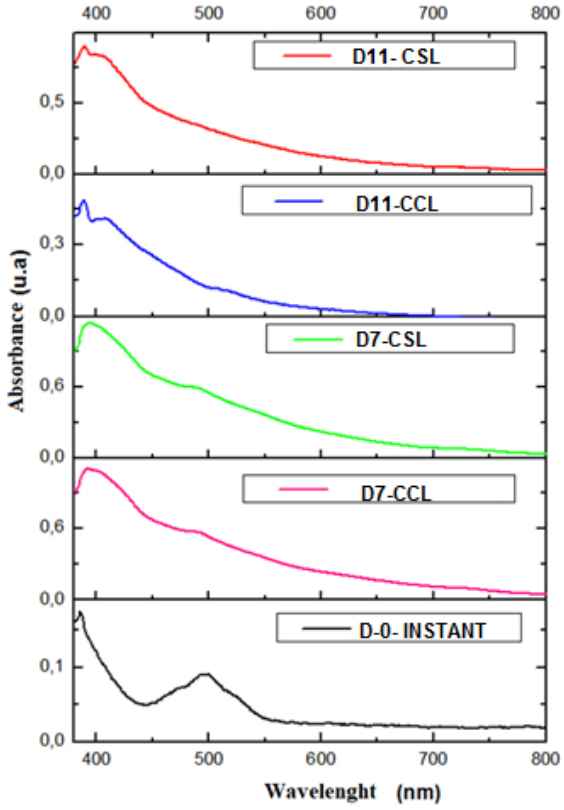

Figure 5. UV-vis spectrum of 1.2 mL AA samples at: 0 days (D-0), 7 days with light exposure (D7-CCL), 7 days without light exposure (D7-CSL), 11 days with light exposure (D11-CCL), 11 days without light exposure (D11-CSL).

Regarding the effect of exposure to light, there are no notable differences in the wavelength that defines the absorbance peak, at seven days both samples (D7-CCL and D7-CSL) have a peak shifted to the right in the visible range of 490 nm, indicative of the oxidation process in progress; similar behavior is observed in the case of the samples with 11 days of aging (D11-CCL and D11-CSL), with a predominance in the order of 386 nm, close to the characteristic peak of cuprous peroxide.
Due to the presentation of two phases that are formed when the sample is left to rest for 14 hours, an atomic absorption spectrophotometry was performed on both the precipitate and the supernatant, this in order to define in which phase we found the highest concentration of the desired metal.

Table 1. Precipitate and supernatant atomic absorption spectrophotometry of the NPS Cu Solution

Samples	**[C]Cu (ppm) Samples NPs**	**[Cu]Real ppm Standard**
Supernatant	0.14	295
Sediment	1519.1	30382

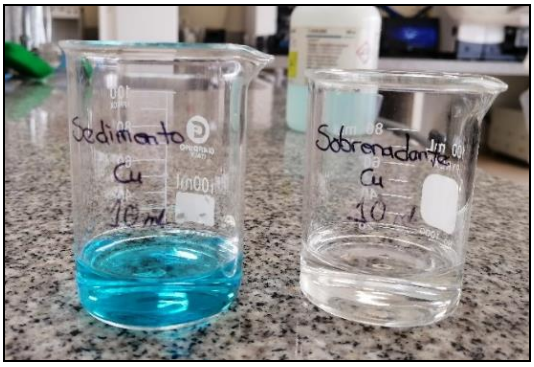

Figure 6. Atomic absorption spectrophotometry NP Cu chemical synthesis method, sediment, and supernatant analysis. (a) Digestated sample of NP Cu sediment cyan color. (b) Colorless supernatant NP Cu digested sample

4. Conclusions

The results obtained in this article suggest that copper nanoparticles are formed by using a volume of 1.2 mL of AA as a reducing agent because it presents a well-defined absorbance peak, which resulted in the order of 501 nm. However, this solution is not stable over time as it shows a shift of peak to the right, evidencing a possible oxidation process that converts copper into cuprous oxide with the passing of days and can even form cuprous peroxide. If the sample is stored exposed to air, the compound formed is not stable and is evidenced by a spectrum whose absorbance peak undergoes a more accelerated shift to the left, stabilizing in the order of 380 nm characteristic of copper peroxide.

It was also determined that the nanoparticles obtained are not photosensitive, as they do not present differences in absorbance in samples exposed to and without light, but they do react to prolonged exposure to air.

Thus, it was also concluded that in the two phases that occur of the colloid, precipitate and supernatant, the highest concentration of the metal is found in the precipitate with 1519.1 ppm compared to 0.14 ppm of the supernatant (Figure 6).

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