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To cite this article: D. Asmat-Campos *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **897** 012014

IOP Conf. Series: Earth and Environmental Science **897** (2021) 012014 doi:10.1088/1755-1315/897/1/012014

Ecological and sustainable synthesis of silver nanoparticles from alcoholic extract of *Eucalyptus globulus*: Evaluation of alcoholic solvent influence (70° and 96°)

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Abstract. The present study provides an ecological and sustainable methodology for obtaining nanostructured material from *Eucalyptus globulus* leaf extract, as a potential value-added alternative and a contribution to circular economy. Silver nanoparticles (NP Ag) were synthesized, through the reducing action of the alcoholic extracts of eucalyptus on the precursor silver nitrate ($AgNO_3$) evaluating the influence of alcoholic solvent (70 ° and 96 °) and pH in the synthesis. The silver colloids obtained were evaluated by UV-vis spectrophotometry, which shows the formation of nanoparticles through the plasmon resonance peak; showing that for pH values 9.9 and 10 with alcohol extract of 70 ° and 96 ° respectively, silver nanoparticles with plasmon resonance peaks at 410 nm and 412.5 nm are obtained. While for pH values 3.86, 11.8 (96°) and 4.7, 8.2 (70°) nanoparticles with higher polydispersity and in a lower proportion are obtained. The results suggest that the alcoholic extracts of eucalyptus can act as reducing agents and that the optimum pH value for the synthesis of silver nanoparticles corresponds to 10.

1. Introduction

Eucalyptus, in different varieties commonly used as wood resource, leaves and bark are used to a lesser extent, and are usually left on the ground. Current research leads to a new use of these resources by developing extracts that are used in the synthesis of various nanoparticles, thereby giving them both economic and environmental added value [1,2].

Nowadays metallic nanoparticles have become an important object of study due to their new and unique properties that arise at this scale. Studies on their magnetic, electrical, and medical properties, among others, provide knowledge for future applications based on these nanometric materials [3,4].

There are various methods for the synthesis of nanoparticles; however, current methods are aimed at green synthesis, a method in which chemical reducing agents, harmful to the environment, are replaced by natural elements, such as plant extract for example. The biological components of these extracts such as polyphenols, alkaloids, flavonoids, reducing sugars, tannic acids, among other components, act as bioreducing agents [5–10]. This green synthesis has the advantage of not generating polluting chemical by-products, and they are lower cost by presenting less energy expenditure and requiring less infrastructure.

Silver nanoparticles are of great interest due to their various applications, among which their bactericidal properties stand out. Various authors have reported the green synthesis of these nanoparticles in which different plant extracts are used, such as blueberries, tomatoes, onions, grapes, cocoa, among many others. These works coincide in the reducing capacity of the extracts, showing characteristic plasmon resonance peaks between 400 nm and 450 nm, and showing nanoparticle size between 9 nm and 50 nm [5,6,11].

Using the aqueous extract of eucalyptus leaves, iron nanoparticles between 20 and 80 nm were synthesized [2]; likewise, it was possible to synthesize zinc oxide nanoparticles with sizes between 20 nm and 40 nm approximately [1]. Works related to the synthesis of silver nanoparticles show us the reducing capacities of this extract; three different varieties of eucalyptus were used (*Eucalyptus urophylla*, *Eucalyptus citriodora* and *Eucaliptus robusta*), achieving evidence of the formation of these nanoparticles through the characteristic surface plasmon resonance peak at 447 nm, 445 nm and 482 nm for each extract respectively, and with mean size 23.25 nm [7]. The ethanolic extract of Eucalyptus citriodora was also investigated as a possible reducing agent in the formation of silver nanoparticles with a spherical shape between 8 and 15 nm, whose UV-Vis absorption peak is at 416 nm [12].

In this study, the results of the green synthesis process of silver nanoparticles are shown, specifically evaluating the influence of the type of solvent (70 ° and 96 ° alcohol) to obtain the extract, and pH in the synthesis process of nanoparticles, to evaluate the reducing potential of the extract and the process of formation of nanostructured material. Results are presented by UV Vis spectrophotometry evaluating the presence of the surface plasmon peak corresponding to the NP Ag.

2. Materials and methods

2.1. Preparation of eucalyptus extract

60 g of dried leaves of eucalyptus (Eucalyptus globulus) was used; the same ones that were washed and dried in an oven at 40 °C. Later, these leaves were ground with the help of a mortar until obtaining a fine powder, which was mixed with 1 L of alcohol (70 ° and 96 °) at room temperature with the help of a magnetic stirrer. Then we proceeded to filter with which the eucalyptus extracts were obtained in both 70 ° and 96 ° alcohol and stored at 4 ° C for later use.

2.2. Green synthesis of silver nanoparticles

The synthesis was carried out using the green chemistry method (biosynthesis), having as a precursor silver nitrate ($AgNO_3$), from Merck, Germany (CAS: 7761-88-8) at a concentration of 1M. The solution was brought to a hotplate with stirring keeping it at 60 ° C for 10 min. at 400 rpm; subsequently, the extracts were added dropwise for evaluation, and finally the pH of the solution was varied by adding sodium hydroxide (CAS number 1310-73-2) dropwise and stirring at 400 rpm.

2.3. Silver nanoparticle characterization

The colloidal samples were characterized by UV-vis spectrophotometry (Shimadzu, UV 1900, Tokyo, Japan) to evaluate the presence of the plasmon peak typical of silver nanostructures, the effect of pH and the stability of the colloid over time. Spectrophotometry measurement was performed for each of the samples, on the day of synthesis (day 1), 17 and 65 days later.

3. Results and Discussion

The silver nanoparticles were synthesized by green synthesis, evaluating the effects of the type of solvent used in the preparation of the extract (70 ° and 96 ° alcohol), as well as the pH values, 4.7, 8.2 and 9.9 for the extracts in alcohol of 70 °, and pH of 3.86, 10 and 11.8 for alcohol of 96 °.

Figure 1 shows the collides obtained for each of the parameters indicated above. As mentioned by various authors, the change in colour towards brown by the collides would indicate the formation of silver nanoparticles [13–15].

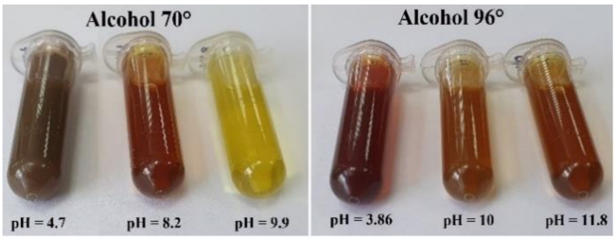

Figure 1. Colloids of silver nanoparticles under the influence of different solvents and pH values.

These same parameters are analysed through their UV-Vis absorbance spectrum (Figure 2), where it is shown that their resonance peaks are between 410 nm and 430 nm, indicative of the formation of silver nanoparticles [16,17]. This graph allows us to note that there are indeed phytochemical compounds capable of the reduction process towards Ag^0, which is evidenced in the previous literature, where polyphenols and flavonoids are indicated as responsible agents for this reduction process [13,15,18].

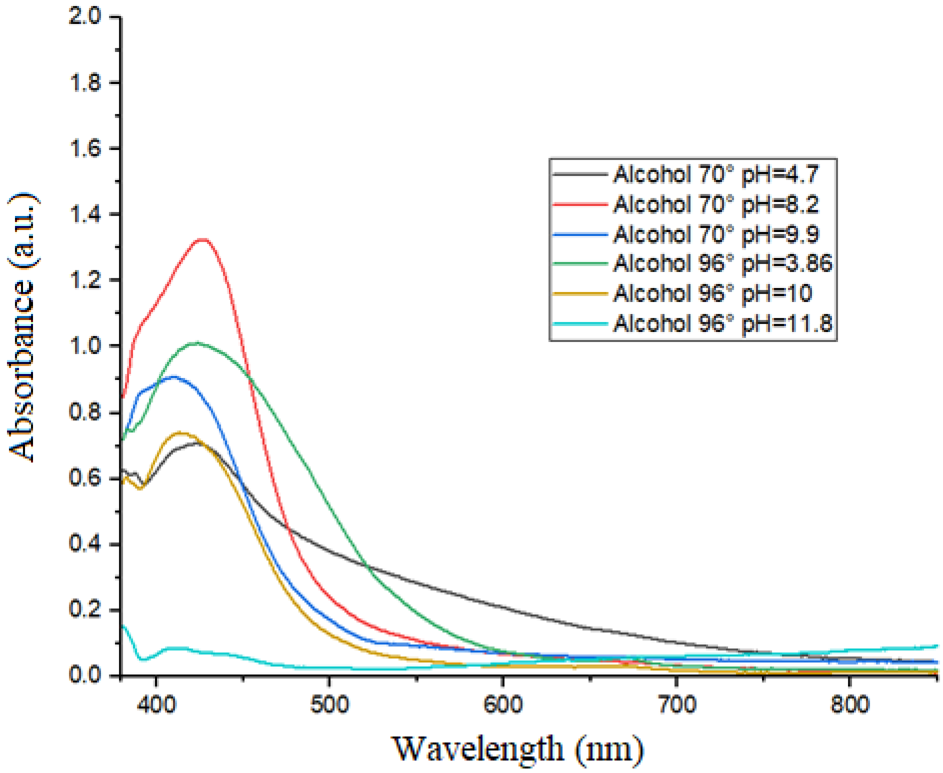

Figure 2. UV-vis spectrophotometry of the influence of type of solvent and pH on the production of Ag nanoparticles.

The pH values intervene in the reaction kinetics with effects on the size and shape of the nanoparticles [19,20]. It is graphically evident (Fig. 2) that the values of pH 9.9 and 10 for the synthesis with alcohol extracts of 70 ° and 96 ° respectively, provide us with a better formation of nanoparticles as their plasmon resonance peaks are better defined, narrow, and with values of 410.9 nm and 412.5 nm.
Regarding the stability analysis, this was carried out from 1 to 65 days. In Figure 3, the UV-Vis absorbance spectra are presented for each of the pH values and type of extract solvent. It can be observed that, over time, the peaks have an increase in absorbance and a shift towards the “red shift”.

IOP Conf. Series: Earth and Environmental Science **897** (2021) 012014 doi:10.1088/1755-1315/897/1/012014

The increase in the absorbance peak is due to the aggregation processes, originating larger silver nanoparticles. The foregoing is a consequence of the still presence of Ag^+ charges, whose surface allows the adherence of other nanoparticles, generating clusters, which in turn provide us with broader peaks, indicative of greater polydispersity in terms of nanoparticle size [21,22].

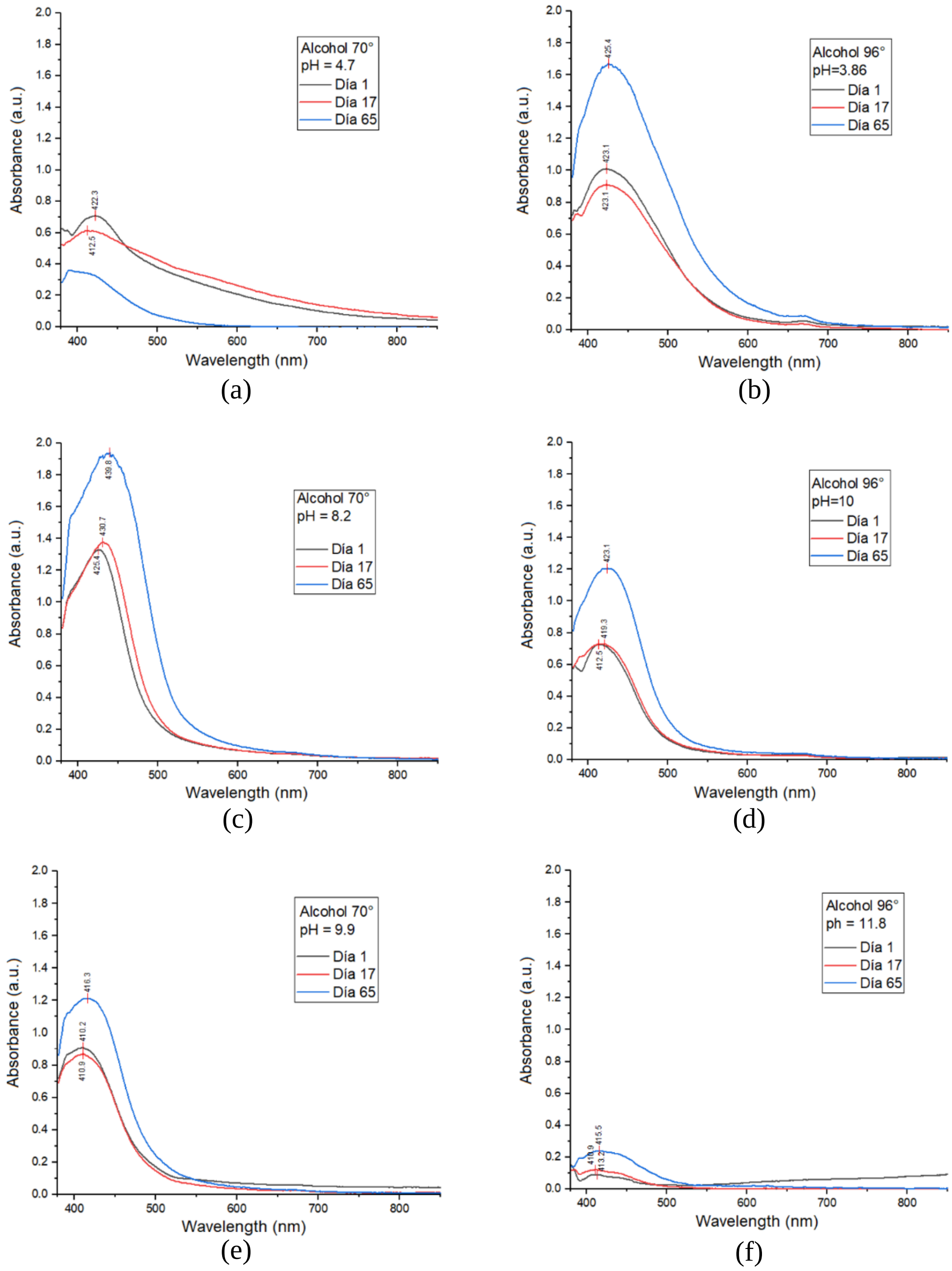

Figure 3. UV-Vis spectrophotometry, stability evaluation using alcoholic extract a) 70 ° - pH 4.7, b) 96 ° pH 3.86, c) 70 ° - pH 8.2, d) 96 ° - pH 10, e) 70 ° pH 9.9 and f) 96 ° - pH 11.8.

Note that although in Figures 3b and 3c the absorbance peaks are higher compared to the rest of the graphs, they also have a higher bandwidth, which would indicate that the nanoparticle sizes are less uniform. The 3d and 3e graphs on the other hand, provide us with more defined resonance peaks with absorbance values of 0.90991 u.a. - 1.21361 u.a. (day 1- day 65) and 0.73981 u.a. - 1.21888 u.a. (day 1 - day 65) respectively, indicative of the formation of nanostructures with less dispersion in size due to having a narrower bandwidth than those mentioned above.

Figure 3 (a) for a pH of 4.7 with eucalyptus extract in 70° alcohol, shows us the little formation of silver nanoparticles, based on the presence of absorbance peaks that are not very well defined, especially over time; in which the aggregation process occurs, leading to the disappearance of the resonance peak due to the low presence of nanostructures. At the other extreme, Figure 3(f), gives us evidence that at these pH values the synthesis by means of the alcoholic extract of eucalyptus provides us with a very low production of nanoparticles, so none of the above parameters is recommended. mentioned.

Comparing all the absorbance spectra, we can see that the best syntheses through the parameters under study occur with approximate pH values equal to 10.

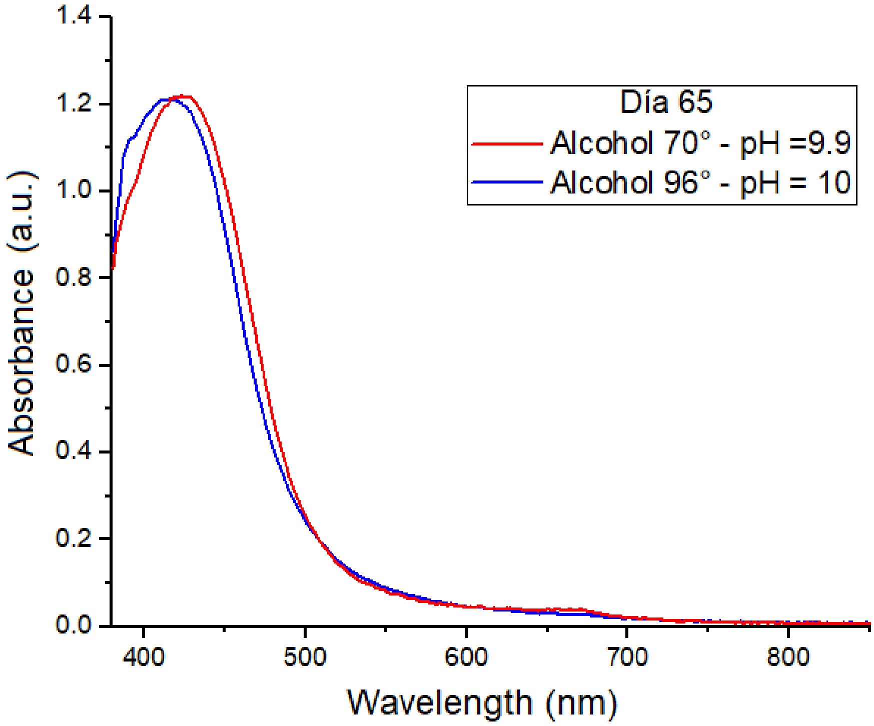

Figure 4. UV-Vis spectrophotometry, stability comparison for synthesis with alcoholic extract of 70 ° and 96 ° with pH values of 9.9 and 10 respectively.

Figure 4 shows the absorbance results 65 days after the synthesis for the pH values 9.9 and 10, in both it can be noted that the absorbance values are very similar 1.21361 u.a. and 1.21888 u.a. for eucalyptus extracts in alcohol of 70 ° and 96 ° respectively. However, the wavelength of the resonance peak for 70 ° alcohol synthesis is 416.3 nm, while for 96 ° it corresponds to 423.1. The above indicates the formation of smaller nanoparticles through the first extract due to the shift of this peak towards the "blue shift" although not with a marked difference.

4. Conclusions

The reuse of eucalyptus leaves is a potential alternative as a reducing agent within the silver nanoparticle synthesis process. However, it is important to establish an adequate methodology for the extraction of reducing compounds; therefore, the solvent plays a fundamental role in the process of making these extracts. In this sense, silver nanoparticles were able to synthesize using the alcoholic extract of eucalyptus, both at 70 ° and 96 °, this process being economic and ecological showing the characteristic plasmon resonance peak for silver nanoparticles around 416.3 nm. Likewise, the management of the pH variable in the precursor reduction process had a significant influence, this after the analysis of the absorbance spectra by means of the surface plasmon resonance peaks, it becomes evident that for pH values of 4.7 or 3.86 for example, although there is nanoparticle production, this is very low or they are large, in the same way with a pH of 11.8. However, it was also possible to determine the optimum pH value, which corresponds to values approximately equal to 10, under which the synthesized nanoparticles show a well-defined characteristic plasmon peak and which remains with good stability over time.

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