ECOFRIENDLY FABRICATION AND CHARACTERIZATION OF ANTIBACTERIAL Ag NANOPARTICLES-*Caesalpinia Spinosa Kuntze* BASED BIOCOMPOSITE FOR THE LEATHER INDUSTRY

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Abstract

an ecofriendly and simple method to prepare monodisperse silver nanoparticles-*Caesalpinia spinosa Kuntze* (tara) powder have been developed in order to let it to be included in leather and bring in addition to an increment in the strength, bactericidal properties. Silver nanoparticles were synthetized in the tara powder by a citrate reduction of silver nitrate, letting the hydroxyl and carbonyl groups present in the tara powder contribute to the silver reduction and disperse well silver nanoparticles showing an average size of 12.5 nm. Nanocomposite was characterized using UV-Visible, FT-IR, TEM and XRD to determine the presence of silver nanoparticles in tara powder and to verify their correct dispersion. Successful antibacterial tests of leather impregnated composites were performed at laboratory level.

1. Introduction

Silver nanoparticles have a growing interest because of its applications in areas like medicine due its antibacterial properties. Those nanoparticles can react with proteins, enzymes of cells, cytoplasm and also with nitrogen bases of nucleic acids destroying structures of simple microorganisms. Bacterium are sensitive to silver ions in very small concentrations (35 ppb) [1].

Caesalpinia spinosa Kuntze (tara) is a tree naturally distributed in the valley area in the middle of the east Andes in South America and in the seashore desert along the Pacific Ocean [2]. Its seeds are used to extract tannins which are rich of pirogalic acid [3,4]. Those tannins are used in leather industry to clear out it and also to make it more resistant to light exposure. Gallic acid is a tannin obtained of tara and it is useful to make leather tougher due its capacity to cause dryness in tissues. That compound calls Tara powder. Tannins are polyphenolic compounds with water solubility and are a powerful antioxidant.

A tara powder containing silver nanoparticles increase their bactericidal properties which could apply to leather industry. The present study is focus on the synthesis and characterization of silver nanoparticles (NPs) in tara powder. The synthesis was carried out in aqueous suspension of tara powder using sodium citrate as reducing agent [5].

2. Materials and Methods

2.1. Preparation of Ag NPs-tara powder

Tara powder was supplied by MASAC (Molinos Asociados S.A.C., Peru). Silver nitrate ($AgNO_3$) (99,9%, Merck) and sodium citrate ($Na_3C_6H_5O_7$) (99%, Merck) were used for the Ag NPs synthesis.

2.2. Synthesis of Ag NPs

To prepare the silver nanoparticles it was used citrate method. First, it was necessary to boiled 50 mL of a 0,001 M of $AgNO_3$. Then it was dropped 5 mL of 1% of sodium citrate solution. The obtained solution was heated until solution turns yellow.

2.3. Synthesis of Ag NPs/Tara powder biocomposite

Tara powder was acquired from MASAC. The powder was dried for 8 hours at 373 K to remove the moisture. After that, a solution of 0.27 g/mL of Tara powder was prepared, at which it was added a heated solution of $AgNO_3$ (0,001 M) with continuous stirring for approximately 10 minutes. Later, a solution of sodium citrate, 1% in volume, was added and stirring. Biocomposite is obtained after the color change is observed.

2.4. Antibacterial Effects of Ag NPs/Tara powder

The disc method was used to study the antibacterial activity of the Ag-tara powder. All materials were sterilized in an autoclave for about 30 min. For the essay it was used *Escherichia coli* (*E. Coli*) (ATCC 25922). Bacterial suspension was prepared by growing E. Coli overnight in nutrient broth. After that, it was diluted and plated on agar. Samples of leather treated with nanocomposite were placed in plates using different dilutions of E. Coli. All samples were incubated at 37 °C for 18 h.

3. Characterization

The Ag NPs/Tara powder characterization was performed by using various techniques like BET, FT-IR, TEM and XRD. X-ray diffraction study of the samples was performed using a X´PERT MPD Philips X-ray diffractometer, which employs a CuKα radiation of 1.5418 Å. Absorption at the visible region within the 200 to 800 nm were study with a UV-visible spectrophotometer Perkin Elmer using a quartz cuvette to sample the composite. The bonding molecular analysis was performed by Attenuated total infrared reflection using a Fourier Transform (FTIR) Prestige 21 Shimadzu spectrometer. To do that the Ag NPs/Tara powder was pressed with KBr powder to form a pellet. Analysis was performed within the range of 4000 – 400 cm^{-1} with a 4 cm^{-1} resolution. The biocomposite microstructural study was performed using a scanning electron microscope (EVO MA 10, SEM, ZEISS) under 20 kV electron acceleration voltage. In order to measure Ag NPs, microscopic analysis of sample was made by TECNAI G2 20 High performance in S/TEM with an accelerating voltage of 200 kV.

4. Results and discussion

The UV-visible spectroscopy is a sensitive technique to determined nanoparticles presence by plasmonic absorption. A brown color suspension was obtained that indicated a silver nanoparticles (Ag°) formation produced by the reduction of silver ions (Ag^{+}) in the tara powder. The presence of silver nanoparticles in tara powder was confirmed by UV-visible spectral analysis. A peak at 434 nm was observed in spectra and it was associated to the silver plasmonic absorption of conducting electrons from the surface of silver nanoparticles [6]. On that way, silver nanoparticles obtained are stable and well dispersed in biocomposite. As the

absorbance intensity of samples increased with higher concentration of silver nitrate due the oxidation of hydroxyl groups by silver ions [7], spectra of biocomposite showed that silver nanoparticles concentration was around 1 mM taking into account the value of the absorbance intensity (1,4) of the biocomposite.

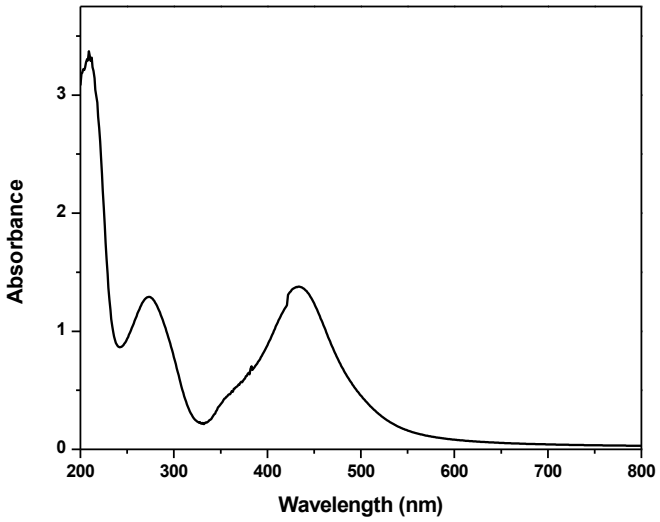

Figure 1.- UV-Visible absorption spectra of Ag Nps/tara poder sample.

FT-IR spectra of nanocomposite Ag Nps-tara powder are showed in Figure 2a and just tara powder in Fig. 2b. A centered band at 3260 cm^{-1} is assigned to strong stretching vibrations of O-H functional group [8]. That peak is shifted to low wavenumbers due degree of polimerization, where hydrogens form external bonds to the phenolic groups. Band centered at 1192 cm^{-1} is assigned to asymmetric vibrations of C-O of phenolic group and the band at 1022 cm^{-1} to symmetric vibrations. At 1702 cm^{-1} it can be seen a peak that corresponds to the stretching of carbonyl group of ester linkages. Also it was detected a peak at 1607 cm^{-1} which could be assigned to the ionized carboxyl groups produced by hydrolysis of ester union [7]. Peaks at 1192, 1315 and 1445 cm^{-1} correspond to C-O symmetric stretching, C-OH stretching and stretching vibration of C-O-C in the Tara Powder. It was reported [9,10] that hydrolysable tannins are basically constituted of gallic acid as is seen in Fig. 2 b. However, when Ag Nps are obtained in the tara powder, Fig. 2a., some absorption peaks at 1083, 869 and 755cm^{-1} are diminishing respect to the ones observed for the tara powder Fig. 2b, this is probably

due to participation of tannins in the $AgNO_3$ reduction which was reported to happen for the reduction of some metal ions [11,12].

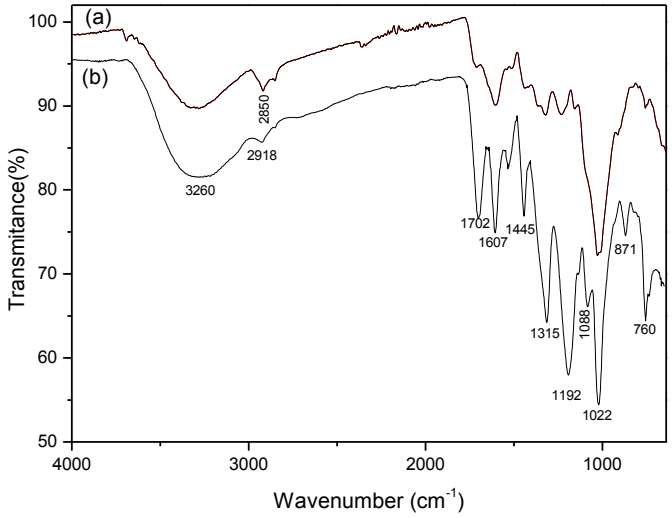

Figure 2.- FTIR spectrum analysis of (a) Ag NPs-tara powder and (b) tara powder

The XRD technique was used to confirm the presence of silver nanoparticles. Spectra obtained showed that intensity of peaks (data not shown) was low due nanoparticles are within tara powder matrix.

TEM micrographs of Ag NPs-tara powder showed that silver nanoparticles are spherical shaped and well distributed with a nil aggregation. As micrographs show, silver nanoparticles have an average particle size of 12,5 nm (Fig. 3). Ag NPs are well dispersed in solution containing tara powder. Nanocomposite was prepared in aqueous solution and it was observed that it is stable for about 4 months after synthesis which was also correlated [4,13].

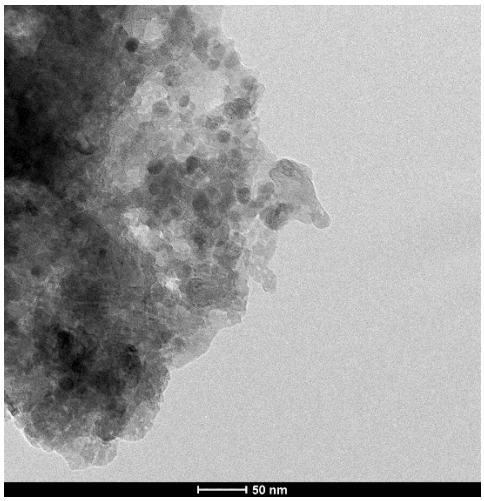

Figura 3.- TEM micrograph of Ag NPs-tara powder sample

Natural leather disc of 18 mm in diameter was immersed in the Ag Nps-tara powder nanocomposite for one minute and then lets dry for 24 h. The treated sample was tested in its bactericide effect by using *E. Coli* bacteria with the disc method to monitoring the inhibition of bacteria growing. It was placed in a plate containing *E. Coli* bacteria solution with a concentration of $1x10^4$ ufc/mL. After incubation for 24 hours at 40°C, growth suppression was observed, showing that the treated natural leather shows significant antibacterial characteristics.

Figure 4.- Antibacterial *E. Coli* activity of natural leather impregnate with Ag NPs-tara powder nanocomposite

5. Conclusions

The present study reports a simple and ecofriendly method to synthesis of silver nanoparticles – tara powder. The citrate method enhanced with the hydroxyl and carbonyl groups present in tara powder allow us to obtain silver spherical and well dispersed nanoparticles with an average size of 12.5 nm. Antibacterial activity studies showed that Ag-tara powder nanocomposite had a significant antibacterial action on *E. Coli*. Stability of Ag-tara powder nanocomposite together with its other studied properties, makes nanocomposite a good candidate for its application in tanneries industry as an inhibitor of growth of bacteria, promoting the use of tara powder, that is currently used in this industry.

6. Acknowledgements

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7. References

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