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Synthesis of silver nanoparticles using aqueous extracts of *Heterotheca inuloides* as reducing agent and natural fibers as templates: *Agave lechuguilla* and silk

Raúl.A. Morales-Luckie [a,*], Aldo Adrián Lopezfuentes-Ruiz [a], Oscar F. Olea-Mejía [a], Argueta-Figueroa Liliana [a], Víctor Sanchez-Mendieta [b], Witold Brostow [c], Juan P. Hinestroza [d]

[a] Universidad Autónoma del Estado de México, Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Atlacomulco Km 14.5, San Cayetano, 50200 Toluca, Estado de México, Mexico
[b] Facultad de Química, Universidad Autónoma del Estado de México. Paseo Colón y Paseo Tollocan, Toluca, Estado de México 50120, Mexico
[c] Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, 1150 Union Circle #305310, Denton, TX, United States
[d] Department of Fiber Science and Apparel Design, Cornell University, 242 Van Rensselaer Hall, Ithaca, New York 14853-4203, United States

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ABSTRACT

Silver nanoparticles (Ag NPs) were synthesized using a one-pot green methodology with aqueous extract of *Heterotheca inuloides* as a reducing agent, and the support of natural fibers: *Agave lechuguilla* and silk. UV–Vis spectroscopy, X-Ray photoelectron spectroscopy XPS and transmission electron microscopy TEM were used to characterize the resulting bionanocomposite fibers. The average size of the Ag NPs was 16 nm and they exhibited low polydispersity. XPS studies revealed the presence of only metallic Ag in the nanoparticles embedded in *Agave. lechuguilla* fibers. Significant antibacterial activities against gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus* were determined. AgO as well as metallic Ag phases were detected when silk threads were used as a substrates hinting at the active role of substrate during the nucleation and growth of Ag NPs. These bionanocomposites have excellent mechanical properties in tension which in addition to the antibacterial properties indicate the potential use of these modified natural fibers in surgical and biomedical applications.

1. Introduction

Replacement of artificial fibers by natural fibers is encouraged for several reasons including a more responsible use of resources, the manufacturing of biodegradable products, and the potential reduction of production costs [1]. Industrial natural fibers are attractive due to their low environmental impact, renewability, biodegradability, relative low cost, lightness, carbon dioxide neutrality, acoustic and thermal insulation properties [2,3]. According to the 2020 Technology Road Map for Plant/Crop Based Renewable Resources, authored by the US Department of Energy (DOE), the application of plant derived renewable resources may increase to 10% as basic chemical building blocks by 2020, and by 50% by 2050 [4]. In fact, the insertion of natural fibers in the industrial, building and commercial markets has experienced a compounded growth rate of 13% over the last 10 years [5].

The use of biocomposites is expected to improve manufacturing and recycling of products with enhanced environmental compatibility [6]. The biodegradability of biocomposites is due to the existence of microorganisms with specific enzyme systems capable of hydrolyzing carbohydrate polymers from the cell wall into digestible units.

It is well known that the properties of nanocomposite materials depend not only on the properties of their individual components but also on the morphological and interfacial characteristics between nanomaterials and substrates [7]. It has been demonstrated that natural cellulose fibers can be used as supports for nanoparticle synthesis using *in situ* approaches and electrostatic assembly methods [8]. However, most literature reports on natural fiber's surface modification with nanoparticles refer to cotton and few references are made to other natural fibers. The use of unconventional natural fibers as solid supports for metal nanoparticles synthesis is attractive as they exhibit heterogeneous and oxygen-rich surface structure [9]. These unique surface properties can result in diverse nanoparticle shapes, sizes and distributions that could confer, due to the shape- and size-dependent properties of the nanoparticles, varied macroscopic properties such as color, conductivity and improved mechanical resistance to the modified fibers [10].

Silver nanoparticles (Ag NPs) have been extensively studied because of their use in antimicrobial gels [11], preservation of fruits and vegetables [12], healing materials [13], and antiseptic sprays [14]. There are

* Corresponding author.
E-mail addresses: rmoralesl@uaemex.mx, ramluckie@gmail.com (R.A. Morales-Luckie).

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several methods of synthesize nanoparticles including laser ablation [15], chemical reduction [16], mechanical synthesis, and biological methods. In recent years, the bio-reduction of noble metal ions with plant extracts to obtain nanoparticles has been gained importance [15, 17–19].The use of bioreductors does not require expensive equipment or chemical reactants while simple methods follow the principles of green chemistry- which refers to the design of products and processes friendly to the environment [20].

Heterotheca inuloides is a medicinal plant that had been used for centuries to heal skin wounds and bruises, as it exhibits anti-inflammatory properties. Several studies have shown that these properties are given by its main compounds: cadalen-15-oic acid, 3,7-dihydroxy-3-isocadalen-4-one, and dicadalenol, which found in the aerial parts of *Heterotheca inuloides* [21].

When a wound is sutured there is a risk of infection [22] which not only delays the healing process but also can cause bigger damages to the wound. When suture threads are used, patients are required to take external antibiotic drugs to avoid infection; however, many of these drugs show undesirable secondary effects [23]. A suture thread that could reduce the risk of infection would also minimize the need to take external antibiotic drugs.

In this work, *Heterotheca inuloides*, also known as *Mexican arnica*, is used for the first time as a bio-reducing agent of silver ions to generate Ag NPs on two natural fibers: *Agave Lechuguilla* and silk. Structural and morphological characterizations, mechanical properties, and their capability to inhibit bacteria growth, were determined for both natural fibers.

2. Materials and methods

2.1. Materials

All reagents used were analytical grade. $AgNO_3$ was purchased from Sigma-Aldrich. *Heterotheca inuloides* (*Mexican arnica*) was purchased from Anahuac Mexican teas, 99.90% of purity. *Agave lechuguilla* fibers were obtained directly from agave producers in the State of Mexico. Commercial suture threads of silk with regular tapered point, black, braided and non-absorbable were obtained from Atramat, Inc. (Mexico).

2.2. Agave lechuguilla fiber preparation

Fibers were boiled in deionized water for 5 min to remove impurities. Because the fibers do not present a uniform diameter along their length, they were cut to eliminate the heart base and the tapering towards the tip to achieve a uniform diameter (400 μm approximately) along 40 cm of length. Additionally, some of these fibers were treated with methylene blue (MB) to soften them and improve their handling for suture applications.

2.3. Synthesis of silver nanoparticles on Agave lechuguilla and silk

1 g of *Heterotheca inuloides* dry leaves was poured into 100 ml of deionized water. The mixture was boiled for 20 min, vacuum filtered and let to cool at room temperature. 1×10^{-2}, 5×10^{-3}, 1×10^{-3}, 1×10^{-4} M $AgNO_3$ solutions were prepared. *Agave lechuguilla* fibers were submerged inside these solutions, at 1, 10, 30 and 60 min and, after the set immersion time, the fibers vacuum filtered. The fibers impregnated with Ag^{1+} ions were soaked in solutions of *Mexican arnica* at room temperature during different times: 1, 10, 30 and 60 min. Fibers were removed and dried at room temperature.

2.4. Characterization of the silver nanoparticles

UV–Vis spectroscopy was performed in a Cary 5000 UV–Vis Spectrophotometer using a quartz cell and the wavelength range was from 300 to 600 nm. Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS) analysis were done in a JSM-6510-LV microscope (JEOL) at 20 kV of acceleration and using secondary electrons.

The samples were coated with a thin film of gold (approx 20 nm) using a Denton Vacumm DESK IV sputtering equipment. Transmission electron microscopy (TEM) was carried on in a JEOL-2100 Microscope (JEOL) at 200 kV of acceleration in the bright field mode. In order to prepare the samples for TEM, the specimens were sonicated during 4 h to detach the nanoparticles from the fibers; Then a drop of the suspension was carefully placed on a carbon coated TEM grid. Thermogravimetric analysis were done on a SDT Q600 from TA Instruments in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from 25 to 600 °C.

TGA and DSC analysis for pyrolysis and combustion were performed at 10 °C/min heating rate. Infrared spectra of the relevant materials have been obtained using a Bruker FTIR spectrometer (IFS 113v) for wavelengths between 2 and 200 μm (5000–500 cm^{-1}).

XPS wide and narrow spectra were acquired using a JEOL JPS-9200, equipped with a Mg X-ray source ($h\upsilon = 1253.6$ eV) at 200 W over an area of 1 mm^2. The spectra was analyzed using the specsurf™ software and the spectra were corrected by means of the carbon signal (C1s) at 284.5 eV. The Shirley method was used for background subtraction, whereas curve fitting was done with the Gauss-Lorentz method.

2.5. Antibacterial activity

The antimicrobial activity was assessed using procedures from the Clinical and Laboratory Standards Institute [22]. For culturing *Staphylococcus aureus* and *Escherichia coli*, mannitol salt agar [23] and eosin methylene blue agar [24], were used respectively. Antimicrobial activity of the synthesized Ag NPs on *Agave lechuguilla* and silk was tested against human pathogenic bacteria *Staphylococcus aureus* and *Escherichia coli* by determining the halo of inhibition following the agar diffusion test using Muller-Hinton agar.

Agar plates were prepared and inoculated with 200 μl of bacterial culture. The culture was adjusted with sterile saline to achieve a turbidity equivalent to a 0.5 McFarland standard. *Agave lechugilla* and silk fibers with and without Ag nanoparticles were firmly placed on the agar plates. Tests were performed three times for each strain. The inoculated petri dishes were incubated at 37 °C for 24 h, and then, the antibacterial halos were observed over the agar plates.

2.6. Mechanical properties

10 fiber samples of *Agave lechuguilla* and *silk* were selected for mechanical testing at an initial deformation speed of 50 mm/s using an universal testing machine MTS Qtest/5. For statistical analysis, the descriptive analysis including mean and standard deviation was performed. For significant differences between the groups, Kruskal-Wallis test and Mann-Whitney U tests were used. Correlations between elastic modulus and stress at break were determined using Spearman correlation analysis. Statistical analysis was performed using SPSS Version 19 (SPSS, Inc., Chicago, IL, USA). *P*-values of ≤0.05 were considered to indicate statistical significance.

3. Results

In order to find the best conditions for obtaining Ag nanoparticles well dispersed throughout the surface of the fibers, without agglomeration and in a sufficient amount to deliver antibacterial properties, the effect of each of the the synthesis parameters was judiciously explored. It was found that the optimum silver ions impregnation time was 30 min. At shorter impregnation times, silver was not detected on the surface of the fibers, while, at longer times big agglomreations of AgNP were found.

Regarding $AgNO_3$ concentration, the optimum concentration was found to be 10×10^{-3} M. A higher concentration would yield big