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Biosynthesis of silver nanoparticles using a natural extract obtained from an agroindustrial residue of the tequila industry

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ABSTRACT

The biosynthesis of silver nanoparticles (AgNPs) using an aqueous extract of an agroindustrial residue of the tequila industry [i.e. leaves of *Agave tequilana* Weber var. *azul* (AT)], and silver nitrate or silver acetate as precursor salts is reported. The presence of AgNPs was confirmed by color change, scanning electron microscopy, ultraviolet visible spectroscopy and X-ray diffraction. AgNPs were tested against clinically important bacteria. The effect of extract concentration and the reaction temperature was investigated. Results revealed that, the concentration of AgNPs increases as temperature and extract concentration increase. AgNPs were found to be mainly spherical shaped and showed antibacterial activity against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. Results demonstrate the possibility of using a natural extract obtained from an abundant agroindustrial residue for the sustainable synthesis of AgNPs.

1. Introduction

Due to the unique set of properties of silver nanoparticles (AgNPs) their use continues to increase, which leads to a wide range of industrial applications. Chemical reduction still is the most common method used to obtain AgNPs, despite it involves the use of toxic compounds. The integration of green chemistry principles into nanotechnology is essential to promote both, efficiency and safety in the production process. Therefore, synthesis routes where biological entities like microorganisms, plant extracts or plant biomass are used, have received vast attention, since they are considered cost-effective and environmentally friendly alternatives to synthesize AgNPs [1,2].

Although a wide variety of plants extracts have been used to synthesize AgNPs [2,3], the use of agroindustrial residues is not common. *Agave tequilana* Weber var. *azul* (AT) is the most widely cultivated agave species in Mexico, its cultivation and industrialization to produce tequila represents an important economic source; but also a serious environmental issue. For tequila production, only the agave head-plant is commercially important, whereas the leaves constitute an agroindustrial residue, despite their high total reducing sugars content (i.e. 13.1–16.1%) [4,5]. Reducing sugars have been demonstrated to efficiently reduce silver ions [6].

On the other hand, silver nitrate ($AgNO_3$) is the most widely used silver precursor in the synthesis of AgNPs as demonstrated by the number of publications [7,8]. However, $AgNO_3$ is a very toxic compound associated with several health issues. According to previous reports, $AgNO_3$ is twice toxic than silver acetate (CH_3-COOAg), which can also be used as precursor salt [9,10]. Thus, it results relevant to evaluate the performance of less toxic Ag° precursor in the biosynthesis of AgNPs.

Therefore, in the present work, we demonstrate the biosynthesis of silver nanoparticles via the reduction in aqueous solutions of $AgNO_3$ or CH_3COOAg using *Agave tequilana* Weber var. *azul* extract (ATE) as reducing agent as well as the antibacterial activity of the synthesized AgNPs.

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Table 1
AgNPs synthesis parameters.

Sample	Silver salt 10 mM (ml)	ATE (ml)	Deionized water (ml)	Reaction time (min)	Temperature (°C)
1 N	5	5	5	5	80
2 N	5	5	5	5	90
3 N	5	5	5	5	100
4 N	5	5	5	5	110
5 N	5	5	5	5	120
6 N	5	1	9	5	80
7 N	5	1	9	5	90
8 N	5	1	9	5	100
9 N	5	1	9	5	110
10 N	5	1	9	5	120
1 A	5	5	5	5	80
2 A	5	5	5	5	90
3 A	5	5	5	5	100
4 A	5	5	5	5	110
5 A	5	5	5	5	120
6 A	5	1	9	5	80
7 A	5	1	9	5	90
8 A	5	1	9	5	100
9 A	5	1	9	5	110
10 A	5	1	9	5	120

N: samples synthesized using $AgNO_3$, A: samples synthesized using CH_3COOAg.

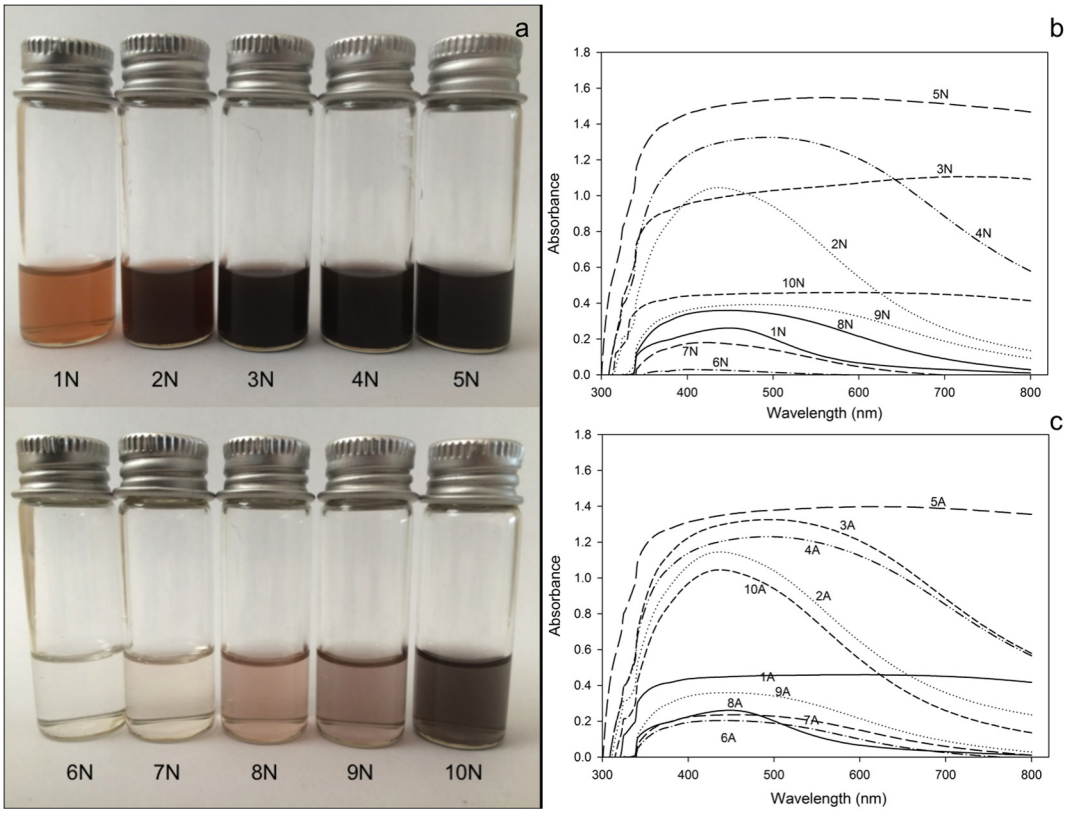

Fig. 1. a) Visual appearance of vials autoclaved at different reaction conditions (1 N to 10 N), using $AgNO_3$ as precursor salt, (b) UV–vis spectra of AgNPs synthesized using $AgNO_3$, (c) CH_3COOAg.

2. Experimental

2.1. Materials

Silver nitrate (99.99%, Sigma-Aldrich), silver acetate (99.99%, Sigma-Aldrich), AT (collected in Tequila, Mexico).

2.2. Preparation of ATE

AT leaves were washed, cut and boiled (30 g in 100 ml of distilled water) for 30 min. The solution was filtered to remove unwanted residues. ATE was stored at 4 °C and used after no longer than 24 h.

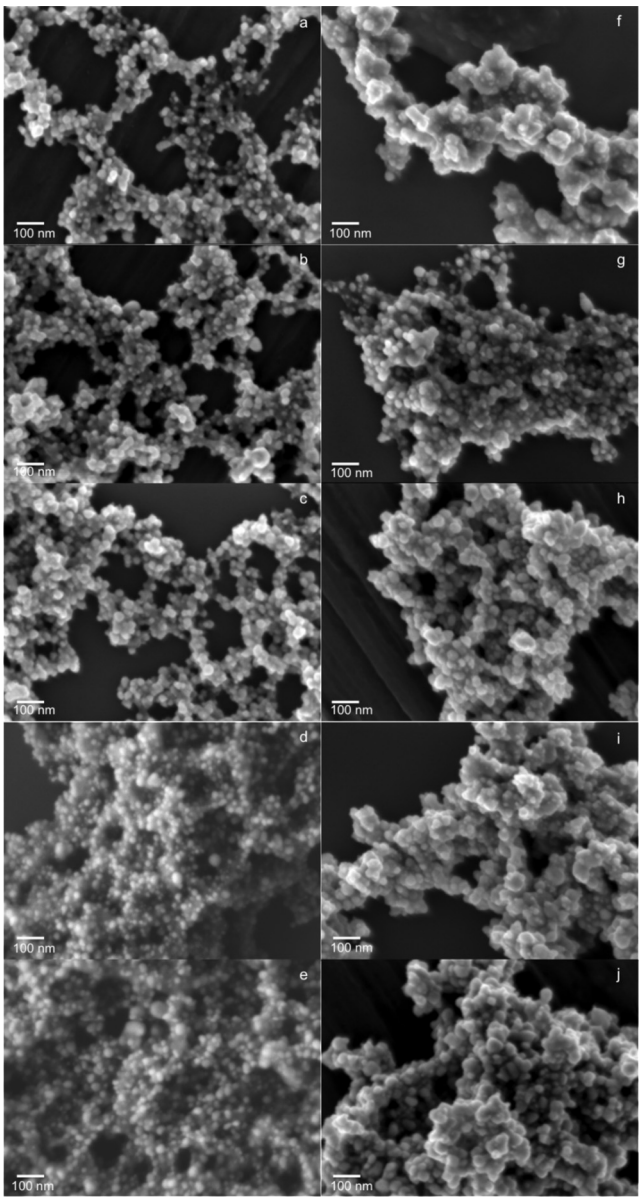

Fig. 2. SEM micrographs of samples synthesized using $AgNO_3$ or CH_3COOAg: a) 1 N, b) 2 N, c) 3 N, d) 4 N, e) 5 N, f) 1 A, g) 2 A, h) 3 A, i) 4 A, j) 5 A.

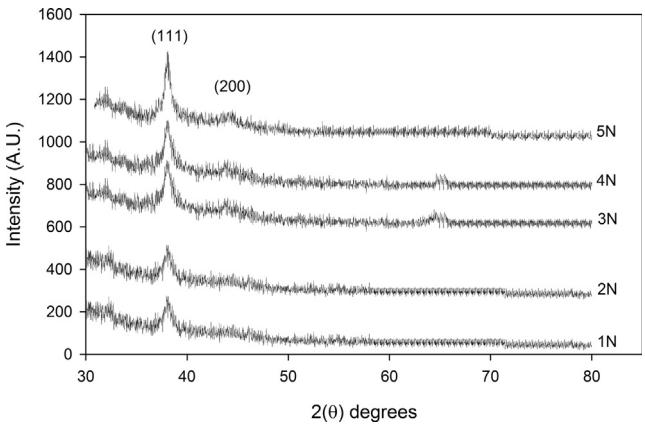

Fig. 3. X-ray diffraction patterns of samples 1 N to 5 N.

2.3. Synthesis of AgNPs

Different ratios of ATE, a 10 mM silver salt solution and deionized water were used as indicated in Table 1. Mixtures were autoclaved during 5 min. Solutions were washed three times with deionized water and centrifuged after each washed at 4000 rpm during 7 min to separate reaction residues from AgNPs .

2.4. Characterization of AgNPs

AgNPs were studied by means of color evolution, UV–vis spectroscopy using a double beam spectrophotometer (Hitachi U-2900), scanning electron microscopy (FE-SEM Tescan MIRA 3 LMU) and X-ray diffraction (Rigaku Dmax2100 device with Co, λ = 1.7889 Å).

2.5. Antibacterial assays (disk diffusion agar method)

AgNPs antibacterial activity was evaluated against *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*. Test bacterial suspensions containing 1.8×10^5 CFU/ml of Mueller-Hinton broth were spread on agar plates. Samples of 30 µl containing 50 or 100 mg/ml of AgNPs were added to disks before placing them on agar plates. Samples were incubated at 35 ± 2 °C for 24 h.

3. Results and discussion

3.1. Optical properties

Fig. 1a shows the color evolution of samples synthesized using $AgNO_3$ as precursor salt. Samples initially yellowish, showed different colors, from slightly pink to deep brown after being autoclaved, indicating the formation of AgNPs at a different extent depending on the reaction parameters. Changes in color are related to strong absorption of visible light due to the excitation of the nanoparticle surface plasmons, which depends on the size, shape and concentration of the nanoparticles [7]. Our results indicate that AgNPs concentration was lower when less ATE was used. Samples 1 N to 5 N show deeper colors than samples 6 N to10 N indicating a higher content of AgNPs. AgNPs production is temperature-dependent since color turned darker as the temperature increased.

UV–visible spectroscopy was used to corroborate the formation of AgNPs. According to the Beer-Lambert law, the maximum absorbance at λ_{max} is directly proportional to the molar concentration of nanoparticles in a solution [7]. Fig. 1b and c show the UV–vis results for samples synthesized using $AgNO_3$ and CH_3COOAg, respectively. Darker samples showed the higher absorbance levels, indicating a higher concentration of AgNPs. UV–vis results indicate that AgNPs concentration increases as the reaction temperature and the volume of ATE increase as well. In general, samples 1 to 5, showed a higher concentration of AgNPs than samples 6 to 10.

Regarding AgNPs morphology, it is known that different-shaped nanoparticles exhibit characteristic absorption peaks [7,11]. AgNPs commonly show a plasmon resonance absorption peak between 392 and 492 nm [7]. Therefore, in this work, UV–vis spectra indicate that samples were mostly spherical (i.e. nanoparticles). Additionally, a tail around 400–800 nm range (samples 5 N, 3 N, 5A, 1A) indicates the presence of silver nanorods [11].

3.2. Morphology

Fig. 2 shows SEM micrographs of selected samples. SEM results confirmed that the morphology of the synthesized samples was predominantly spherical. It seems that, as the reaction temperature increased particle agglomeration decreased, indicating higher

AgNPs stability [7]. Stability is considered a crucial issue respecting to the application of AgNPs, since the generation of aggregates leads to a loss of their antibacterial activity [12]. Regarding the size of AgNPs, no particular trend is observed since a wide nanoparticle size distribution is observed. It can be observed that higher temperatures increased the yield of AgNPs biosynthesized using ATE.

3.3. Crystal structure

XRD analysis was used to determine the crystalline nature of synthesized AgNPs. XRD results for samples 1 N to 5 N are presented in Fig. 3 showing the major peaks corresponding to the diffraction of (1 1 1) at $2\theta = 38.42^\circ$ and (2 0 0) at $2\theta = 44.53^\circ$ planes of face centered cubic (fcc) silver [13]. According to our results, the crystalline structure of silver is barely noticed, indicating that synthesized AgNPs showed no preferential growing direction.

3.4. Antibacterial assays

Tested bacteria were inhibited to a different extent by selected samples, synthesized with 5 ml of ATE (i.e. 1 N to 5 N, and 1A to 5A). Results indicate that at a concentration of 50 mg/ml, *S. aureus* and *P. aeruginosa* were more resistant than *E. coli*., which shows inhibition zones of around 1 cm for most of the samples, but 1 N and 1 A, which caused no inhibition. However, at a concentration of 100 mg/ml, all microorganisms were sensitive to AgNPs. Samples 1 N and 1A did not inhibited bacterial growth. For the rest of the samples, the diameter of the inhibition zone (cm) was as follows: 3 N (1.1, 0.9, 1.1), 5 N (0.9, 0.9, 1.1), 3A (0.9, 0.9, 1.0), 5A (0.8, 0.8, 0.8); respectively for *S. aureus, E. Coli* and *P. aureginosa*. Regarding precursor salts, it is known that $AgNO_3$ shows higher solubility than CH_3COOAg, which could originate a higher concentration of Ag°, affecting the final concentration of AgNPs in a particular sample. Although it has been indicated that Ag° cause bacterial death rather than AgNPs [7], according to our results bacterial inhibitory capacity is directly related to AgNPs concentration.

4. Conclusions

In the present work, AgNPs were obtained using a natural extract of *Agave tequilana* Weber var. *azul* leaves as reducing agent. Results indicate that both, the reaction yield and the morphology of the synthesized AgNPs using CH_3COOAg or $AgNO_3$, were similar for the same reaction conditions. Samples synthesized using CH_3COOAg showed similar antibacterial activity than samples obtained using $AgNO_3$. Our results provide an eco-friendly, simple, and low cost method for the synthesis of AgNPs using an agroindustrial residue.

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