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Lantana camara berry for the synthesis of silver nanoparticles

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ABSTRACT

Objective: To synthesize the silver nanoparticles (AgNPs) by reduction of silver ions into nano silver, using ripened berry extract of *Lantana camara* and evaluate its antioxidant activity against 1, 1-diphenyl-2- picrylhydrazyl.

Methods: The prepared AgNPs were characterized by visual, UV-visible spectrophotometer, dynamic light scattering and transmission electron microscopy with selected area electron diffraction.

Results: Transmission electron microscopy and dynamic light scattering analysis confirmed the AgNPs are spherical and 75.2 nm average sized. Selected area electron diffraction analysis supports that the obtained nanoparticles were in crystalline form. In addition, the antioxidant efficacy of prepared AgNPs was found to be higher than berry extract against 1, 1-diphenyl-2-picrylhydrazyl.

Conclusions: From the results obtained it is suggested that surface modified AgNPs at lower concentration, showed higher antioxidant activity than berry extract against 1, 1-diphenyl-2-picrylhydrazyl and could be used effectively in future ethno pharmacological concerns.

1. Introduction

The recent interest of nanobiotechnology, is the development of environmentally benign technology for the synthesis of metal nanoparticles with significant applications in the pharmaceutical, cosmetics, food, agriculture, health, environment and defense. Metallic nanoparticles exhibit unusual optical, thermal, chemical, and physical properties due to large surface atom, large surface energy, spatial confinement and reduced imperfections. The reduction of material dimensions has pronounced effects on the physical properties that may be significantly different from the corresponding bulk material[1]. Among all metals, synthesis of functionalized silver nanoparticles (AgNPs) using phytochemicals transformations in test tube play an indispensable role, because the functional groups of various phytochemicals enhance the reduction of silver ions to elemental silver. Hence, plant-based methods for AgNPs synthesis using *Zingiber officinale* root extract[2], soybean[3], sacha inchi oil[4], agricultural wastes[5], leaves[6], *Citrus sinensis* peel extract[7], edible mushroom extract[8], clove extract[9]and extracts from *Passiflora tripartita*[10], are widely growing in popularity. Due to a straightforward synthesis, stability, and ease of incorporating functional groups for targeting capabilities, silver nanoparticles have great application in antifungal[11], antibacterial[12], anti-inflammatory[13], antiviral[14], antiangiogenesis[15], *etc*.

Lantana camara L. (*L. camara*) is a notorious weed and a popular ornamental garden plant, growing at elevations up to 2000 m in tropical, sub-tropical and temperate regions[16]. It has found

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various uses in folk medicine in many parts of the world against fever, influenza, stomachache, chicken pox, measles, rheumatisms, asthma, vermifuge, leprosy, scabies and high blood pressure[17-19]. The ripe blue-black berries (Figure 1) are also eaten in some tropical country, but ingestion of the green berry has led to human fatalities[17,19]. The major phyto constituents of *L. camara* is mono- and sesquiterpenes, triterpenes, iridoid glycosides, flavanoids, *etc*[16]. However, there have been no reports on the preparation of the AgNPs using ripened berry of *L. camara* and its antioxidant activity against 1, 1-diphenyl-2- picrylhydrazyl (DPPH•).

Figure 1. *L. camara* ripened berry.

2. Materials and methods

2.1. Synthesis of silver nanoparticles

All chemicals were of analytical grade and used without any purification. Silver nitrate ($AgNO_3$, 99%) was purchased from Spectrum (USA) and ripened *L. camara* berrys were collected from the local garden of Universidad de las Fuerzas Armadas, Sangolqui, Ecuador. DPPH• (>99.5%) was purchased from Sigma Aldrich, USA. The collected fresh black color *L. camara* fruits (2 g) were washed thoroughly with Milli-Q water and heated (55-60 ℃) in 20 mL of ethanol (95%) for 10 min. After cooled, the light greenish-yellow color extract was filtered using Whatman No.1 paper. For the green synthesis, 2 mL of filtrate was mixed with 18 mL of 1 mmol/L $AgNO_3$ solution at room temperature (22-25 ℃). Reduction occurs slowly by the appearance of a pink color after 6 h.

2.2. Characterization of silver nanoparticles

The *L. camara* berry mediated AgNPs were confirmed by UV-visible, single beam spectrophotometer (Thermo Spectronic, GENESYSTM 8, England, Quartz Cell, path length 10 mm and graph plotted on the Origin 6.1 program). The particle size distributions of nanoparticles were determined using the HORIBA, Dynamic Light Scattering Version LB-550 program. Size and selective area electron diffraction (SAED) pattern of nanoparticles are studied on transmission electron microscopy, TEM (FEI, TECNAI, G2 spirit twin, Holland).

2.3. Evaluation of antioxidant activity

The scavenging activity of AgNPs was measured by using DPPH• as a free radical model based on the method adapted from Kumar *et al.*, 2014[6]. An aliquot (1.0-0.2 mL) of AgNPs or control and (1.0-1.8 mL) of H_2O was mixed with 2.0 mL of 0.2 mmol/L (DPPH•) in 95% ethanol. They were mixed vigorously by vortex mixer and allowed to stand at room temperature for 30 min in the dark. Absorbance of the mixture was measured spectrophotometrically at 517 nm, and the free radical scavenging activity was calculated using equation:

$$\text{Scavenging effect } (\%)=[1-(\text{absorbance}_{\text{sample}}/\text{absorbance}_{\text{control}})]\times 100 \quad (1)$$

The scavenging percentage of all samples were plotted. The final result was expressed as % of DPPH• free radical scavenging activity (mL).

3. Results

3.1. Visual and UV-vis study

The visual signature for the formation of AgNPs using an ethanolic extract of *L. camara* berry is shown in the Figure 2. It presents the color changes with addition of berry extract of *L. camara* to $AgNO_3$ solution during the reaction time. Figure 3 displays the UV-vis spectra of AgNPs as a function of reaction time and the progress of two new absorbance band at 390 nm and 520 nm.

3.2. Dynamic light scattering study

In order to determine the particle size distribution of AgNps in solution, dynamic light scattering measurements were carried out over 120 h of reaction time. The mean particle sizes of AgNps are 75.2 nm shown in Figure 4.

3.3. Ttransmission electron microscopy (TEM) and selected area electron diffraction (SAED) study

Figure 5 shows the TEM images of AgNps recorded after 120 h of reaction time. It can be seen that the average size of the AgNps was around 40-70 nm. With spherical shapes, the bright circular spot in SAED pattern reveals that the synthesized AgNps are crystalline.

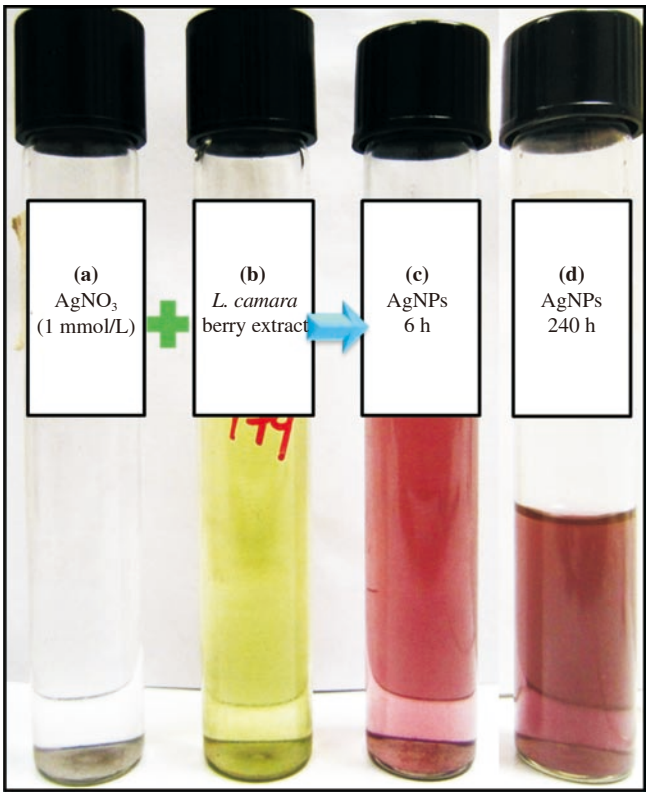

Figure 2. Color changes with addition of berry extract of *L. camara*.

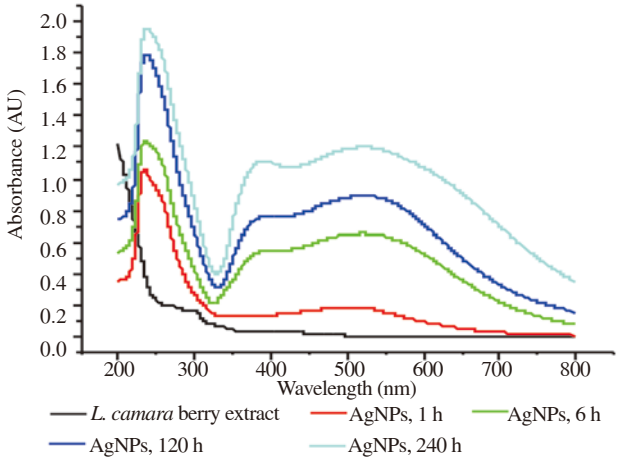

Figure 3. UV–vis absorbance spectra of prepared AgNPs at different time interval.

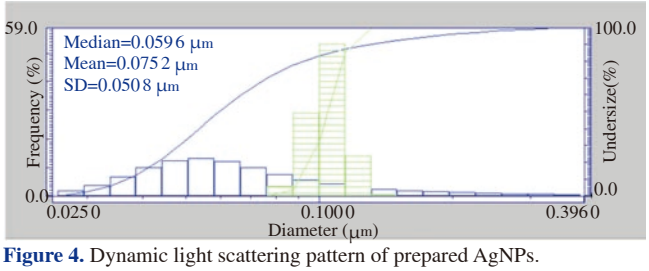

Figure 4. Dynamic light scattering pattern of prepared AgNPs.

3.4. Antioxidant study

Antioxidant study is an important area for phytochemist and biologist. The antioxidant efficacy of *L. camara* berry extract and AgNPs were quantified spectrophotometrically by changing the DPPH• color from purple to yellow. The DPPH• radical scavenging activity was presented in Figure 6. It was found that the DPPH• activity of the berry extract of *L. camara* was increasing from 0.2 mL to 0.6 mL and saturated for 0.8-1.0 mL whereas AgNPs has higher scavenging activity for 0.2-0.4 mL with slight deviation at higher dose. The maximum scavenging efficacy for the *L. camara* berry extract was 6.03% in 0.6 mL and for AgNPs was found to be 10.57% in 0.2 mL.

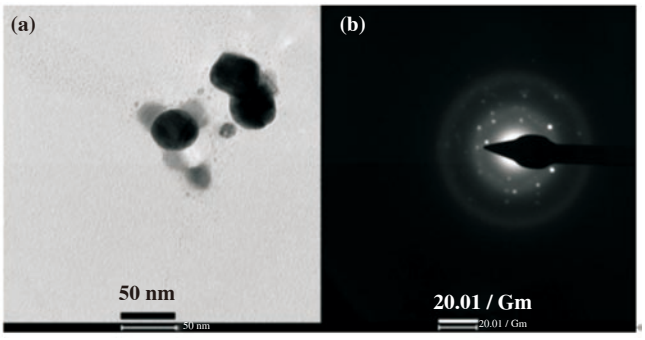

Figure 5. TEM and SAED images of AgNPs.
a: TEM; b: SAED.

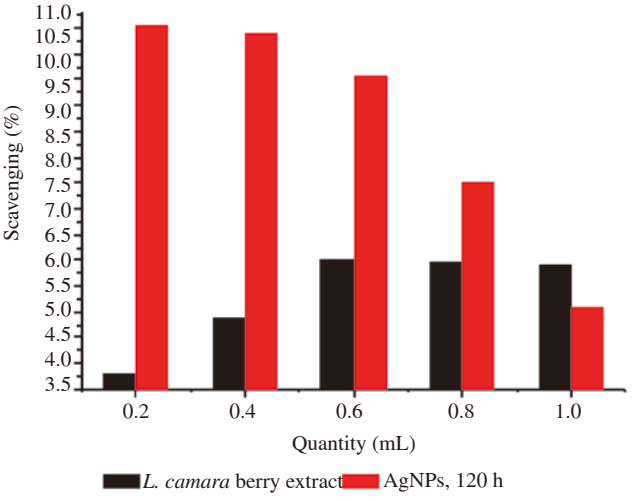

Figure 6. Antioxidative properties of *L. camara* berry extract and AgNPs.

4. Discussions

The visual color changes with addition of berry extract of *L. camara* to $AgNO_3$ solution, indicated the reduction of Ag^+ via complexation and formation of AgNPs. The progress of two new absorbance band at 390 nm and 520 nm, supports the preliminary synthesis and aggregation of AgNps with the lapse of time. It might arise from the extent of charge transfer between the medium and the particle in the solution[20]. The hydrodynamic analysis of the particle size distribution of AgNps reveals the particle sizes of AgNps is 75.2 nm and coincides with the TEM results. It also confirmed that the AgNPs are spherical shapes with a small

degree of aggregation due to capping effect of berry extract and a bright circular spot in SAED pattern supports the crystallinity. The AgNPs in lower concentration, showed higher antioxidant activity than berry extract against DPPH•. It was due to the involvement of phytochemicals for the stabilization and surface modification of AgNPs. The antioxidant efficacy may be hypothesized, due to encapsulation of bioactive molecules on the spherical surface of AgNPs through the electrostatic attraction between negatively charged bioactive compounds (COO^-, O^-) and neutral or positively charged nanoparticles[21,22]. The effect of activity depends on the site of attachment of metals and its consequent impact on the activity of antioxidant agent.

Conflict of interest statement

The authors declare that there is no conflict of interests regarding the publication of this article.

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References

[1] Albrecht MA, Evans CW, Raston CL. Green chemistry and the health implications of nanoparticles. *Green Chem* 2006; **8**: 417–432.

[2] Velmurugan P, Anbalagan K, Manosathyadevan M, Lee KJ, Cho M, Lee SM, et al. Green synthesis of silver and gold nanoparticles using *Zingiber officinale* root extract and antibacterial activity of silver nanoparticles against food pathogens. *Bioprocess Biosyst Eng* 2014; **37**: 1935-1943.

[3] Sasikala D, Govindaraju K, Tamilselvan S, Singaravelu G. Soybean protein: a natural source for the production of green silver nanoparticles. *Biotechnol Bioprocess Eng* 2012; **17**: 1176-1181.

[4] Kumar B, Smita K, Cumbal L, Debut A. Sacha inchi (*Plukenetia volubilis* L.) oil for one pot synthesis of silver nanocatalyst: an ecofriendly approach. *Ind Crops Prod* 2014; **58**: 238–243.

[5] Kumar B, Smita K, Cumbal L, Debut A. Sacha inchi (*Plukenetia volubilis* L.) shell biomass for synthesis of silver nanocatalyst. *J Saudi Chem Soc* 2014; doi: 10.1016/j.jscs.2014.03.005.

[6] Kumar B, Smita K, Cumbal L, Debut A. Synthesis of silver nanoparticles using Sacha inchi (*Plukenetia volubilis* L.) leaf extracts. *Saudi J Biol Sci* 2014; **21**: 605-609.

[7] Kaviya S, Santhanalakshmi J, Viswanathan B, Muthumary J, Srinivasan K. Biosynthesis of silver nanoparticles using *Citrus sinensis* peel extract and its antibacterial activity. *Spectrochim Acta A Mol Biomol Spectrosc* 2011; **79**: 594-598.

[8] Philip D. Biosynthesis of Au, Ag, and Au-Ag nanoparticles using edible mushroom extract. *Spectrochim Acta A Mol Biomol Spectrosc* 2009; **73**: 374-381.

[9] Vijayaraghavan K, Kamala Nalini SP, Udaya Prakash N, Madhankumar D. Biomimetic synthesis of silver nanoparticles by aqueous extract of *Syzygium aromaticum*. *Mater Lett* 2012; **75**: 33-35.

[10] Kumar B, Smita K, Cumbal L, Debut A, Camacho J, Hernández-Gallegos E, et al. Pomosynthesis and biological activity of silver nanoparticles using *Passiflora tripartita* fruit extracts. *Adv Mater Lett*. Forthcoming 2015.

[11] Wiley BJ, Im SH, Li ZY, McLellan J, Siekkinen A, Xia Y. Maneuvering the surface plasmon resonance of silver nanostructures through shape-controlled synthesis. *J Phys Chem B* 2006; **110**: 15666-15675.

[12] Sondi I, Salopek-Sondi B. Silver nanoparticles as antimicrobial agent: a case study on *E. coli* as a model for Gram-negative bacteria. *J Colloids Interface Sci* 2004; **275**: 177-182.

[13] Nadworny PL, Wang J, Tredget EE, Burrell RE. Anti-inflammatory activity of nanocrystalline silver in a porcine contact dermatitis model. *Nanomedicine* 2008; **4**: 241-251.

[14] Elechiguerra JL, Burt JL, Morones JR, Camacho-Bragado A, Gao X, Lara HH, et al. Interaction of silver nanoparticles with HIV-1. *J Nanobiotechnol* 2005; **3**: 6.

[15] Gurunathan S, Lee KJ, Kalishwaralal K, Sheikpranbabu S, Vaidyanathan R, Eom SH. Antiangiogenic properties of silver nanoparticles. *Biomaterials* 2009; **30**: 6341-6350.

[16] Ghisalberti EL. *Lantana camara* L. (Verbenaceae). *Fitoterapia* 2000; **71**: 467-486.

[17] Ross IA. Chemical constituents, traditional and modern medical uses. *Medicinal plants of the world*. New Jersey: Humana Press; 1999.

[18] Sharma VS, Kaul KN. Indian 59418. *Chem Abstr* 1959; **23**: 652.

[19] Irvine FR. *Woody plants of Ghana with special reference to their uses*. London: Oxford University Press; 1961.

[20] Aswathy Aromal S, Philip D. Green synthesis of gold nanoparticles using *Trigonella foenum-graecum* and its size-dependent catalytic activity. *Spectrochim Acta A Mol Biomol Spectrosc* 2012; **97**: 1–5.

[21] Du L, Suo S, Wang G, Jia H, Liu KJ, Zhao B, et al. Mechanism and cellular kinetic studies of the enhancement of antioxidant activity by using surface-functionalized gold nanoparticles. *Chem Eur J* 2013; **19**: 1281-1287.

[22] Kumar B, Smita K, Cumbal L, Debut A. Green approach for fabrication and applications of zinc oxide nanoparticles. *Bioinorg Chem Appl* 2014; doi: 10.1155/2014/523869.