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Shora (*Capparis petiolaris*) fruit mediated green synthesis and application of silver nanoparticles

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Abstract: This report describes a rapid, facile and an eco-friendly synthesis of silver nanoparticles (AgNps) using fruit extracts of Shora (*Capparis petiolaris*) and further as-synthesized AgNps were characterized by UV-vis spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques. The effects of various other parameters such as pH, concentration of fruit extract, time, and change of light sources are studied. Analytical characterizations revealed that the sunlight-induced AgNps appeared at $\lambda_{max} = 423$ nm, had a spherical shape and varied in the range of 10–30 nm. Furthermore, AgNps showed moderate antioxidant activity against 2, 2-diphenyl-1-picrylhydrazyl (DPPH·) (38.98%, 0.125 mM) and photocatalytic activity for the degradation of methylene blue (MB) (>58%, 240 min). The results indicated that as-synthesized AgNps could be used in future engineering and biomedical products.

Keywords: antioxidant; *Capparis petiolaris*; ecofriendly synthesis; nanoparticles; photocatalysis; TEM; XRD.

1 Introduction

In recent years, green synthesis of nanoparticles has been one of the most attractive areas in nanotechnology for modern science research. Noble metal nanoparticles such as gold, silver and platinum are widely used in different fields due to their unique size and shape dependent properties [1]. Among all noble metal nanoparticles, silver nanoparticles (AgNps) are preferred due to their cost effectiveness and optical, catalytic, sensor, antibacterial and antioxidant properties [2]. The synthesis of AgNps uses high energy, toxic and expensive chemicals, and poses serious economic and environmental problems. For that reason, the goal of green chemistry is to foster the use of an ecofriendly solvent, reducing and stabilizing agents [3].

In the past few years, there has been an increasing interest in the synthesis of AgNps using biological systems, including bacteria, fungi, algae and plants have become more significant [4, 5]. Among the different biogenic methods, green synthesis of AgNps using plant materials, like the stem, leaves, roots, seeds, fruits, etc. have received more attention in comparison to the use of microorganisms, due to low cost and mild experimental conditions without maintaining complicated cell culture procedures [6]. In addition, plant extracts containing polyphenols, flavonoids, proteins, saponins, sugar, etc., replacing hazardous chemicals as reducing as well as capping agents. The green synthesis method employing leaf and fruit extracts of *Vaccinium vitis*, *Taraxacum officinale*, *Alchemilla vulgaris*, *Urtica dioica* [7], *Prunus serotina* [8], *Solanum trilobatum* [9], *Emblica officinalis* [10], *Rubus glaucus* [11], *Crataegus douglasii* [12], *Sorbus aucuparia* [13], *Ficus carica* [14], *Tanacetum vulgare* [15], etc. has been already reported by many research groups. However, the green synthesis of AgNps using Shora (*Capparis petiolaris*) fruit extract has not been reported yet.

Shora belongs to the Capparaceae plant family, a species of arid woodlands and dry forests between 1100 m and 2000 m of the lower, western slopes of the Ecuadorian and Peruvian Andes [16]. It has 10–25 m high tree and its fruits (Figure 1) are yellow-orange and commonly used for human nutrition [17].

Since our results [8, 11, 14] in the synthesis of AgNps had been successful using different fruit extracts, it was of great interest to take advantage and explore a new Andean fruit in the field of nanoscience, that could be generating an additional source of revenue for farmers. So, we decided to work with Andean Shora fruit. The main aim of this paper is green synthesis of AgNps using an aqueous extract of Shora fruit as a reducing agent and stabilizer. Further, the influence of pH, concentration

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Figure 1: Andean Shora fruit.

of the extract and sunlight on the synthesis of AgNps was assessed by using visual, UV-vis, transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. Finally, the antioxidant and photocatalytic properties of AgNps are evaluated against 2, 2-diphenyl-1-picrylhydrazyl (DPPH·) and methylene blue (MB) as a model reagent.

2 Materials and methods

2.1 Materials

Silver nitrate ($AgNO_3$, 99.0%) and MB (99.5%) were purchased from the Spectrum, USA. DPPH· (>99.5%) was purchased from Sigma-Aldrich, USA. Fresh Shora fruit was purchased from the traditional market of Loja, Ecuador. Millipore Milli-Q water was used in all experiments. Thoroughly washed Shora fruit was dried in shade for 15 days. A total of 9 g of dried Shora fruit were added to 100 ml of 10% ethanol-water solution and heated at 65–70°C for 1.5 h. After cooling, a yellowish-white extract was filtered using Whatman paper no. 1 and the filtrate was collected in a 100 ml Erlenmeyer flask and stored at 4°C for further use.

2.2 Synthesis of AgNps

For the green synthesis of AgNps, different concentrations of the Shora fruit extract were added (1000–100 µl) to a 10 ml silver nitrate solution (1 mᴍ) at different pH (4–11). The reaction mixture (a) was kept at room temperature (21~23°C) and exposed to sunlight (950–1085 cd/m²). Based on the best results obtained, we performed other characterizations.

2.3 Antioxidant activity

The antioxidant activity of the Shora fruit extract and AgNps was measured by using the DPPH· method adapted from Kumar et al. [8, 14] with slight modifications. The Shora fruit extract/AgNps (1000–200 µl) or control and (1000–1800 µl) of H_2O was mixed with 2.0 ml of 0.2 mᴍ (DPPH·) in 95% ethanol. The mixture was vigorously vortexed and allowed to reach a steady state in dark incubation at room temperature for 30 min. The absorbance of the mixture was measured spectrophotometrically at 517 nm, and the free radical scavenging activity was calculated using Eq. (1):

$$\text{Scavenging activity}(\%) = \left(\frac{A_0 - A_1}{A_0}\right) \times 100 \quad (1)$$

where A_0 is the absorbance of the control, (blank, without extract, or AgNps) and A_1 is the absorbance in the presence of the extract or AgNps. The final result was expressed as% of DPPH· free radical scavenging activity (ml).

2.4 Photocatalytic degradation of MB

Two separate sets of experiments were performed for studying the photocatalytic degradation of MB in the sunlight (950–1085 cd/m²). In set 1 (control), 5 ml of MB (5 mg/l) and 500 µl of H_2O were mixed in a glass vial and kept in the sunlight. In sets 2 and 3, 5 ml of MB and 500 µl of AgNps (prepared using sunlight) were added and kept in sunlight. Both sets of reactions were observed after different time intervals. The progress of dye degradation was monitored at different time intervals and the values of the absorption maxima (λ_{max} = 664 nm) were compared with that of the MB. Photocatalytic degradation% of MB was calculated using Eq. (2) and catalytic efficiency of the AgNps was quantified by calculating the respective first-order rate constants (k) according to Eq. (3):

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\,(\%) \quad (2)$$

$$kt = \ln\left(\frac{A_0}{A_t}\right) \quad (3)$$

where η is the rate of decomposition of MB in terms of percentage, A_o is the initial absorbance of MB solution and A_t is the absorbance of the dyes at time t [18].

2.5 Characterization of AgNps

The synthesized AgNps were primarily characterized with the help of a UV-vis spectrophotometer (SPECORD S600, Analytik Jena, Germany). TEM and selected area electron diffraction (SAED) were performed in support film of 2% polyvinyl formal solution stabilized with carbon and recorded digitally (Tecnai G2 Spirit TWIN, FEI, Holland). The hydrodynamic size distributions of nanoparticles were analyzed by using dynamic light scattering instrumentation (LB-550, HORIBA, Japan). XRD analysis was performed to examine the crystallographic structure of the nanoparticles. XRD studies were carried out using a diffractometer (EMPYREAN, PANalytical) and a θ–2θ configuration (generator-detector), wherein a copper X-ray tube emitted a wavelength of λ = 1.54 Å.

3 Results and discussion

3.1 Visual and UV-vis studies

3.1.1 Effect of pH on AgNps synthesis

Recently, green synthesis of AgNps via the wet chemical method has been the most widely used procedure because it involves a low cost for high volume synthesis. Figure 2 (Inset) shows the visual effect of $AgNO_3$ (10 ml) after treatment of Shora fruit extract (250 µl) at different pH values for 18 h incubation at room temperature. The color change from colorless to a brownish color confirms the formation of AgNps at pH = 11. UV-vis spectra show the absorption maximum at 413 nm and confirm the formation of AgNps predominantly at pH 11, due to the appearance of surface plasmon resonance of AgNps in the visible region. The surface plasmon resonance absorption band depends on the shape, size and the surrounding medium of the particle [19]. There is no absorption peak observed in the range of 380 nm to 450 nm for the Shora fruit extract and its treated $AgNO_3$ at pH 4, 5.6, 7 and 9. This clearly indicates that preliminary synthesis of AgNps is feasible at pH 11. This is attributed to the weakening of the H-bonding at the very high alkaline conditions, thereby diminishing its templating potential to support binding of Shora fruit extract with Ag^+ for the synthesis of small sized AgNps [20].

3.1.2 Effect of concentration of Shora fruit extract on AgNps synthesis

Figure 3 shows the color change and UV-vis pattern of AgNps synthesized with different concentrations of

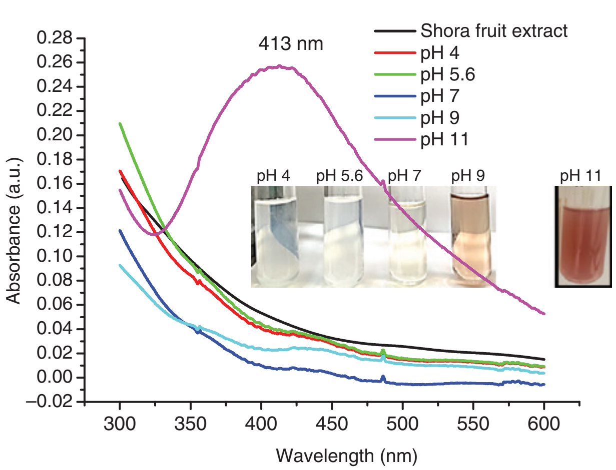

Figure 2: Visual and UV-vis spectrum of Shora fruit mediated silver nanoparticles (AgNps) at different pH.

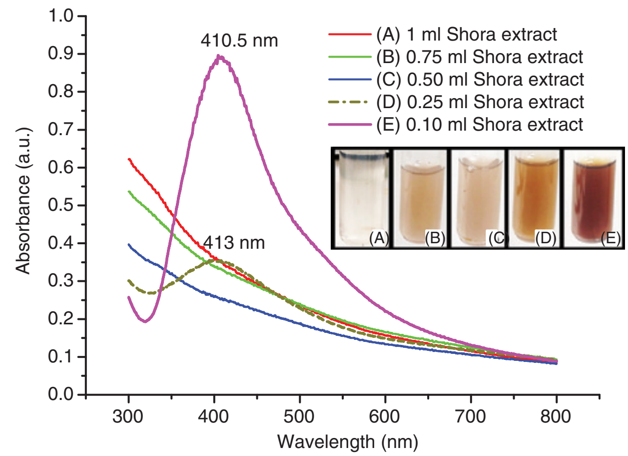

Figure 3: Visual and UV-vis absorption spectra of the synthesized silver nanoparticles (AgNps) at pH 11 with different concentration of Shora fruit extract.

Shora fruit extract at pH 11. When 100 µl or 250 µl of Shora extract was added to $AgNO_3$ (10 ml), the maximum absorption peak for the AgNps is located at 410–413 nm after 24 h, whereas no absorption peak was observed in the range of 400–450 nm when 500 µl, 750 µl or 1000 µl of the extract was added to $AgNO_3$. Increasing the concentration of Shora fruit extracts from 100 µl to 250 µl is accompanied by a decrease of absorption from 0.9 a.u. to 0.36 a.u., broadening of absorption peak and shift of maximum absorption wavelength from 410 nm to 413 nm. Overall results reveal that the production of AgNps is the highest and the size is smaller for 100 µl (blue shift) of Shora extract [15] added $AgNO_3$.

3.1.3 Effect of sunlight on AgNps synthesis

Figure 4 represents the visual and UV-vis absorption spectra for colloidal AgNps synthesized under sunlight at pH 5.6 using Shora extract (100 µl) and $AgNO_3$ (1 mм, 10 ml). The appearance of the brown color of the reaction mixture after exposure in the sunlight for 1 h and maximum absorption peak at 423 nm confirms the formation of AgNps. It indicated that the sunlight also influences the production of AgNps and is more ecofriendly in comparison to the pH based AgNps synthesis. However, the broad peak at 423 nm in comparison to 410.5 nm can be attributed to a wide size distribution of the particles with different shapes formed in the solution [8]. The above results also suggest that sunlight irradiation shortens the reaction time for the preparation of AgNps.

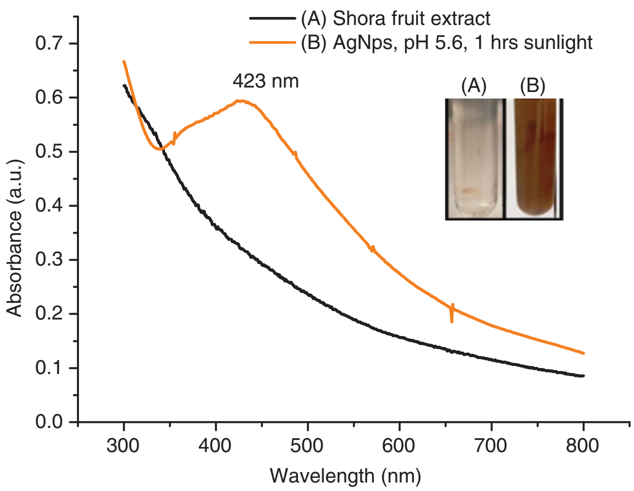

Figure 4: Visual and UV-vis absorption spectra of the synthesized silver nanoparticles (AgNps) using sunlight and Shora fruit extract.

3.2 TEM and SAED studies

TEM analysis is useful to characterize the morphology and exact particle size of the green synthesized AgNps. TEM images and SAED pattern of as-synthesized AgNps are depicted in Figure 5. The results suggest that the average size of AgNps produced by pH 11 (Figure 5A) and sunlight at pH 5.6 (Figure 5B) are 5–30 nm. Both AgNps correspond to the spherical shape, but AgNps synthesized at pH 11 are less polydisperse than sunlight influenced AgNps. This result agrees with the interpretations of the UV-vis study (410.5 nm and 423 nm). The diffuse spherical rings in the SAED pattern (Figure 5C) clearly reveal that the synthesized AgNps are spherical and partially crystalline in nature. The partial crystalline nature of AgNps is due to the capping of nanoparticles with phytoconstituents of the Shora fruit [8, 14].

3.3 XRD studies

In order to determine the crystallographic structure of AgNps (i.e. synthesized by sunlight), XRD measurements were carried out. The four distinct diffraction peaks (Figure 6) at 38.04°, 44.03°, 64.23° and 77.22° originated from the (111), (200), (220) and (311) Bragg reflections of crystalline AgNps [7, 11], respectively, which are identical with those reported for the standard Ag metal (ICSD No. 98-018-0878). Interestingly, the relative growth of the (111) plane was higher than of the other crystal planes, indicating that there was an oriented growth along the (111) direction [21]. The extra peaks near to 27–31° are due to the presence of a bio-organic phase on the surface of particles. Generally, the broadening of peaks in the XRD patterns of solids signifies smaller particle size and reflects the effects of the experimental conditions on the nucleation and growth of the crystal nuclei [22]. From the results of the XRD and TEM studies, it could be inferred that the sunlight-induced AgNps are small and partially crystalline.

3.4 Antioxidant activity

Antioxidants are widely used to reduce or prevent oxidation in natural food systems and suppress pathological disorders like cancer, heart attack and aging [23]. The antioxidant activity of AgNps was assayed using a DPPH· scavenging test. DPPH· is an unstable compound and it will be reduced by accepting the hydrogen or electrons.

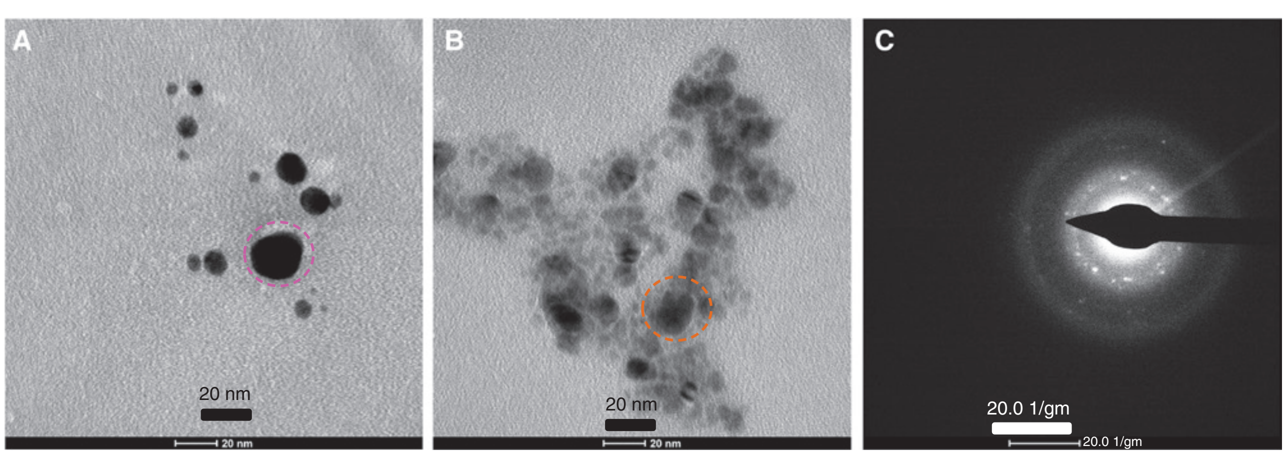

Figure 5: Transmission electron microscopy (TEM) images of silver nanoparticles (AgNps) derived from a Shora fruit extract at pH 11 (A) and influence of sunlight (B). Selected area electron diffraction (SAED) pattern (C) of AgNps synthesized from Shora fruit extract and sunlight.

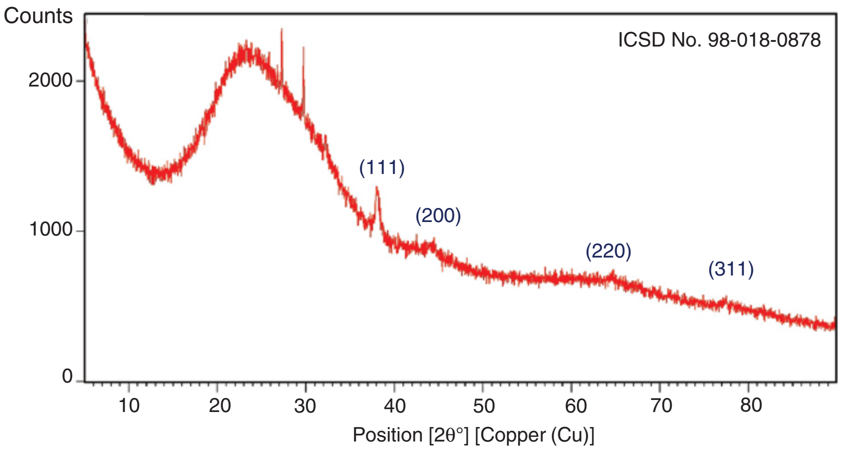

Figure 6: X-ray diffraction (XRD) spectra of as-synthesized silver nanoparticles (AgNps) using Shora fruit extract and sunlight.

Figure 7 shows the result of DPPH· assay, demonstrating a dose-response relationship between the amount of Shora extract and sunlight-induced AgNps. The increase in the concentration of AgNps increased the DPPH· scavenging activity and AgNps (38.98%) had higher antioxidant activity than Shora fruit extract (25.94%) for 0.5 ml, respectively. The enhanced antioxidant activity of the AgNps might be the result of an active physicochemical interaction of Ag atoms with the functional groups of the Shora fruit extract that may be synergistic, antagonistic or additive [23].

3.5 Photocatalytic activity of AgNps

Metal nanoparticles have excellent photocatalytic activity, including AgNps, and are expected to vary with the

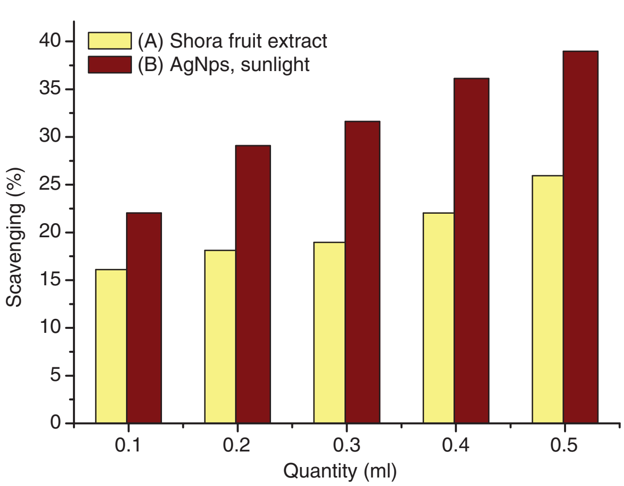

Figure 7: Scavenging activity of (A) Shora fruit extract and (B) silver nanoparticles (AgNps).

size [24]. Figure 8 shows the UV-vis absorption spectra of MB degradation and their kinetics using AgNps as a catalyst under solar light. Figure 8A shows that the addition of AgNps to MB can cause a slight increase of absorption spectra at $\lambda_{max} = 664$ nm with respect to MB alone due to the interaction/adsorption of MB with AgNps. Further, the absorption spectra indicated that the intensity of the absorption peak for MB dye with AgNps gradually decreases with increase in sunlight irradiation time. The calculated η (%) of MB was 7.54%, 12.48%, 20.23%, 28.31%, 33.62%, 50.05% and 58.90% in 30 min, 60 min, 90 min, 120 min, 150 min, 180 min and 240 min. Figure 8B showed that the photocatalytic rate of MB degradation using AgNps shows a linear relationship and is assumed to be fitted by a first order rate law. The corresponding degradation rate (k) of MB is 0.0025293163 min^{-1}. The decrease in the absorption intensity of the band at $\lambda_{max} = 664$ nm during the irradiation also expresses the loss of the conjugation of the organic molecule in MB and the formation of leuco-MB [18, 24]. This is due to the activity of the superoxide anions and the valence band holes and the conduction band electrons, that caused the oxidation and reduction of the dye. The high specific surface area of AgNps provided maximum exposure for the reactant to the active surface and showed excellent photocatalytic activity [18, 24, 25].

4 Conclusions

Herein, we demonstrated that the extract of Shora (*C. petiolaris*) fruit is capable to produce small AgNps (10–30 nm) at $\lambda_{max} = 423$ nm by a rapid reduction of silver ions using sunlight. The sunlight irradiation step is of prime importance and is more ecofriendly in comparison to pH, concentration or temperature maintenance procedure

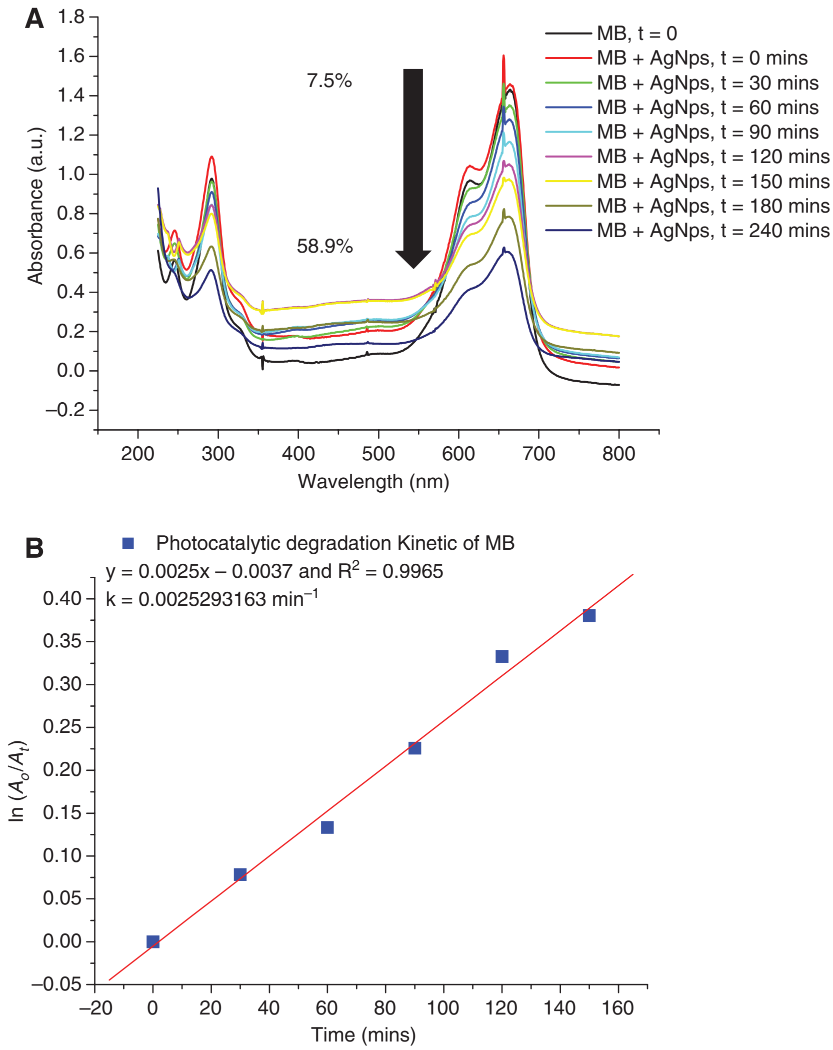

Figure 8: Methylene blue (A) degradation pattern and (B) ln(A_o/A_t) v/s time kinetic plot using silver nanoparticles (AgNps) as a photocatalyst.

for the rapid fabrication of AgNps. Shora fruit exhibited a moderate antioxidant activity (25.94%), whereas as prepared AgNps enhance antioxidant activity (38.98%) and are also able to degrade MB (>58%). Shora mediated nanoparticles could be used in future studies for many applications. The results showed that Shora fruit extract mediated AgNps synthesis is a fast, simple, inexpensive and selective method that could be used in future studies for many applications.

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Conflict of interest statement: The authors declare that there is no conflict of interest regarding the publication of this article.

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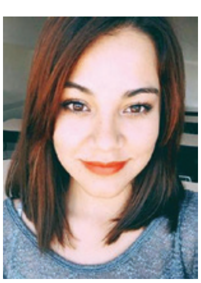

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