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Silver nanoparticles: Green Synthesis using *Derris trifoliata* Seed Extract and It's Applications as a Sensor, Photocatalyst and Antibacterial agent

RESHMA AUGUSTINE[1], NAVYA S. KOLLAMPARAMBIL[1], KRISHNARAJ M. V.[2], USHAMANI M.[1] and SARITHA CHANDRAN A.[1]*

[1]Department of Chemistry and Centre for Research, St. Teresa's College (Autonomous), Ernakulam, Kerala-382220, India.
2Department of Botany, Baselius College, Kottayam, Kerala Kerala-382220, India.
*Corresponding author E-mail: sarithachandran@teresas.ac.in

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ABSTRACT

This work focuses on the preparation of silver nanoparticles (AgNPs) by a green synthesis using the seed extract of *Derris trifoliata*. The optimum time and temperature for the extraction of seeds were determined using FTIR analysis. The seed extract acted as a reducing agent and silver nitrate was used as the metal precursor for the preparation of AgNPs. Optimization of reaction conditions for the preparation of AgNPs and its characterization was done by UV-Vis spectroscopy, FTIR, HRTEM and SAED images. The UV- Visible spectrum of AgNPs revealed a characteristic SPR peak at 433nm. HRTEM and SAED images confirmed nearly spherical nature of the AgNPs with a diameter of 2–20nm. H_2O_2 sensing capacity and the photocatalytic dye degradation of the AgNPs was investigated using UV-Vis spectroscopy. Antibacterial activity of silver nanoparticles on E-coli bacteria was also studied using microtitre plate method.

Keywords: Green synthesis, Silver nanoparticles, *Derris trifoliata*, Hydrogen peroxide sensing, Dye degradation.

INTRODUCTION

Nanotechnology is one of the most prominent field of research in modern science giving emphasis to non-polluting technology with production of wide range of environment friendly and safe nanomaterials[1]. Nanoparticles synthesized using metals have wide range of applications as antibacterials and therapeutics[2-3], optoelectronics[4], catalysis[5], biosensors, drug delivery, nanodevice fabrication and medicine[6].

Different nanomaterials like alginate[7], gold[8], magnesium[9], titanium[10], copper[11], zinc[12] and silver[13] are known. But AgNPs have more popularity than others when researchers found they could produce it at nanoscale. It exhibits distinctive morphologies[14-15] and characteristics[16]. AgNPs are commonly used in many applications because of their relative high stability[17], unique optical properties[18-19] and strong

conjugation ability with biomolecules[20]. They also possess anti-inflammatory[21], antimicrobial and anticoagulant[22] antifungal[23-24], anti-bacterial[25,26], antiviral[27,28], antitumor[3,29] and anti-platelet[22,30] properties.

For the synthesis of AgNPs, different methods like radiation assisted process[31], microwave assisted process[16], electro chemical methods[32], sonochemical process[33] and thermal decomposition[34] of Ag compounds are available, however poor conversion of materials, high energy demands, challenging and wasteful purifications, associated environment toxicity etc are the major defects. As a result, plant extract-based green synthesis of AgNPs has emerged as a quick and effective substitute for physical and chemical synthetic processes[37,38,39].

Now-a-days, synthesizing silver nanoparticles using a number of microorganisms like bacteria[40-41] and fungi[42-43], as well as by using different plant extracts like the seed extract of *Avicennia marina*[44], tuber of *Curcuma longa*[2], berry of *Solanum xanthocarpum*[26], stem bark of *Callicarpa maingayi*[45], leaf extract of *Carica papaya*[46], fruit of *Citrus lemon*[47], callus of *Sesuvium portulacastrum*[48] and seed extract of *Artocarpus heterophyllus*[49] are in practice. The rate of synthesis of nanoparticles by plant extracts is proportional to the chemically done process and are faster than green synthesis done by microorganisms. According to studies, seed extracts are the most efficient reducing agents for the synthesis of AgNPs that exhibit antifungal and antibacterial action[49,50]. This paved the way for the biosynthesis of silver nanoparticles using Derris trifoliata seed extract.

Derris trifoliata is liana, belonging to the flowering plant family Leguminosae. It is distributed in coastal parts of East Africa, Tropical Asia and Australia. Fruits are 3-4 cm, flat, pale yellow in color. Seeds are proven to have antibacterial, antiplasmodial properties and are larvicidal agents[51,52]. Photo induced and phytomediated synthesis of AgNPs using *Derris trifoliata* was also established[52]. This species also have bioactive compounds like flavonoids, isoflavanoids, phenolic acids and polysaccharides[53]. AgNPs prepared from *Derris trifoliata* is known to degrade dyes[54] and also known as a sensor of mercury ions in aqueous solutions[55].

In the present study, we prepared AgNPs using *Derris trifoliata* seed extract as reducing agent and silver nitrate as metal precursor. We have optimized the conditions of seed extraction and preparation of silver nanoparticles using FTIR, UV-Vis spectroscopy, HRTEM and SAED. We studied the possibility of the use of AgNPs as a sensor for Hydrogen peroxide and in the photodegradation of a hazardous dye, methylene blue. Since silver nanoparticles are known to have antibacterial properties, this property was also investigated on *E-coli* bacteria.

MATERIALS AND METHODS

Materials

The seeds of *Derris trifoliata* were collected from marshy areas of Paravur, Kerala, India. Silver nitrate, Hydrogen peroxide (30% w/v), and Methylene blue were procured from Nice Chemicals Pvt. Ltd. Kochi, Kerala, India and used without further purification.

Preparation of AgNPs

Preparation of *Derris trifoliata* seed extract at optimized conditions

Derris trifoliata seeds were dried and ground into fine powder. 5 g of this finely powdered seed was soaked in 25 mL distilled water for 30 min and filtered using Whatman no.1 filter paper. The process of extraction was done under room temperature, 35°C, 40°C, 45°C, and 50°C. Optimum temperature for the extraction process was investigated using FTIR spectra of each sample. Likewise, extraction was repeated at the optimum temperature for 15, 30, 45, 50, 55 and 60 min to find optimum time for the extraction. Later, the extract was prepared at these optimized reaction conditions.

Preparation of AgNPs at optimized conditions

Optimum temperature for the preparation of AgNPs was determined using UV-Vis spectroscopy. For this, 250 µL of seed extract was added to 5 mL of 1 mM silver nitrate solution. It was kept under room temperature, under sunlight and at 35°C, 40°C, 45°C, and 50°C for 15 minutes. Absorption spectra of each sample of AgNPs were recorded and optimum condition for the synthesis of AgNPs was determined.

At the optimized condition, preparation of AgNPs was done by keeping the reaction mixture for 15, 30, 45 min and 1 hour. From the absorption spectra, optimum time of preparation was also determined. Later, AgNPs were prepared at these optimum conditions.

Characterization of synthesized AgNPs

Characterization of the AgNPs was done using FTIR, UV-Vis spectroscopy, HRTEM and SAED. The FTIR spectra of the prepared AgNPs were recorded on a Thermo Nicolet, Avatar 370 spectrophotometer using KBr pellets. UV-Visible spectra of the prepared AgNPs were recorded on Thermo Scientific Evolution 201 UV-Visible spectrophotometer with wavelength range 200nm-1000nm. HRTEM & SAED photographs were taken using Joel/ JEM 2100 spectrometer with resolution point: 0.23nm, lattice: 0.14nm.

AgNPs as Hydrogen peroxide sensor

Hydrogen peroxide sensing of AgNPs was investigated[56]. UV-Vis absorption spectrum of AgNPs was recorded. 1 mL of 20 mM hydrogen peroxide was then added to the AgNPs solution and thoroughly mixed. The absorption readings were taken at regular intervals of time and the changes in absorption was noted.

AgNPs as catalyst for photo degradation of methylene blue

The photo degradation of the dye can be followed by measuring the absorbance of the dye at its λ_{max} 660nm. Photo degradation of methylene blue was studied in the presence and absence of of AgNPs. Methylene blue solution was prepared by adding 10 mg of the dye to 1000 mL distilled water. To this solution, 5 mL of AgNPs was added and stirred well. This dispersion was kept under sunlight. At specific intervals of time, absorbance of the solution was measured using UV-Vis spectrophotometer. The same process was done for a blank solution of methylene blue.

AgNPs as Antibacterial agents

Antibacterial activity of the synthesized AgNPs was checked on E-coli bacteria using microtiter plate method. Using aseptic techniques, a single pure colony was transferred into a 10 mL of nutrient broth, capped and placed in incubator overnight at 37°C. The turbidity of suspensions was calculated and adjusted using McFarland standards as a reference. A sterile 96-well plate was labelled. A volume of 10 µL, 20 µL, 30 µL, 40 µL of test material was pipetted into the wells. 100 µL of nutrient broth was added to each well. Finally, 100 µL of microbial suspension was then added to each well. The plates were incubated at 37°C for 24 h and Optical Density (OD) reading was taken (OD600) after sufficient incubation. Optical density was obtained as follows.

$$\% \, inhibition = \frac{(OD_{Control} - OD_{Test})}{OD_{Control}} \times 100$$

RESULTS AND DISCUSSION

Optimization of reaction conditions for Derris trifoliata seed extraction using FTIR

The reduction of metal salts to nanoparticles can be mediated by the biological components in the *Derris trifoliata* seed extract[57]. The functional groups of these components may encapsulate the surface of silver ions by stabilizing the nanoparticles as capping agents[57]. The FTIR spectra of the seed extracts prepared at different temperatures are depicted in Fig. 1a. Only the sample prepared at room temperature showed a peak at 1061 cm^{-1} which arises due to –CN stretching of amines. –CN group can aid the reduction of Ag^{+} to metallic Ag during the formation of AgNPs. Thus we assume that room temperature is the optimum temperature condition for the preparation of seed extract. After optimizing the temperature for the preparation of the seed extract, we investigated the optimum time for the same. For this, the extraction was carried out at room temperature which is the optimum temperature condition for different time durations. Fig. 1b represents the corresponding IR spectra. The peaks in the range 3417-3469 cm^{-1}, 2067-2079 cm^{-1}, 1636 cm^{-1}, 537-566 cm^{-1} was present in all reaction conditions. –CN stretching of amines at 1061.97 cm^{-1} was present in sample extracted for 30 min and not found in any other reaction conditions. The same peak was seen for room temperature extraction during optimization of temperature for extraction. Hence the time of extraction was optimized at 30 min for the preparation of the seed extract.

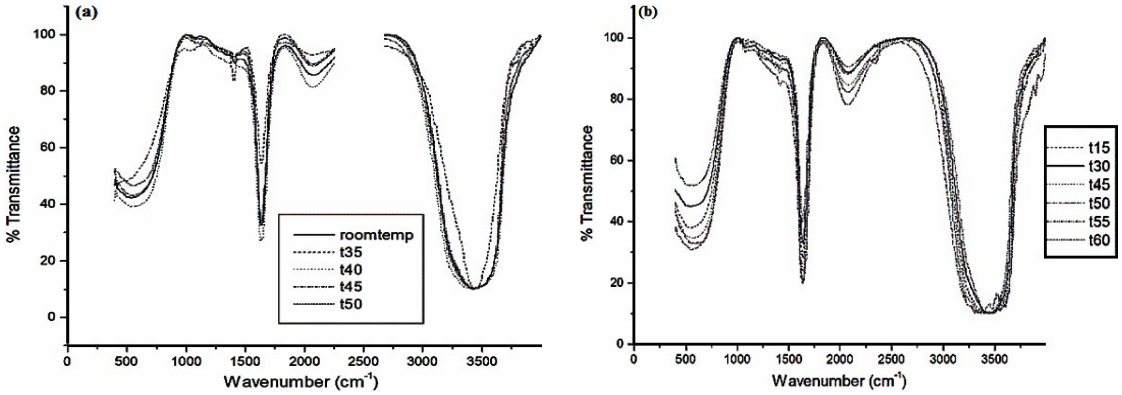

Fig. 1. FTIR spectral analysis of *Derris trifoliata* seed extract for a) temperature optimization b) time optimization

Optimization of reaction conditions for the synthesis of AgNPs using UV-Vis spectroscopy

AgNPs were prepared under sunlight and also at different temperatures. The UV-Vis spectrum of these reaction mixtures is given in Fig. 2. It shows an absorption peak between 400–450nm. This absorption peak represents the presence of AgNPs. None of the samples prepared under different temperature conditions gave the absorption peak corresponding to the formation of AgNPs. So, sunlight irradiation is the optimum condition for the preparation of AgNPs using the seed extract.

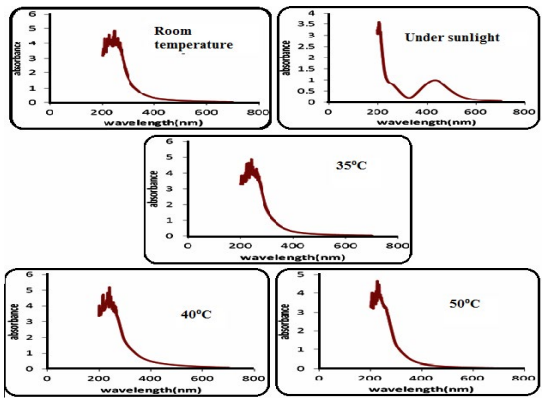

Fig. 2. Absorption spectrum of AgNPs prepared under different temperature conditions

Figure 3 shows the absorption spectrum of the AgNPs recorded for optimization of time of reaction. Metallic nanoparticles show characteristic UV-Vis absorption spectra at 433 nm due to Surface Plasmon Resonance (SPR). The SPR bands are influenced by size, shape, morphology, composition and dielectric environment of the prepared nanoparticles[55]. Intensity of absorption peak indicates the concentration of AgNPs. The appearance of the SPR increased with increase in reaction time. Irradiation for one hour shows maximum absorbance of 1.483 at 433nm. Thus, we optimized this condition -1 h for the synthesis of AgNPs.

Optimized process for the preparation of AgNPs

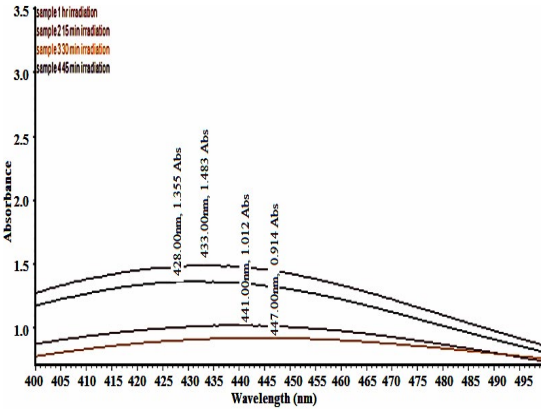

Fig. 3. Absorption spectra of AgNPs for optimization of time of reaction

5 gram of finely ground seeds was soaked in 25 mL distilled water for 30 min at room temperature, filtered and the extract was collected. This seed extract was used as reducing agent for the synthesis of AgNPs. The seed extract was treated with 1 mM $AgNO_3$ solution and kept under sunlight for 1 hour. Appearance of reddish-brown colour specifies the formation AgNPs.

Characterization of synthesized AgNPs

Characterization of AgNPs were done using UV-Vis spectroscopy, FTIR spectroscopy and HRTEM- SAED images.

UV-Visible spectrum

The UV-Vis absorption spectrum of the AgNPs prepared under optimum conditions is given in Figure 4.

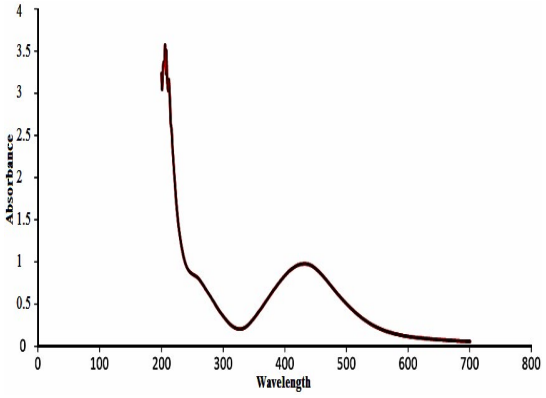

Fig. 4. Absorption spectrum of AgNPs prepared at optimum conditions

The AgNPs showed a broad characteristic absorption peak at a wavelength of 433nm because of SPR. According to Mie theory[58], a single SPR band shows the formation of small spherical or quasi-spherical nanocrystals. A broad peak indicates that the AgNPs are spherical and polydispersed. The spherical shape of the AgNPs was thus confirmed.

FTIR spectrum

The FTIR spectrum of the AgNPs prepared under optimum conditions are given in Fig. 5. The important peaks present in FTIR spectrum of AgNPs were at 3448.20 cm^{-1}, 2101.46 cm^{-1}, 1637.0 cm^{-1}, 1384.61 cm^{-1} and 543.50 cm^{-1}. They correspond to the -OH stretching or -NH stretching of amines, alkyne group present in phyto constituents, carbonyl stretching in carboxyl group of proteins, germinal methyl of secondary metabolites and halide, respectively. The peak at 1061.97 cm^{-1} corresponding to -CN stretching of amines seen in the FTIR spectrum of the seed extract was absent here. The disappearance of this peak in the FTIR spectrum of synthesized AgNPs indicates that the amine groups present in bioactive compounds or secondary metabolites cause the reduction of Ag^{+} to Ag_0. This reveals the role of biological molecules in the synthesis and stabilization procedures[59]. The stabilization of AgNPs is due to surface bound proteins through free amine group[60].

HRTEM

Figure 6 gives the HRTEM and SAED images of AgNPs. The size of the synthesized AgNPs obtained were found in the range of 2-20nm. Nearly spherical shape of the prepared AgNPs that is assumed from the absorption spectrum was also confirmed here.

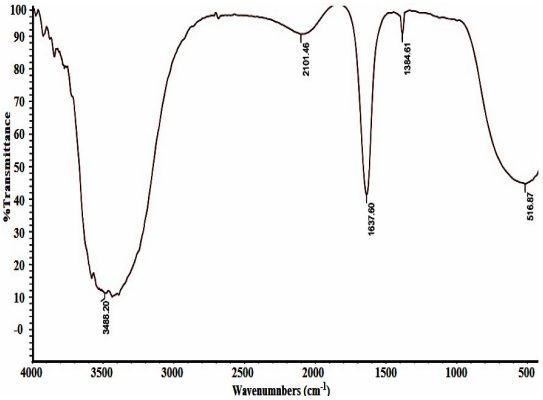

Fig. 5. FTIR spectrum of AgNPs

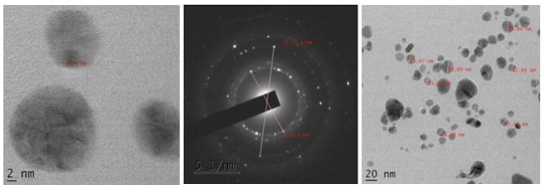

Fig. 6. The HRTEM and SAED images of AgNPs

AgNPs as Hydrogen peroxide sensor

The absorption spectra of the reaction mixture of the AgNPs and hydrogen peroxide at regular intervals of time are given in Fig. 7. As time increased, the absorbance at 433nm of the samples decreased. Finally, this SPR peak vanished and the brown colour of the reaction mixture became completely colourless. These results are in accordance with the results obtained by Tagad *et al.*,[61]. According to Mohan and coworkers[62], "the addition of AgNPs to H_2O_2 resulted in the formation of free radicals which initiated the degradation of the AgNPs. This led to the oxidation of silver to silver ions and resulted in a decrease in absorbance." These findings suggest that the AgNPs can be successfully used to sense the concentration of H_2O_2 present in various samples.

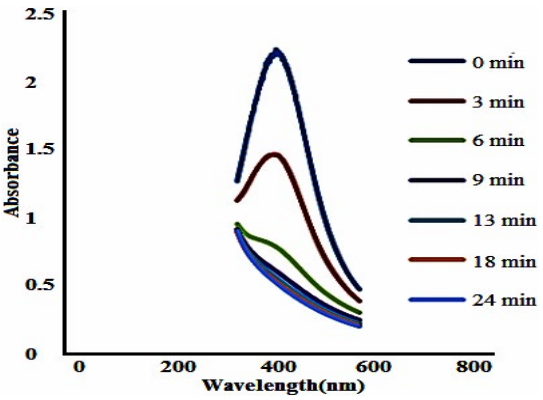

Fig. 7. Absorption spectra of AgNPs and H_2O_2 reaction mixture at regular intervals of time

AgNPs as catalyst for photo degradation of methylene blue

Figure 8 a and b shows the photograph of blank solution of methylene blue and methylene blue solution with AgNPs at different time intervals. The colour remained same throughout the time of study of the blank solution. For the solution with AgNPs, the deep blue colour of the methylene blue solution started to fade during irradiation of sunlight and the degradation of was complete within 12 h of irradiation.

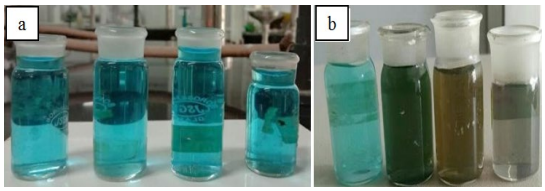

Fig. 8. Photograph of methylene blue at varying time intervals (a) blank solution (b) solution with AgNPs

Figure 9 indicates the absorption spectra of the blank solution at different time intervals. Methylene blue shows an absorption band at 660nm. It is clear from the graph that the absorbance of methylene blue in the blank solution decreases only slightly with time.

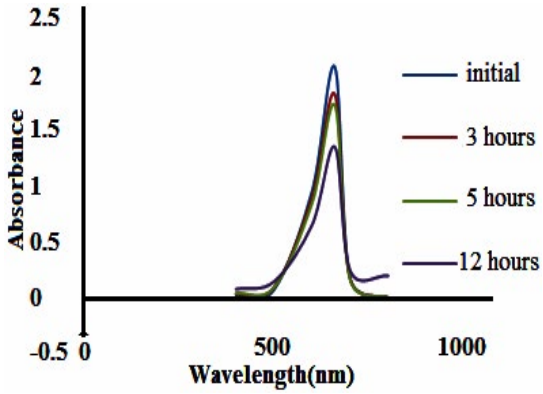

Fig. 9. Absorption spectrum of methylene blue (blank solution) at varying time intervals

Figure 10 indicates the UV-Vis spectra of methylene blue in the presence of AgNPs at varying time intervals. With increase in time, the absorption of methylene blue decreased with simultaneous increase of absorption of AgNPs. After 12 h of exposure, the absorbance of methylene blue dye almost approached the base line and the absorbance of AgNPs was maximum. This may be due to the photocatalytic degradation of methylene blue dye by AgNPs. Thus the degradation of the hazardous dye methylene blue can be enhanced by using AgNPs.

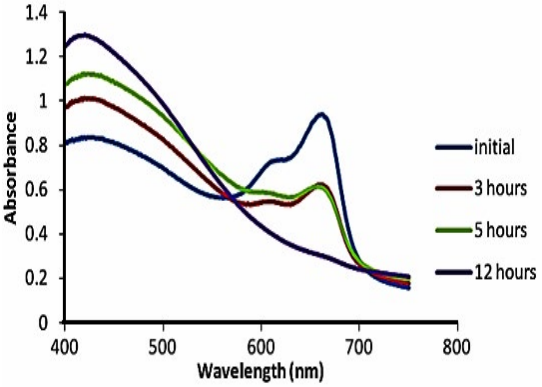

Fig. 10. Absorption spectrum of methylene blue in the presence of AgNPs at different time intervals

AgNPs as antibacterial agents

Table 1 lists the percentage inhibition of the AgNPs on *E.coli* bacteria. An increase in percentage of inhibition with respect to concentration of AgNPs was found. The percentage of inhibition has highest value for the 40 µL mixture. The antibacterial action of synthesized AgNPs was thus proved.

Table 1: Analysis of % of inhibition of synthesized AgNPs on *E.coli* bacteria

Concentration of AgNPs(µL)	Optical Density	% of inhibition
Control	1.422	
10	0.371	73.7%
20	0.32	77.5%
30	0.253	82%
40	0.24	83%

CONCLUSION

Our study reports a cost effective, non-toxic, ecofriendly and easy method for the preparation of AgNPs, where Derris trifoliata seed extract act as a reducing and stabilizing agent. The preparation of seed extract and synthesis of AgNPs were optimized through spectroscopic methods. UV-Visible spectrum of AgNPs showed a characteristic Surface Plasmon Resonance peak at 433nm. HRTEM and SAED images confirmed nearly spherical nature of the AgNPs with a diameter of about 2–20nm. FTIR spectra of the seed extract and silver nanoparticles revealed that the seed extract can act as a biological agent which can perform the dual function of reduction and stabilization. Ability of AgNPs to sense hydrogen peroxide was demonstrated using UV-Visible absorption spectra which would find applications in the development of sensors to detect the presence of hydrogen peroxide in samples. The

use of the prepared AgNPs in the photodegradation of one of the hazardous dyes, methylene blue was investigated using UV-Vis spectroscopy. The decrease in methylene blue absorption with increase in exposure time indicates the photocatalytic activity of AgNPs. Also, we analysed the antibacterial activity of the AgNPs on *E-coli* bacteria which would find applications in development of new antibacterial drugs.

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