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Sunlight induced rapid synthesis and kinetics of silver nanoparticles using leaf extract of *Achyranthes aspera* L. and their antimicrobial applications

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ABSTRACT

Sunlight induced strategy for the rapid green synthesis of silver nanoparticles (AgNPs) is reported for the first time using aqueous leaf extract of *Achyranthes aspera*. On exposing a mixture of silver nitrate solution and aqueous leaf extract of *A. aspera* to sunlight, stable silver nanoparticles were obtained within few seconds. The water soluble biomolecules from the *A. aspera* served as both reducing and capping agents in the synthesis of silver nanoparticles. The nanoparticles were characterized using UV–Vis., Fourier transform infrared (FTIR), transmission electron microscopy (TEM), and EDAX techniques. . The pseudo first order rate constant $k_{obs,}$ for the formation of AgNPs was found to be 3.49 x 10^{-2} min^{-1}. The particles were stable for 3 months. The nanoparticles were mono-dispersed, spherical in shape with the average size of 12.82 nm. FT-IR analysis revealed that the -OH groups, possibly, from saponin were responsible for the reduction of silver ions to silver nanoparticles (AgNPs). Thus prepared AgNPs have desirable cytotoxicity towards bacterial strains and fungus and the effect was compared with standard drugs, Amikacin and fluconazole respectively. This green and mild technique can be used for the large scale extracellular synthesis of silver nanoparticles and the AgNPs thus prepared may be used for biological applications.

Keywords: Silver nanoparticles; *Achyranthes aspera*; sunlight induced; green synthesis.

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Introduction

Metal nanoparticles show various applications in medicine, biotechnology and electronics **[1]**. In the past various synthetic routes like chemical reduction **[2]**, electrochemical method **[3]**, sonochemical method **[4]**, templating **[5]**, and photochemical method **[6, 7]** have been reported for the preparation of the metal NPs. The reduction of metal precursors in aqueous solution by different reducing agents is the easy and convenient method for the preparation of the noble metal NPs, and the resulting particles were stabilized by capping agents such as surfactants, polymers and dendrimers **[8-10]**. However, the excess of the oxidized products of the reducing agent contaminate the nanoparticles and are not suitable for biological applications. Hence green chemistry approaches for designing environmentally benign

materials and sustainable methods for total elimination or minimization of generated waste that are hazardous to the environment and human health are envisaged by researchers. An eco-friendly reducing and capping agent, an environmentally suitable solvent system and synthetic processes are essential criteria for an absolutely green nanostructured synthesis. Biosynthesis of metal nanoparticles is the current field of material science **[11-15].**

Among various green synthetic methods proposed for the preparation of metal nanoparticles, sunlight irradiated route is an important and economical one. Recently many articles were published in this field. The rates of biosynthesis and chemical reduction of AgNPs were found to increase by visible **[16-17]** and ultraviolet light **[18]** respectively and solar irradiation is effective in the synthesis of Au **[19]** and Ag nanoparticles **[20]**. Sunlight-induced synthesis of Ag/Au bimetallic nanostructures on DNA template was reported by Liu and co-workers **[21].** Synthesis of gold nanodecahedra using sunlight irradiation was reported by Chien et al. **[22].** The sunlight-induced method for the rapid biosynthesis of AgNPs using ethanol extract of *Andrachnea chordifolia* has been reported by Shahverdi and co-workers **[23].** Annadhasan et al. reported the sunlight induced synthesis of AgNPs suing sodium salt of N-cholyl amino acids **[24].** Recently we have reported the biogenic synthesis of silver nanoparticles by leaf extract of *Cassia angustifolia* **[25]** in which it was observed that sunlight had profound influence on the rate of formation of AgNPs. This observation made us to study the effect of sunlight on the rate of formation of AgNPs using regionally available resources. The prime objective of the present work is to use of natural sunlight for the synthesis of AgNPs using the leaves of *Achyranthes aspera* L., an abundantly available weed. This process is non-toxic, nonpolluting and would reduce energy costs and the sunlight is traceless in this process and hence the AgNPs can be used for biological applications.

Achyranthes aspera L. (Family *Amaranthaceae*) **(Fig. 1)** is an erect, annual or perennial herb of about 1-2 meter in height and is found on road sides, field boundaries and waste places as a weed throughout India up to an altitude of 2100 m and in South Andaman Islands.

Fig. 1. *Achyranthes aspera*

It is known as "Prickly chaff flower" in English and "*Chirchita*", "*Onga*", "*Latjeera*" or "*Apamarga*", *Nayuruvi* in local languages and dialects **[26]**. Traditionally, the plant is used in asthma and cough. It is pungent, antiphlegmatic, antiperiodic, diuretic, purgative and laxative, useful in oedema, dropsy and piles, boils and eruptions of skin etc. Crushed plant is boiled in water and is used in pneumonia. The flowering spikes are used as external application for bites of poisonous snakes and reptiles, used in night blindness and cutaneous diseases. Ash of the plant is used for ulcers and warts. Paste of the roots in water is used in ophthalmia and opacities of the cornea. The plant is useful in liver complaints, rheumatism, scabies and other skin diseases. It also possesses tranquillizing properties **[27].**

Experimental

Materials

All the chemicals and reagents used in this study were of analytical grade. Silver nitrate ($AgNO_3$, 99.9%) was obtained from Sigma-Aldrich (USA) Chemicals. All glassware were washed in dilute HNO_3 acid and rinsed thoroughly with double-distilled water prior to use and dried in a hot air oven. pH was adjusted to the required value with 0.1M NaOH or 0.1M H_2SO_4. The leaves of *Achyranthes aspera* used in the present study were procured from N. Muthaiyapuram in Tiruchendur Taluk (Tamil Nadu) India.

Preparation of leaf extract

The dirt and other foreign materials in the leaves were removed by thorough washing with tap water and finally with double-distilled water. To prepare the leaf extract, 10 g of thoroughly washed and finely cut leaves were boiled in 100 mL sterile distilled water for 5 min in a 250 mL Erlenmeyer flask and the solution was finally filtered through Whatman no.41 filter paper. All the experiments were carried out with this extract unless otherwise mentioned. Fresh leaf extract was always used to do the experiments.

Development of AgNPs

About 10 mL of the leaf extract was added to 100 mL of 1 mM aqueous silver nitrate solution (1:10 ratio) and the solution was immediately kept under bright sunlight. The formation of AgNPs was indicated by the development of its characteristic reddish brown colour within a minute. In the variation of pH, first the pH of the extract was adjusted before adding silver nitrate solution. In all the variations, the reaction mixture was exposed to sunlight for 5 min unless otherwise mentioned. To study the reaction in the absence of light, all the reactants were taken in an Erlenmeyer flask, covered with black paper and kept in the dark.

Characterization of AgNPs

UV–Vis spectral analysis was performed on a JASCO, V-530 spectrophotometer at a resolution of 1 nm. IR measurements were performed in a Thermo scientific Nicolet 6700 FT-IR spectrometer with the resolution of 0.2 cm^{-1}. HR-TEM measurements were performed on a JEOL 3010 instrument with a UHR polepiece which gives a lattice resolution of 0.14 nm and a point to point resolution

of 0.12 nm. EDAX analysis was done using FEI Quanta 200 ESEM. Particle size distribution was determined by photon correlation spectroscopy, which analyzes the fluctuations in light scattering due to Brownian motion of the particles, using a Zetasizer 1000 HS (Malvern Instruments, UK) at Defence Food Research Laboratory (DFRL), Mysore. Light scattering was monitored at 25°C at a 90° angle. Particle size distribution studies were performed at a fixed refractive index of the respective formulation and also the stability of the prepared particles was assessed by measuring Zeta potential. pH was measured using H1 211 pH/ORP meter, Hanna instruments.

Antibacterial and antifungal activities of AgNPs

Antibacterial activity of the synthesized AgNPs was determined using the agar well diffusion assay method. Approximately 20 mL of molten and cooled nutrient agar media was poured into sterilized Petri dishes. The plates were left overnight at room temperature to allow any contamination to appear. The bacterial test organisms were grown in nutrient broth for 24 hours. 100 mL nutrient broth culture of each bacterial organism was used to prepare bacterial lawns. The diameter of zones of inhibition was measured using a meter ruler, and the mean value for each organism was recorded and expressed in millimeters.

Results and discussion

UV–Visible spectral analysis

The formation of silver nanoparticles at different time intervals, leaf extract volume, silver nitrate concentrations and pH was monitored by UV–Visible spectrophotometer at 200-800 nm. An intense band observed around 419 nm was identified as a ‘‘surface plasmon resonance (SPR) band’’ and attributed to the excitation of free electrons in the nanoparticles. Since the intensity of absorbance of SPR band was much higher, the solutions in all the cases were diluted 10 times with double distilled water before measuring the absorbance. **Fig. 2a** represents the UV-Vis spectra recorded from the sunlight exposed silver nitrate - *Achyranthes aspera* reaction mixture as a function of time.

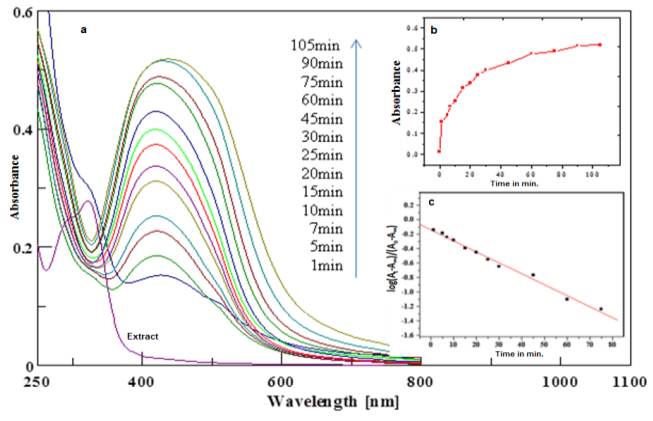


Fig. 2. (a) UV–Visible spectra recorded as a function of interaction time of *A. aspera* extract with an aqueous solution of 1 mM $AgNO_3$; (b) variation of absorbance with time (inset); (c) plot of $\log(A_t-A_\infty)/(A_o-A_\infty)$ Vs time (inset).

The colour changed from colourless to reddish brown within 1 min of exposure to sunlight indicating the formation of AgNPs. The intensity of SPR band initially increased exponentially with time after that it tended to attain a constant absorption value **(Fig. 2b inset)** indicating the completion of the reaction. The AgNPs were stable in solution for 3 months with a small red shift with broadening of SPR band. The SPR band at 419 nm indicates the formation of spherical nanoparticles which was further confirmed by TEM analysis.

The λ_{max} of the SPR band at 1 min was observed to be 429 nm which gradually decreased up to 60 minutes and then increased with broadening of the SPR band, indicating the formation of different sized AgNPs with the different time of exposure to sunlight. These results indicate an optimum time of exposure to sunlight is required to form small and monodispersed Ag nanoparticles; in this case it appears to be 20-30 minutes. The pseudo first order rate constant k_{obs} was obtained from the slope of the plot of $\log(A_t-A_\infty)/(A_o-A_\infty)$ vs time t **(Fig. 2c inset)** according to the equation $A_t = A_\infty+(A_o - A_\infty)\exp(-k_{obs}t)$, where A_o and A_∞ are the initial and final absorbance respectively **[28]**. The k_{obs} was found to be 3.49×10^{-2} min^{-1} with R = 0.995.

Effect of volume of extract

To study the effect of the extract *of A. aspera*, the volume of the extract was varied from 1 to 9 mL at 1 mM $AgNO_3$ solution. The total volume was maintained as 20 mL by the addition of required amount of double distilled water and the solution was exposed to sunlight. With the increase of the volume of extract the SPR band was shifted to lower wavelengths signifying the formation of smaller sized nanoparticles. The plot of absorbance versus volume of extract tended to attain a constant value signaling completion of reaction at higher volumes of *A. aspera* extract.

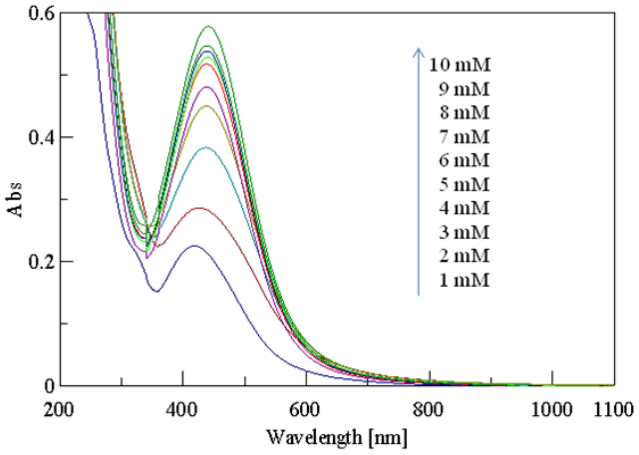


Fig. 3. UV-Visible spectra of silver nanoparticles obtained using leaves extract of *A. aspera* in different concentration of $AgNO_3$.

Effect of silver ion concentration

The effect of silver ion concentration was assessed by varying the concentration from 1 to 10 mM. The formation of AgNPs was found to be slow at lower metal ion concentrations and hence the absorbance was also less

compared to higher metal concentrations. From the UV-Visible spectra **(Fig. 3)**, it was seen that with increasing the concentration of silver nitrate, the formation of nanoparticles was also increased.

Sharp peaks were observed at higher concentration of silver ion which indicates that the particles were monodispersed. There was steady increase in absorbance up to 4 mM after that it tended to attain a maximum value, with increasing the concentration of silver ions up to 3 mM, a red shift in λ_{max} (from 418 to 435 nm) was noticed after that it was almost same. The variations in λ_{max} values signify changes in particle size owing to changing concentration ratios between plant extract and silver ions. These results show that as the concentration of metal ion increases the particle size also increases.

Effect of pH

To study the effect of pH on the formation and stability of AgNPs the reactions were carried out at different pH, ranging from 3 to 11 by adjusting with 0.1M sulphuric acid or sodium hydroxide in acid and alkaline medium respectively at 20 mL of 1mM silver nitrate solution. At acidic pH the formation of AgNPs was less indicated by less intensity of SPR band and also the λ_{max} was high signifying the formation of large nanoparticles. With the increase of pH the rate of formation of AgNPs was quick and the intensity of SPR band steadily increased and the λ_{max} was also shifted to lower wavelength with the narrowing of the peak **(Fig. 4)**. This may be due to the formation of monodispersed small sized AgNPs at high pH conditions.

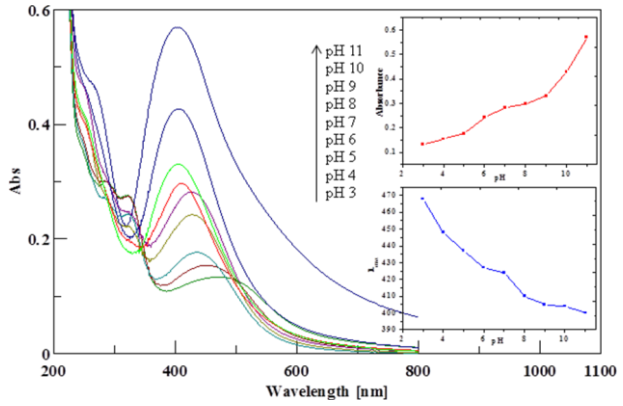


Fig. 4. UV-Visible spectra of AgNPs obtained using leaves extract of *A. aspera* at various pH.

At pH 10 and 11 the formation of AgNPs was instantaneous with very dark reddish brown colour. This may be due to the free availability of large number of functional groups for silver binding and subsequent reduction. The AgNPs so formed do not get time to aggregate, resulting in the formation of large number of small sized nanoparticles (λ_{max}=400 nm). From pH 3-9 absorbance increased gradually there after a sudden increase in absorbance from pH 10 to 11 **(Fig. 4(a) inset)**. From the plot of λ_{max} Vs pH **(Fig. 4(b) inset)**, it was seen that with increasing pH from 3 to 12, a blue shift in λ_{max} from 468 to 400 nm occurred. The broad SPR bands observed at lower pH values may be due to large anisotropic particles.

Fourier transform-infrared spectroscopy

FTIR analysis was performed to identify the biomolecules responsible for the reduction of Ag^+ ions into Ag^0 and its stabilization. FTIR spectra of the synthesized solid silver nanoparticles along with the solid biomaterial obtained by natural evaporation of the aqueous extract are shown in **Fig. 5**. The AgNPs showed characteristic bands similar to those of the *A. aspera* extract **(Figure 5(b))** indicating that silver nanoparticles were coated with the biomolecules from the extract. There was a major shift from 3416 to 3391cm^{-1} showed that the corresponding functional group may be responsible for the reduction of silver ions to silver nanoparticles. The broad absorption band located at around 3391 cm^{-1} may be attributed to -O-H stretching. The presence of three peaks in the region of 2850-3000 cm^{-1} is due to aliphatic -C–H stretch. The peak at 1633 may be assigned to C=C.

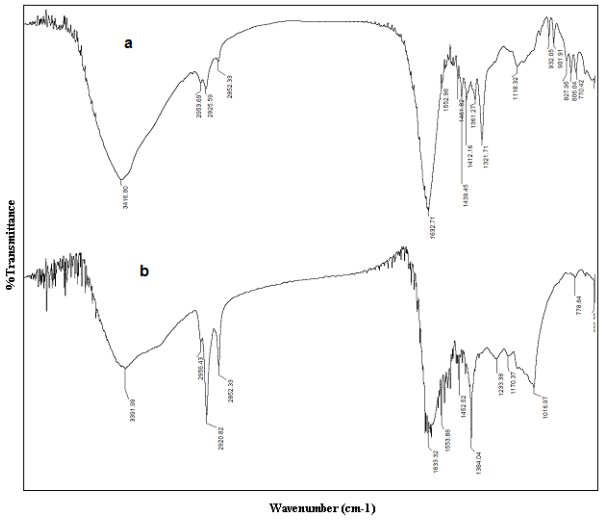


Fig. 5. FT-IR spectra of (a) *A. aspera* extract (b) Solid silver nanoparticles obtained using leaves extract of *A. aspera*.

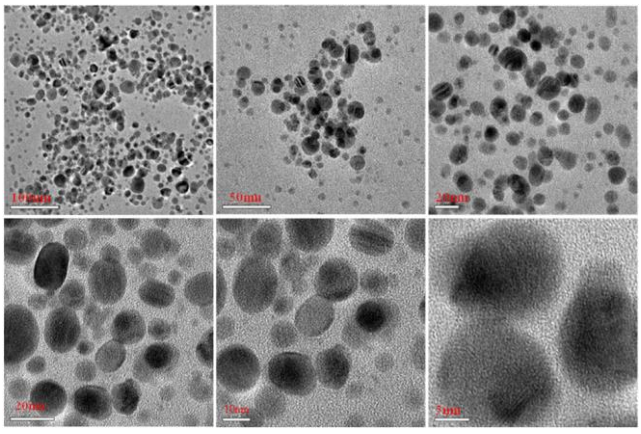


Fig. 6. HRTEM micrograph of AgNPs synthesized using leaves extract of *A. aspera*.

Transmission electron microscopy

HRTEM images of silver nanoparticles showed monodispersed spherical nanoparticles **(Fig. 6)**. Large density of silver nanoparticles could be seen as supported by

the high absorbance value in UV-Vis. spectra. The result showed narrow particle size distribution, the average size of AgNPs was calculated to be 12.82 nm.

EDAX analysis of silver nanoparticles

The elemental analysis of biologically synthesized nanoparticles was done by EDAX **(Fig. 7)** where strong optical absorption peaks were observed approximately at 3 keV, which is typical for the absorption of metallic silver nanoparticles (92.67%) **[29]**. Traces of O (7.33%) atom was also noticed which might be from the attached biomolecules.

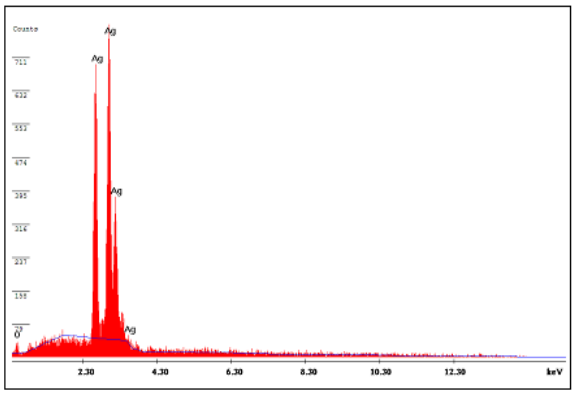


Fig. 7. EDAX analysis of silver nanoparticles synthesized using leaves extract of *A. aspera*.

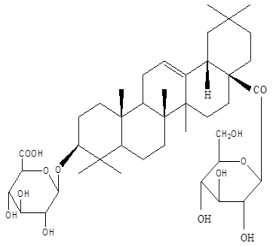
Particle size analysis and zeta potential measurements

Dynamic light scattering (DLS) was used for measuring the average hydrodynamic diameters and polydispersity indexes (PDI). Each sample was analyzed in triplicate at 25˚C and pure water was used as a reference dispersing medium. Zeta potential data was collected through electrophoretic light scattering at 25˚C in triplicate for sample in pure water. DLS data showed that the mean diameter of the AgNPs was 64 nm, PDI was 0.221 and zeta potential was - 30.9 mV.

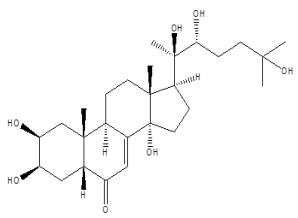
Discussion

Chemical composition of Achyranthes aspera

Leaves and roots of *A. aspera* contain triterpenoid saponins A and B which possess oleanolic acid as the aglycone. The carbohydrate components are the sugars D-glucose, L-rhamnose, D-glucuronicacid (= Saponin A). Saponin B is the β-D-galactopyranosyl ester of Saponin A **[30]**, Ecdysterone, an insect moulting hormone, and long chain alcohols are also found in *A. aspera* **[31].** The structures of important chemical compounds present in *A. aspera* are given below:



Bisdesmosidic Saponin



Ecdysterone

Saponins from medicinal plants showed characteristic infrared absorbance of the hydroxyl group (-OH) ranging from 3429 to 3316 cm^{-1}; C-H ranging from 2929 to 2922 cm^{-1}; C=C absorbance ranging from 1651 to 1619 cm^{-1}; C=O ranging from 1740 to 1736 cm^{-1}. Oligosaccharide linkage absorptions to sapogenins, that is C-O-C, were observed from 1072 to 1034 cm^{-1}. The OH, C-H, C=C, and C-O-C peaks found are suggestive of oleanane triterpenoid saponin in the plant extract and AgNPs. These oleanane-type triterpenoid saponins are characterized by the C=O infrared absorbance due to oleanolic acid/ester. Such triterpenoid saponins may be bidesmosides or monodesmosides depending on number of attachments of glycones (i.e. glycosidic and ester groups) to the sapogenin. Monodesmosidic saponins found in many medicinal plants do not show C=O infrared absorbance due to ester linkages **[32]**. In this study FT-IR spectra of the extract and the prepared AgNPs do not show absorption peak due to C=O group in the range 1740-1736 cm^{-1} suggesting the involvement of monodesmosidic saponins in the reduction and capping of silver nanoparticles.

No considerable reduction was observed in the dark but the reduction was observed within a minute when the solution was exposed to sunlight. In the past synthesis of AgNPs in the absence of light by the extract of *A. aspera* was demonstrated without giving any process details **[33]** and the absorbance reported was very less (Abs ~0.0004). In our study, even after 14 days of the reaction in the absence of light the intensity of colour developed is negligible (~0.03, without dilution) in comparison to reaction carried out by exposing to sunlight for 5 minutes (Abs ~2, considering 10 times dilution of the solution before measurement). All these observations suggest that sunlight has very strong influence on this reaction. The UV-Visible spectrum of aqueous plant extract has absorbance peaks at 288 nm and 322 nm **(Fig. 8a)** whereas the silver nanoparticles have absorbance peak at 414 nm only **(Fig. 8b)**.

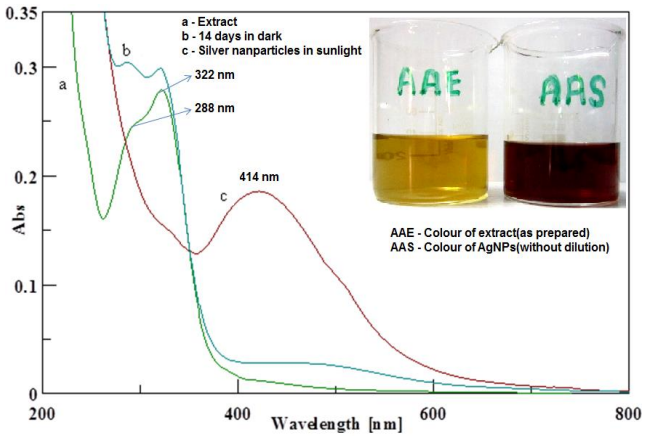


Fig. 8. UV-Visible spectra of (a) extract and (b) AgNPs prepared in dark and (c) AgNPs prepared in sunlight.

More over the peaks at 288 and 322 nm have completely disappeared after the formation of silver nanoparticles suggesting the involvement of these functional groups in the reduction of Ag^{+} to Ag^{0} but these

peaks remain even after 14 days in the dark reaction. π-π* and n-π* electron transitions generally observed at 280-350 nm range indicating the presence of π bonds and nonbonded electrons possibly from the oxygen atom of OH group. The FTIR spectrum of the extract of *A. aspera* has a broad band at 3416 cm^{-1} but in the AgNPs it is shifted to 3392 cm^{-1} which further support the role of OH group in the reaction. It is difficult to exactly identify the molecules responsible for the reduction and capping but the involvement of OH group can be predicted.

Antibacterial and antifungal activities of AgNPs

The disk diffusion assay method is used to test the sensitivity of bacterial strains *(P. aeruginosa, S. aureus and E.coli*) and fungus (*Candida albicans*) towards AgNPs **(Fig. 9)** and the zone of inhibition (ZOI) was compared with standard drugs Amikacin and fluconazole respectively. The clear zone around the disk reflects the bacterial sensitivity towards AgNPs**.** The wells filled with *A. aspera* extract (at the concentrations used for synthesis of silver nanoparticles) did not show any ZOI suggesting at these concentrations it is not antibacterial. It is noticed that AgNPs are almost equally sensitive towards *P. aeruginosa* (12 mm) and *S. aureus* (13 mm) and less in *E.coli* (4 mm). In *Candida albicans* the standard drug fluconazole have no activity, but the prepared AgNPs have cytotoxicity (12 mm). The bactericidal activity of synthesized nanoparticles is found to be much higher than other reports **[34-36].**

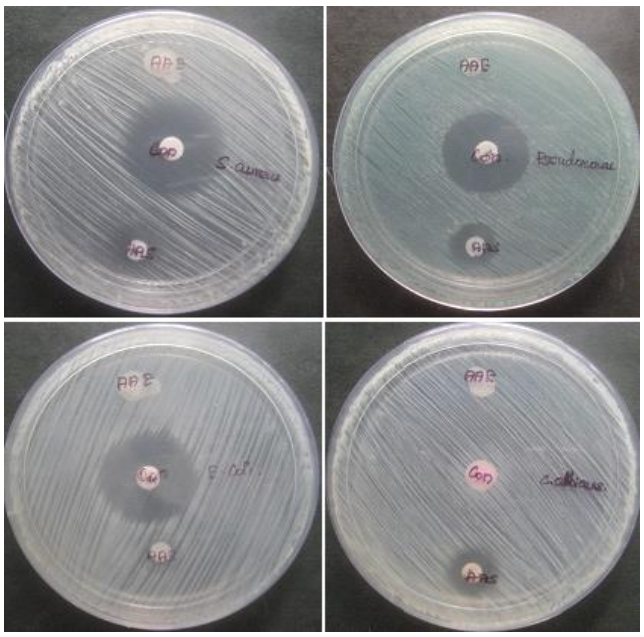


Fig. 9. Antimicrobial activity of AgNPs against various pathogenic bacterial strains AAE - *Achyranthes aspera* Extract, AAS - AgNPs, Con - Control (drugs).

Proposed mechanism of AgNPs formation

Kinetic studies of the reduction process revealed that the synthesis of nanoparticles starts within a minute and reaches the plateau after 60 min **(fig. 2b inset)**. In the first 10 min there is exponential increase in absorbance followed by slow and linear increase in the absorbance values which finally flattens out after 60 min thus, suggesting very fast reaction kinetics of nanoparticles synthesis. The similar control solution kept in a dark for 14 days did not show much colour formation, suggesting that light has crucial role in the synthesis of nanoparticles. The photochemical synthesis of AgNPs in the presence of amino- and carboxylate-terminated PAMAM dendrimers was reported by Zsuga et al. **[37].** While Park et al. reported the photochemical reduction of Ag^+ ions in the presence of sodium citrate at room temperature without using a reducing agent **[38].** In their reports, the formations of AgNPs were due to the decomposition of carboxylate ion into carbon dioxide and electrons, which subsequently reduces the Ag^+ ions to Ag^0. In the present study, it is proposed that after the addition of the extract into aqueous $AgNO_3$, the Ag^+ ion were attracted by the - O^- group of biomolecules, possibly saponin through electrostatic interactions. This is further supported by instantaneous formation of AgNPs in alkaline pH with an intense SPR band. The increase of pH presumably facilitated the ionization of –OH and –COOH groups of biomolecules (probably saponin) present in the extract, the thus formed – O^- could reduce Ag^+ ions into AgNPs **(Fig. 10)**. The AgNPs thus formed are stabilized by $–COO^-$ groups present in the molecules, which is evidenced by the better stability of particles formed under alkaline pH. Andreescu *et al* **[39]** reported a similar pH effect and instantaneous reduction at elevated pH. The exposure of the reaction medium to sunlight would have facilitated the quick transfer of electrons from O^- to Ag^+ ion resulting in the complete reduction of Ag^+ ion.

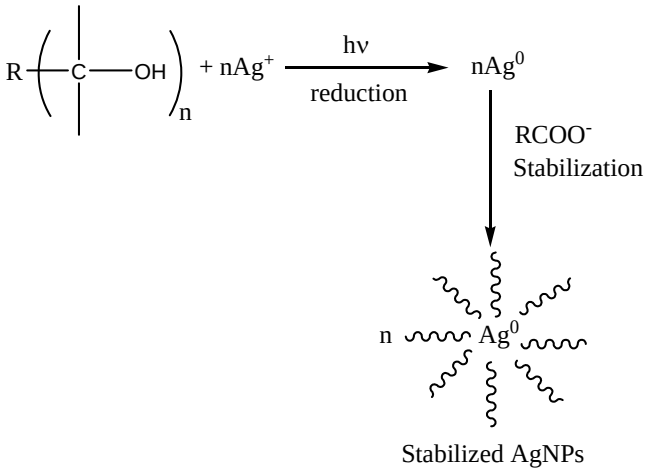


Fig. 10. Proposed scheme for the formation of AgNPs.

Conclusion

Sunlight induced green synthetic method for the preparation of spherical silver nanoparticles was demonstrated using leaves extract of *Achyranthes aspera*. This method excludes the use of external stabilizing/capping agents. Spherical and monodispersed AgNPs were formed in 1 min exposure to sunlight and the amount of AgNPs formed was also much higher. The silver ion and reductant concentrations, pH and interaction time had profound influence on the stability and size of silver nanoparticles. The biomolecules present in the *A. aspera*, probably, saponins were responsible for the reduction of

silver to silver nanoparticles. *A. aspera* could be an excellent bioreductant and easily available plant source for the large scale green synthesis of silver nanoparticles.

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