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Photo-Induced Synthesis of Silver Nanoparticles using, *Syzygium cumini* Fruit Peels Extract Characterization and Antibacterial Activity Studies

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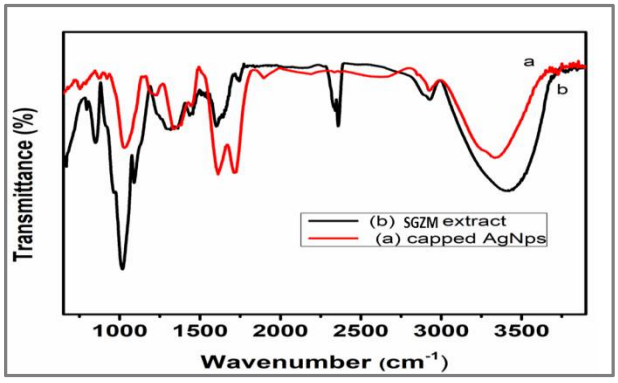
ABSTRACT

Nanomaterials are playing an important role in the emerging field of nano technology. In the present work, silver nanoparticles (AgNPs) were prepared by adopting photo-induced reduction green synthesis from silver nitrate ($AgNO_3$) and Syzygium cumini fruit peelings extract, which can act as a reducing as well as capping/stabilizing agent. It is a simple and low cost and eco-friendly technique in which an external stabilizing agent is not required. The synthesized particles were characterized by using Powder X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), FT-IR, UV-Vis spectroscopy and Scanning Electron Microscopy–Energy Dispersive X-ray Analysis (SEM-EDX). The antibacterial activity of synthesized AgNPs was evaluated on both gram positive and gram negative bacteria using agar well diffusion method.

Graphical Abstract



Keywords: Silver nanoparticles, *Syzygium cumini* fruit peels extract, Photo-induced reduction, Antibacterial activity.

INTRODUCTION

Silver nanoparticles (AgNPs) are most important metallic nanoparticles due to their characteristic SPR (surface plasmon resonance) band in UV-Visible region of electromagnetic radiation[1]. AgNPs are having wide range of applications in various fields, such as sensor technology [2], food processing processes and biological activity. The wavelength of SPR band is depending on the size, shape and distribution of nanoparticles. The AgNPs also have antibacterial and catalytic microbial activities [2].

There are different methods for synthesis of AgNPs, such as chemical reduction, photo-induced reduction, biological and green methods. Green synthesis is the significant and most utilized method for the synthesis of AgNPs, since it is rapid, non-toxic and eco- friendly method [**3**]. Generally, the plant extracts are used for the reduction of metal ions and also act as capping agent for stabilization of metallic nanoparticles [**4, 5**]. The bioactive compounds of plant materials are containing hydroxyl, carboxyl and amino groups, which are responsible for the reduction and stabilization of silver Nps [**6**]. Determination of trace amount of metal ions in biological systems, environment and industrial waste waters, is the most demanding thing for controlling the systems and processes [**7, 8**]. The Fe^{+3}, Hg^{+2}, Pb^{+2} and As^{+3} ions have some positive and negative effects in many biological and environmental processes [**9**]. Thus detection and determination of these ions present in industrial waste water and environment are very important in chemical analysis. In this green synthesis technique, the *Syzygium cumini* fruit peelings extract are used as reducing and stabilizing agent for the reduction of silver unstable **(Ag^+)** ion into silver stable atom **(Ag^0)** [**10**]. The antibacterial activity of synthesized AgNPs is evaluated, on both gram positive (*Bacillus subtilis*) and gram negative (*Proteus vulgarism*) bacteria using agar well diffusion method. The optical and physicochemical properties of synthesized nanoparticles are thoroughly characterized by using various analytical techniques, such as UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction Spectroscopy (XRD), Scanning electron Microscopic and Energy Dispersive Spectroscopy (SEM-EDX), Transmission Electron Microscopy (TEM) and catalytic activity [**11**].

MATERIALS AND METHODS

Materials: The *Syzygium cumini* fruit peelings were collected from a local fruit market. Silver nitrate ($AgNO_3$) was purchased from Sigma-Aldrich. All the chemicals and reagents are of analytical grade and they are used without further purification in this study. Milly-Q water is used throughout the experiment.

Preparation of *Syzygium cumini* peelings extract (SGM): *Syzygium cumini* fruit peelings were cut into small pieces and dried in a hot air oven **[12**]. Then the dried peelings were ground into fine powder and stored. For the preparation of extract, an appropriate amount of *Syzygium cumini* peelings powder is added to Milly-Q water and the solution is stirred for 2 h at 500 rpm. Then the solution was filtered through Whatman filter paper to get clear and transparent extract. Then this extract is stored in refrigerator at 4^oC for further usage.

Synthesis of silver nanoparticles: An aqueous solution of $AgNO_3$ (2 mL) was mixed with 5 mL of *Syzygium cumini* fruit extract. The mixture was stirred and then subjected to a photo-induced reduction with a solar radiation. During this process, the colour of the reaction mixture has changed slowly from pale yellow to brown colour indicating the reduction of $AgNO_3$ to AgNPs. The reaction mixtures were analyzed by UV–Vis spectroscopy to confirm the formation of AgNPs. The formation of AgNPs was investigated by $Fe+^3$ and $Hg+^2$ ions at 0.5 mM concentration of $AgNO_3$ and 0.5 mM concentration of *Syzygium cumini* fruit extract. The synthesized AgNPs solution was centrifuged at high speed (20,000 rpm) and the pellet and supernatant liquid were separated. The pellets were again dispersed in Milly Q water.

Characterization: The analysis of *Syzygium cumini* capped AgNPs solution was carried out on a dual beam UV-Visible spectrophotometer (Shimadzu-3600 Japan). Fourier transforms infrared (FTIR) spectra of *Syzygium cumini* and *Syzygium cumini* capped AgNPs were recorded separately by using an FTIR spectrophotometer (Bruker Optics-TENSOR 27, Germany). The scan was performed in the wave number range of 400–4000 cm^{-1}. Powder X-ray diffraction (XRD) measurements of *Syzygium cumini* -capped AgNPs were carried out on X'pert Pro powder X-ray diffractometer (PAN analytical BV, Netherlands) operating at 40 kV and a current of 30 mA at a scan rate of 0.388 min^{-1}. The morphology and size distribution measurements of the *Syzygium cumini* capped AgNPs were carried out with transmission electron micro scope (TEM, model TECHNAI G2 F30 S-TWIN, FEI Company,

USA) operated at an accelerating voltage of 200 kV). SEM analysis was carried out by casting nanoparticle dispersion on carbon-coated copper grids and allowing for drying at 27°C temperature.

Antibacterial activity test: Agar well diffusion assay was performed according to the method described by earlier reports [**13**]. The target pathogenic bacteria (10^7 CFU mL^{-1}) were spread on the Mueller Hilton Agar plates. The agar wells were made by using clean and sterile borer, then 50 µL of sample was added inside the well. The plates were incubated at 37° C for 24 h. Finally the diameter of the inhibition zone was measured (mm). The pathogens Bacillus subtilis and *proteus vulgarism* were used in this study.

RESULTS AND DISCUSSION

In the present study, we have synthesized the AgNPs by exposing to solar radiation (photo-induced reduction) the mixture of silver nitrate and *Syzygium cumini* fruit peelings extract, which can act as reducing as well as stabilizing agent. The photo-induced reduction is used as energy source for the rapid production of nanoparticles within few minutes [**14**].

UV-Visible spectroscopic analysis: The UV- Visible spectroscopy is one of the most widely useful techniques for the determination of AgNps formation. The formation of AgNps further confirmed by its Surface Plasman Resonance (SPR) peak at around 420nm [**15**], in absorption spectra of AgNPs. The silver nitrate solution of different concentrations (0.1 to 0.5 mM) are mixed with 0.5% concentration of *Syzygium cumini* fruit peelings extract and then exposed to solar radiation (photo-induced reduction) for 5 min [**16**]. The intensity of SPR peak increased gradually and reached to a maximum value upto0.5 mM concentration of $AgNO_3$, (Figure 1a), since the SPR peak intensity is directly proportional to the concentration of AgNPs in the solution. The increase in the $AgNO_3$ concentration up to 0.5 mM, leads to increase in the number of formation of AgNPs, This is due to the addition of more and more number of silver ions into the solution, which are readily undergo reduction by the polyphenol compounds of the extract to produce AgNPs [**17**]. However, the further increase in the concentration from 0.5 to 0.6 mM of $AgNO_3$, did not increase in the intensity of SPR peak intensity and in turn the formation of AgNPs, this may be due to unavailability of polyphenols in the mixture.

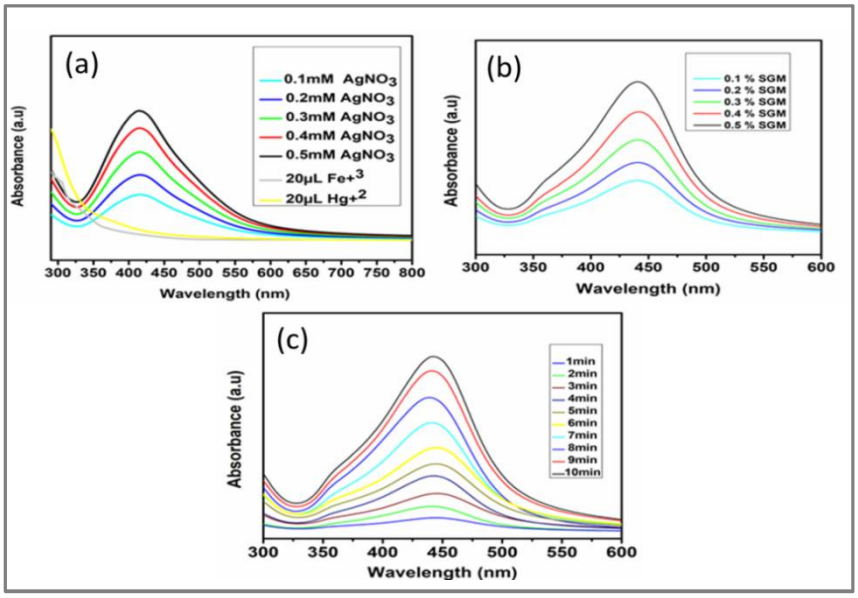


Figure 1. UV-Vis spectra of AgNPs synthesized at(a) different concentrations of $AgNO_3$ and 20 µL Fe^{+3} and 20µL Hg^{+2}, (b)different concentration of SGM extract (c)different time interval.

The mixtures are prepared by mixing 0.5 mM concentration of $AgNO_3$ and different concentrations of extract (0.1% to 0.5%). The UV-Vis spectroscopy for these mixtures (Figure 1b), the SPR peak intensity increased with the increase in concentration of extract. This may due to increase in formation of AgNPs with increase the polyphenol compounds. But, further increase in concentration of extract from 0.5% to 0.6%, did not increase in the SPR peak intensity, this may be due to unavailability of silver ions in the mixture.

Finally, photo-induced reduction time is optimized by keeping other parameters as constant. The increase in the irradiation time also leads to increase in the SPR peak intensities (Figure 1c). This is due to the increased photo-induced reduction[**18**]. Further increase in the irradiation time, did not improve the formation of AgNPs. This is due to complete utilization of Ag^{+} ions and polyphenol compounds present in the mixture, which are responsible for the formation and stabilization of AgNPs [**19**]. However, in this method metal ion detection is observed when different concentrated $AgNO_3$ ions are treated with Hg^{+2} and Fe^{+3}, the peaks intensities are reduced to ground level due to formation of metal complexes with Hg^{+2} and Fe^{+3} ions, which are having size more than Nano particles size.

FT-IR Analysis: FTIR spectra is recorded to provide an evidence for the interaction of functional groups of *Syzygium cumini* involved in the reduction of $AgNO_3$ and the capping of subsequently formed AgNPs. The FTIR spectra of *Syzygium cumini* exhibited stretching vibrations at 3400, 2927, 1737, 1328 and 1020 cm^{-1} [**20**], while the *Syzygium cumini* capped AgNPs showed characteristic stretching frequencies at 3340, 2953, 1716, 1612, 1340, 1030 cm^{-1} [**21**].

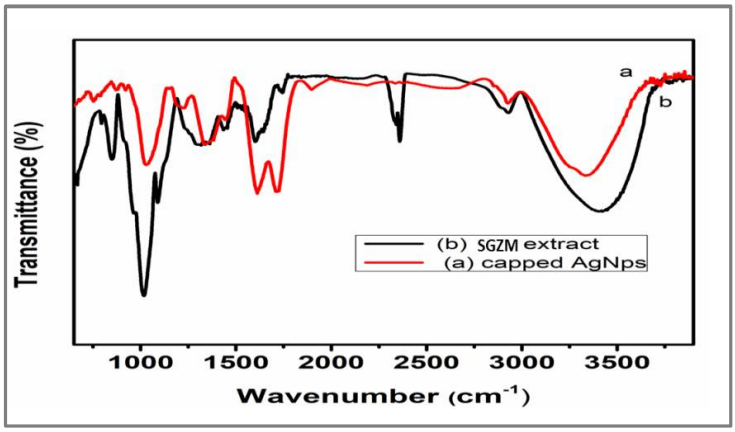


Figure 2. FTIR spectra of (a) Sygyzium capped AgNPs and (b) Sygyziumalone.

The broad peak at around 3400 cm^{-1} corresponds to the O–H stretching vibrations of polyphenols. The peak at around 2900 cm^{-1} corresponds to C–H stretching and strong peak at around 1700 cm^{-1} can be assigned to the carbonyl stretching. Further the peaks at around 1050 cm^{-1} can ascribed to the C–O stretching. FTIR spectra of *Syzygium cumini* capped AgNPs presented some clear distinctions from that of *Syzygium cumini* alone. Most importantly, the intensity of O–H stretching vibrations is decreased and the intensity of carbonyl stretching got increased, which suggests that the hydroxyl groups get oxidized to carbonyl groups. This may be due to the reduction of Ag^{+} ions by the hydroxyl groups of polyphenol compounds and simultaneously phenolic groups undergo oxidation. Further a clear shift in the peak positions were also observed, which confirms the binding of these functional (reducing) groups with the AgNPs [**22**].

Powder XRD pattern of *Syzygium cumini* capped AgNPs: The XRD analysis was performed to determine the crystallite and crystalline structure of *Syzygium cumini* capped AgNPs. As shown in the figure 3, four well defined peaks at scattering angles (2θ) of 38.35, 44.25, 64.54 and 78.28 were observed. These peaks corresponds to the (111), (220), (200) and (311) lattice planes sets respectively. These lattice planes confirm the Face centered cubic (FCC) crystal structure of the

Syzygium cumini capped AgNPs. High intensive peak is observed for (111) lattice plane and broadening of these peaks suggests the Nano size of the synthesized particles.

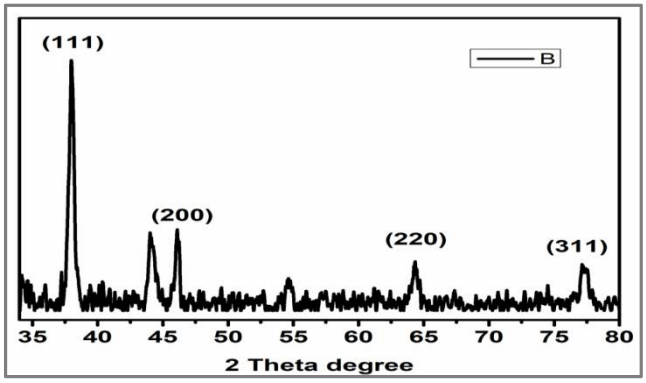


Figure 3. Powder XRD pattern of PMG capped AgNPs.

SEM-EDX analysis: The nanoparticle size and its morphological studies were carried out by using scanning electron microscopy (SEM). The SEM image presented the AgNPs with approximately 20 nm in size with nearly spherical morphology (Figure 4(a)). The purity of *Syzygium cumini* fruit peels extract capped AgNPs and the presence of elemental Ag atoms was studied by Energy dispersive X ray analysis (EDX). As shown in figure 4(b), the EDX spectrum revealed the presence of only carbon, oxygen and silver in *Syzygium cumini* capped AgNPs, which implies the purity of nanoparticles formed (the C and oxygen are from the extract).

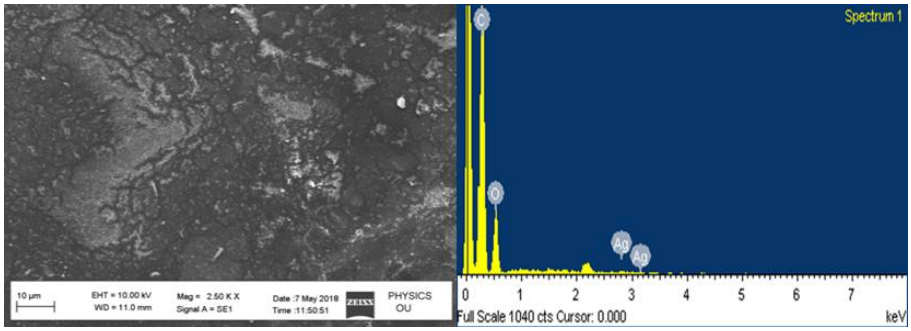


Figure 4. (a) SEM image of Sygiziumcapped AgNPs (b) corresponding EDX spectrum.

TEM analysis: TEM analysis was carried out to examine the particle shape and size of the AgNPs, which are synthesized by using *Syzygium cumini* fruit peelings extract. TEM analysis indicates that the size of AgNPs ranges from 5 to 20 nm.

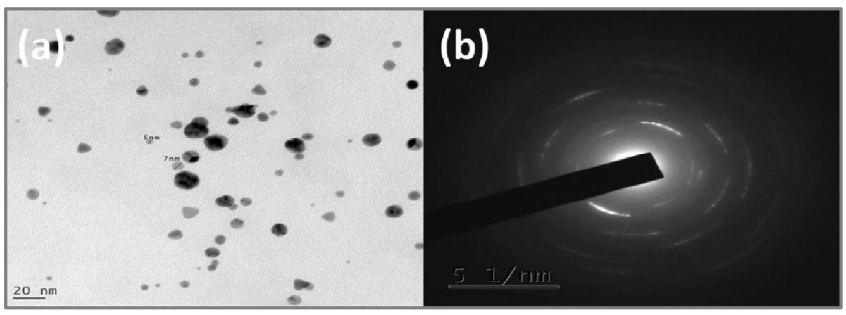


Figure 5. (a) TEM image of Sygizium capped AgNPs and (b) corresponding SAED pattern.

TEM analysis also suggests that the synthesized *Syzygium cumini* fruit peelings extract capped AgNPs are spherical in shape and the average size of the AgNPs is 10±2 nm. The selected area of electron diffraction pattern of concentric rings exhibited with intermittent bright dots, indicating that these Nano particles are highly crystalline in nature.

APPLICATION

Antibacterial Activity: The *Syzygium cumini* fruit peelings extract capped AgNPs had shown a significant antibacterial activity against Gram-negative *Proteus vulgaris* and Gram-positive *Bacillus*. As the concentration of AgNPs is increased, the growth of both bacteria has decreased. The zone of inhibition of AgNPs against proteus vulgarism and *Bacillus subtilis* bacteria has decreased. These results suggest that the AgNPs synthesized from *Syzygium cumini* fruit peelings extract shows the effective antibacterial activity against gram positive than in Gram-negative bacteria. A small zone of inhibition was observed for the *Syzygium cumini* fruit peels extract alone. AgNps make holes in the cell wall, resulting in the fact that leakage of cell contents leads to death of bacteria. The silver nanoparticle can bind with the DNA of bacteria and inhibit the DNA transcription. Because of AgNPs closely bind to the surface of the microorganism causing visible damage to the cells wall; AgNPs can minimize the damage of cell wall and side effects of drugs. It was reported that silver nanoparticles can penetrate and disrupt the membranes of bacteria. Based on these results, it can be concluded that the green synthesized AgNPs had significant antibacterial action on both these Gram-negative proteus vulgarism and Gram-positive Bacillus bacteria.

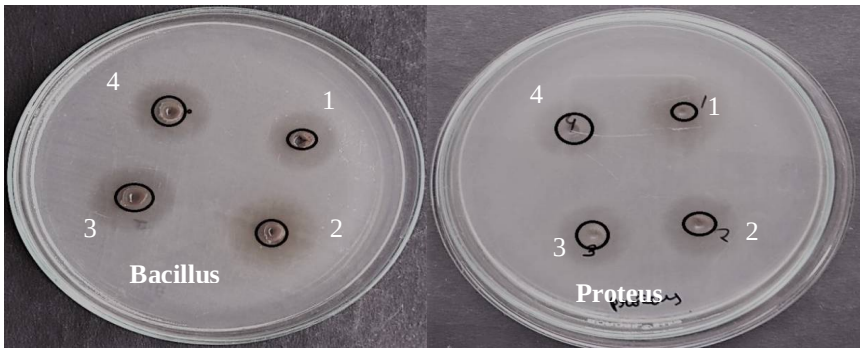


Figure 6. Antibacterial activity of PMG capped AgNPs using (a) Bacillus subtilis (b) Proteus vulgarism.

CONCLUSION

In this study, a simple, efficient and eco-friendly renewable ‘‘green’’ approach has been established for the synthesis of AgNPs. The synthesis was carried out in an aqueous medium using silver nitrate and *Syzygium cumini* fruit peelings extract as a reducing and stabilizing agent without using any harsh, synthetic reducing agents, and then mixture is exposed to solar radiation (a photo-induced reduction).The amount of *Syzygium cumini* fruit peelings extract and lighting time affected the formation of AgNPs. The study shows that photo-induced reduction can accelerate the formation of AgNPs. The antibacterial activity studies revealed that the AgNPs formed are active against both gram positive and gram negative bacteria.

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