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Green synthesis of Silver and Gold nanoparticles using *Shorea tumbuggaia* bark extract and screening for their Catalytic activity

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Abstract

Green synthesis is a novel and cost effective as well as ecofriendly process than physical and chemical methods to synthesize metallic nanoparticles. In the present study silver and gold nanoparticles (AgNPs and AuNPs) were green synthesized using the stem bark extract of *Shorea tumbuggaia*. When the plant extract of 10ml and 2ml added to $AgNO_3$ and $HAuCl_4$ solutions the amalgamated solutions turned reddish brown and deep purple in colour respectively after 48hrs incubation. Later in UV-Visible analysis the amalgamated solutions have shown absorption maximum at 440.15nm and 544.30nm confirming the formation of *S. tumbuggaia* AgNPs and AuNPs. Further the green synthesized AgNPs as well as AuNPs were characterised using Dynamic light scattering, Zeta potential, Energy dispersive X-ray spectroscopy and Scanning electron microscope studies. Imperatively in the present study the plant mediated AgNPs and AuNPs were examined for their catalytic activity in the degradation and removal of methylene blue. Both nano solutions (AgNPs and AuNPs) have shown remarkable catalytic activity in the respective studies.

Keywords: *Green synthesis, S. tumbuggaia, AgNPs, AuNPs, Methylene blue, Catalytic activity*

1. Introduction

In the field of nanobiotechnology metallic nanoparticles have gained extreme attention because of their unique physical and chemical properties which made them suitable candidates for application in catalysis, electronics and optics as well as antimicrobial, anticancer and insecticidal agents in medicine and agriculture (Ahmed *et al*., 2016; Kumar *et al*., 2018). In general metallic nanoparticles are synthesized by physical, chemical and biological methods. However biosynthesis of metallic nanoparticles gained eminence when compared to physical and chemical methods because of their cost effective and ecofriendly nature. In biosynthesis metallic nanoparticles are synthesized using the extracts of bacteria, fungi, algae and plants as reducing and stabilizing agents (Bodaiah *et al*., 2016a).

Green synthesis is a major research area in biosynthesis in which extracts of plants are used in the synthesis of metallic nanoparticles. The secondary metabolites i.e alkaloids, terpenoids, alcohols, phenols and flavanoids etc present in the plant extracts acts as reducing agents and capping agents in the process of metallic nanoparticles synthesis (Ahmed *et al*., 2016). In the present decade many number of metals like silver, gold, platinum, zinc and iron were used for the synthesis of nanoparticles by green route method (Makarov *et al*., 2014; Bodaiah *et al*., 2017). According to the research literature among all types of green synthesized metallic nanoparticles silver nanoparticles (AgNPs) have shown promising results as antibacterial, antifungal, anticancer, pesticidal and catalytic agents (Veerasamy *et al*., 2011). Presently next to green synthesized AgNPs more number of research records of green synthesized gold nanoparticles (AuNPs) was found in the fields of medicine and agriculture. AuNPs were shown to exhibit unique physical, chemical and biological properties. Gold nanoparticles were used in catalysis, biochemical sensors, drug delivery and tissue or tumor imaging (Bodaiah *et al*., 2018a).

In the present study AgNPs and AuNPs were green synthesized using the stem bark extract of *S. tumbuggaia*, a native plant of Andhra Pradesh and Tamilnadu of the family Dipterocarpaceae (Venkateswarlu *et al*., 2010). Methylene blue is a

thiazine cationic dye often used as coloring agent of fabrics in the textile industry. This synthetic dye is also used as antimalarial agent, surgery, diagnostic field, in the analysis of trace levels of sulfide ions in aquatic samples and chemotherapeutic agent in aquatic industry (Bodaiah *et al*., 2016b). In the present the synthesized AgNPs and AuNPs of *S. tumbuggaia* were examined for their catalytic activity in the degradation and removal of methylene blue.

2. Materials and Methods

2.1. Collection of the plant material

The stem bark of *S. tumbuggaia* was collected from Tirumala hills, Tirupathi, Andhra Pradesh, India. The plants were taxonomically identified and authenticated by Prof. M. Vijayalakshmi, Dean and Professor, Dept of Botany and Microbiology, Acharya Nagarjuna University, Guntur, Andhra Pradesh, India. Molecular grade water (Millipore milli Q) was used throughout the experimental studies. All the glass ware used in the present study was carefully acid washed and rinsed with Milli Q water.

2.2. Green synthesis of *S. tumbuggaia* AgNPs and AuNPs

The collected plant material was washed thrice with distilled water to remove the dust and dried under the shade to remove the moisture. The dried plant material was then cut in to pieces and crushed in to fine powder with a suitable pulveriser. 3 grams of finely crushed dried powder was mixed to 100 ml of molecular grade water, boiled at 100^0C for 10 minutes and the extract was filtered with Whatman No 1 filter paper to remove impurities. 10ml of filtered *S. tumbuggaia* extract was added to 190ml of 1mM Silver nitrate ($AgNO_3$) solution and kept for incubation at room temperature. Where as to synthesize AuNPs 2ml of *S. tumbuggaia* aqueous extract was added to 48 ml of 0.5mM Gold (III) chloride trihydrate ($HAuCl_4$) solution and kept for incubation at room temperature.

2.3. Characterization of *S. tumbuggaia* AgNPs and AuNPs

The formation and stability of AgNPs and AuNPs using *S. tumbuggaia* extract was confirmed by UV-Visible spectroscopic studies after 48hrs using $AgNO_3$ and $HAuCl_4$ solutions as blank respectively and the values were recorded within the range of 200 to 800 nm. Dynamic light scattering technique was applied for determining the size, distribution and particle's motion in the medium. Z-average hydrodynamic diameter of the AgNPs as well as AuNPs was measured by using *Dynamic Light Scattering* HORIBA Z100 Nanopartica at a scattering angle of 173°. The analysis was executed at 25°C in a standard mono dispersed medium maintained at a viscosity of 0.892m Pa.s. The plant mediated AgNPs and AuNPs were examined in HORIBA Z100 zeta potential analyzer based on the principle of Laser Doppler electrophoresis to know their stability and the measurements were obtained in the range of -200 to +200mV. Later *S. tumbuggaia* AgNPs and AuNPs were purified by repeated centrifugation from their solutions at 10,000 rpm for 15 min. The pellets of both AgNPs and AuNPs were transferred into separate china dishes and kept for shade evaporation. The dried nanoparticles were washed with distilled water, allowed for shade drying and the process was repeated thrice. The purified and dried nanoparticle samples were collected and used for further characterization. Energy dispersive X- ray spectroscopy study was performed to determine the elemental composition of biosynthesized AgNPs and AuNPs with Field Emission Scanning Electron Microscope equipped with dispersive analysis of X-rays. Scanning electron micrographs of the purified and dried AgNPs as well as AuNPs were taken using Zeiss SEM machine. Thin films of the sample were prepared on a glass slide by just dropping a very small amount of the sample on the grid, allowed to dry by placing it under a mercury lamp for 10 minutes. After drying SEM images of *S. tumbuggaia* AgNPs and AuNPs were taken.

2.4. Catalytic activity of AgNPs and AuNPs

The catalytic activity of *S. tumbuggaia* AgNPs and AuNPs were studied in individual experiments using milli Q water as blank and the absorbance values were recorded using Thermo scientific UV-Visible spectrophotometer. 1ml of 0.1mM methylene blue was mixed with 2ml of milli Q water and the absorbance maximum was recorded. In the first reaction 1ml of 0.1mM methylene blue was mixed with 0.2ml of plant extract and 1.8ml of milli Q water and kept for incubation. In the second reaction 1ml of methylene blue of same concentration was mixed with 0.2ml of plant extract and 1.8ml of nanosolution (AgNPs or AuNPs) and kept for incubation. In all the reactions the total volume was made up to 3ml. The absorption maximum of incubated first reaction was recorded after 30, 40 and 50 minutes intervals. Later the absorption maxima of second reaction containing AgNPs as well as the second reaction containing AuNPs were recorded after 30, 40 and 50 minutes intervals (Ashokkumar *et al*., 2014). The values obtained were compared with the absorption maximum of pure methylene blue.

3. Results and Discussion

Addition of *S. tumbuggaia* plant extract with aqueous solution of silver nitrate led to observable clour change from yellowish to dark reddish brown solution (Fig. 1c) after 48 hrs incubation due to Surface Plasmon Resonance indicating AgNPs formation (Lateef *et al*., 2016). Whereas the

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amalgamated solution of $HAuCl_4$ and plant extract turned in to deep purple in colour after 48 hrs incubation. In general gold nanoparticles exhibit ruby red to dark purple colour in aqueous solutions due to excitation of surface plasmon vibrations. Thus the formation of deep purple colour in the reaction mixture (Fig. 1e) indicated the formation of AuNPs (Singh *et al*., 2016).

3.1. Characterization of *S. tumbuggaia* AgNPs and AuNPs

UV-Visible analysis

After 48hrs incubation both amalgamated solutions were examined for their Surface Plasmon Resonance in UV-Visible spectrophotometer. Surface Plasmon Resonance band for *S. tumbuggaia* AgNPs and AuNPs (Fig. 2a and 2b) were obtained with absorption maximum at 440.15nm and 544.30nm (Malhotra *et al*., 2013) respectively.

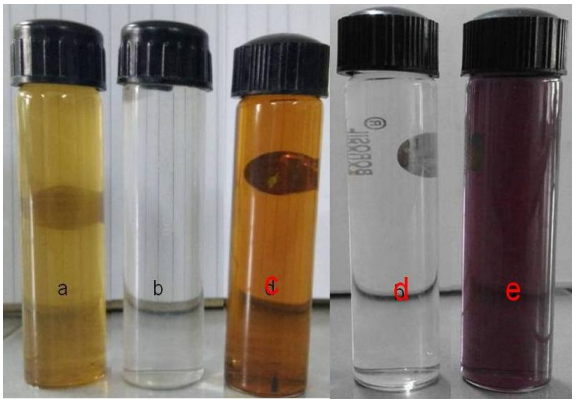

Fig. 1: (a) *S. tumbuggaia* bark extract (b) $AgNO_3$ solution (c) *S. tumbuggaia* AgNPs (d) $HAuCl_4$ solution (e) *S. tumbuggaia* AuNPs

Dynamic light scattering studies

In DLS study the particles exhibit Brownian motion when dispersed in the medium which is measured by the fluctuations in the intensity of scattered light in the system from which translational diffusion co-efficient is calculated by applying Stokes-Einstein equation which determines the hydrodynamic size (Barbara, 2001). The graphs obtained to AgNPs and AuNPs in the analysis (Fig. 3a and 3b) displayed their mean size as 9.5nm and 18.8nm respectively. Polydispersity index (PDI) represents the ratio between different sizes to total number of particles. A PDI value more than 0.5 refers to the aggregation of the particles. The AgNPs and AuNPs of *S. tumbuggaia* showed the PDI values of 0.264 and 0.209 which clearly indicates that the particles are in mono dispersed phase with very low chances of aggregation (Kalainila *et al*., 2014).

Zeta potential analysis

In Zeta Potential analysis the charged nanoparticles were attracted to oppositely charged electrode and their velocity was measured and expressed in Unit field strength as their mobility (Bodaiah *et al*., 2018b). The AgNPs of *S. tumbuggaia* have exhibited a mean negative zeta potential of -22.9mV (Fig. 4a) indicating that the particles are moderately stable. Whereas the AuNPs of *S. tumbuggaia* were shown to exhibit zero zeta potential (Fig. 4b) indicating their unstable nature (Singh *et al*., 2014).

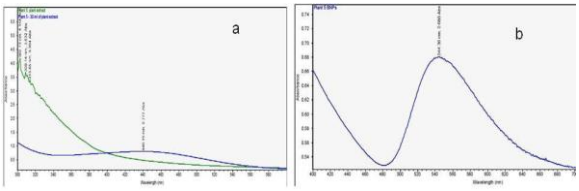

Fig. 2: UV-Visible analysis of *S. tumbuggaia* (a) AgNPs (b) AuNPs

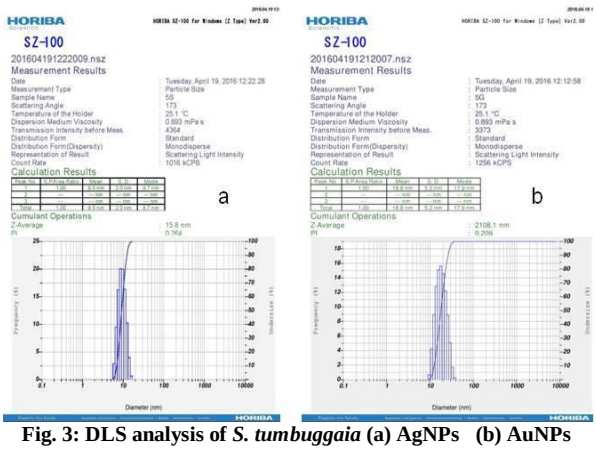

Fig. 3: DLS analysis of *S. tumbuggaia* (a) AgNPs (b) AuNPs

EDX analysis of S. tumbuggaia AgNPs and AuNPs

The EDX spectrum showed highest peak at 3 keV for purified green synthesized AgNPs (Ravichandran *et al*., 2016) and 2.15 keV for green synthesized AuNPs (Kuppusamy *et al*., 2015) and the results were depicted in the Fig. 4c and 4d. The other peaks obtained in both the figures were may be to the protein capping over the AgNPs and AuNPs or may be the element composition of glass that holds the samples or may be the other elements in the respective salts.

SEM images of Plant mediated AgNPs and AuNPs

The SEM analysis revealed that AgNPs were spherical to irregular in shape. The SEM images also revealed that AgNPs were not aggregated and mean diameter was found to be 10-50nm (Fig. 5a&b) (Ravichandran *et al*., 2016; Zhang *et al*., 2016). The SEM images of AuNPs (Fig. 5c&d) indicates that the particles were irregular in shape with the mean diameter in the range 20-100nm (Kuppusamy *et al*., 2015; Tahir *et al*., 2015).

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3.2. Catalytic activity of AgNPs and AuNPs

In the present study the AgNPs and AuNPs of *S. tumbuggaia* were examined for their catalytic activity and the results were depicted in the figure 6. Pure methylene blue of 0.1mM concentration has shown a lambda max value at 664nm. When the first reaction was studied in UV-Visible spectrophotometer the absorbance is decreased and shifted to higher wave length compared to pure methylene blue. It indicates that the stem bark extract of *S. tumbuggaia* has degraded the methylene blue (Bodaiah *et al*., 2016b). Further the second reaction of *S. tumbuggaia* AgNPs was examined for lambda max value after 30 minutes. The absorption gradually decreased and shifted to higher wave length when compared to first reaction. The second reaction of *S. tumbuggaia* AuNPs were also exhibited same result when studied in UV-Visible spectrophotometer after 30 minutes. Later the second reaction of AgNPs as well as AuNPs again examined for absorption maximum after 40 minutes incubation. Second reaction of AgNPs as well as AuNPs was again studied in UV-Visible spectrophotometer finally after 50 minutes incubation. In the case of both AgNPs and AuNPs the absorption gradually decreased and shifted to higher wave length after 40 as well as 50 minutes incubation. From the above results it can be known that both AgNPs and AuNPs of *S. tumbuggaia* have exhibited catalytic activity in the degradation and removal of methylene blue (Ashokkumar *et al*., 2014).

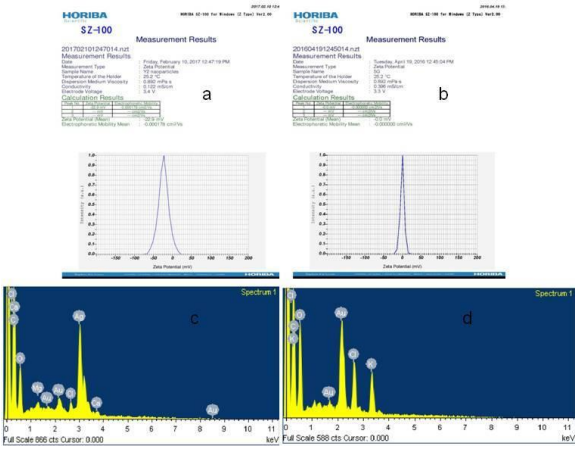

Fig. 4: (a) Zeta potential of *S. tumbuggaia* AgNPs (b) Zeta potential of *S. tumbuggaia* AuNPs (c) EDX of *S. tumbuggaia* AgNPs (d) EDX of *S. tumbuggaia* AuNPs

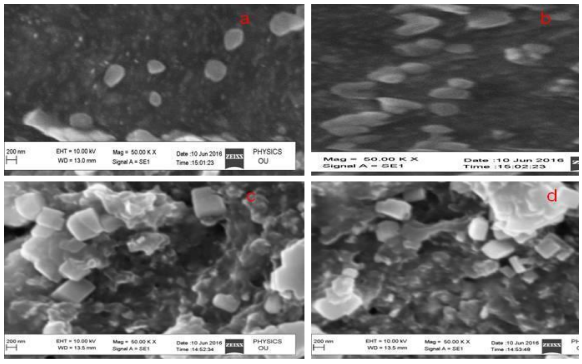

Fig. 5: SEM images of *S. tumbuggaia* (a&b) AgNPs (c&d) AuNPs

4. Conclusion

Biosynthesis is an ecofriendly approach and gained prominence in the present decade for the synthesis of metallic nanoparticles. In the present study AgNPs and AuNPs were biosynthesized using the aqueous extract of *S. tumbuggaia* and their formation was confirmed in UV-Visible spectroscopic analysis. The respective nano solutions were further characterized using DLS, Zeta potential, EDX and SEM studies. The plant mediated AgNPs and AuNPs were exhibited their mean size as 9.5nm and 18.8nm respectively in DLS analysis. Further the AgNPs and AuNPs were shown to exhibit Zeta potential of -22.9 and Zero indicating that AgNPs are more stable than AuNPs. EDX studies confirmed the presence of pure silver and gold in the respective synthesized nanoparticles. While the images obtained in SEM analysis indicated that both AgNPs and AuNPs were irregular in shape with no aggregation with one another and their mean size in the range of 10-50nm and 20-100nm. Crucially in the further study the AgNPs and AuNPs of *S. tumbuggaia* were studied for their catalytic activity. AgNPs as well as AuNPs were exhibited potential catalytic activity in the degradation and removal of methylene blue.

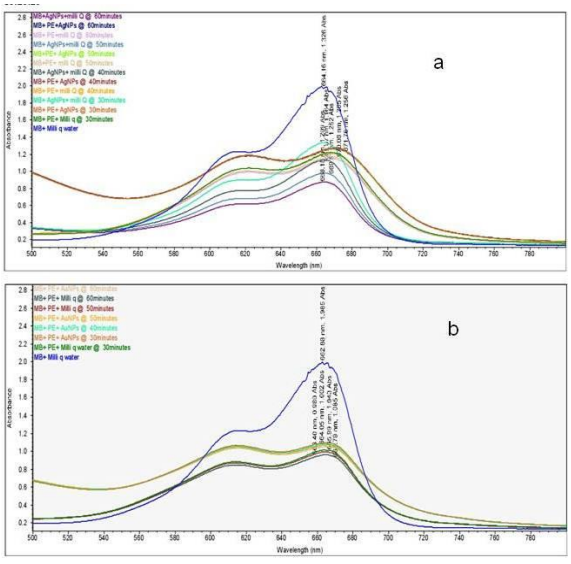

Fig. 6: Catalytic activity of *S. tumbuggaia* (a) AgNPs (b) AuNPs

Conflict of Interest: All the authors declare that there is no conflict of interest.

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