Green Synthesis of Silver Nanoparticles using two Apocyanaceae plants and Screening for their Catalytic activity

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Abstract

The catalytic activity of biosynthesized silver nanoparticles (AgNPs) gained an importance in removal of synthetic dyes from waste water released form textile industries. In this study aqueous leaf extract of *Cascabela thevetia* and *Wrightia tomentosa* were used to synthesize silver nanoparticles. Further the catalytic activity of newly synthesized particles in reducing 4-Nitrophenol, Methylene blue, Methyl orange and Methyl red using $NaBH_4$ was screened. It was observed that the respective amalgamated solutions of $AgNO_3$ and leaf extract turned reddish brown in colour after 48 hours incubation. The formation of AgNPs from *C. thevetia* and *W.tomentosa* were conformed by absorption maximum at 443.07nm and 440.05 nm in UV-Visible analysis. The absorption maxima results in UV-Vsible analysis of respective dyes clearly indicate total degradation by $NaBH_4$ and the AgNPs of both plants have exhibited remarkable catalytic activity in dye reduction reactions.

Key words: Green synthesis, AgNPs, 4-Nitrophenol, Synthetic dyes, Catalytic activity

Introduction

Nanobiotechnology is an emerging research field applying for next generation development in agriculture, environment and medicine sciences. Nanoparticles are usually referred as particles with a maximum size of 1 to 100nm (1) and exhibit novel and improved properties with respect to their size, distribution and morphology (2). In general metallic nanoparticles are often prepared using Silver (Ag), Gold (Au), Zinc (Zn) and Platinum (Pt) etc. Indeed silver nanoparticles (AgNPs) gained prominent research interest among metal nanoparticles due to their *in vitro* antimicrobial activity and cytotoxic activity (3). Biological synthesis of AgNPs is ecofriendly and cost effective process compared to physical and chemical methods (4, 5).

Dyes are the major synthetic organic compounds used in textile industries. However 15% of dye used is wasted and released into water bodies resulting significant pollution (6). Waste water treatment by physical and chemical methods is costly process and require more energy. The nano silver particles have shown remarkable catalytic activity in dye reduction and removal and exhibited the degradation activity on certain toxic chemicals like 4-Nitrophenol (7, 8, 9).

The phenolic and polymorphic compound 4-Nitrophenol is used to darken the leather, in the manufacture of drugs, fungicides, insecticides and dyes. Ingestion and inhalation of 4-Nitrophenol leads to nausea, drowsiness, headache and cyanosis (10). Methylene blue or methylthioninium chloride is a synthetic heterocyclic aromatic dye and dark green powder when dissolved in water turns in to blue colour (11). Methyl orange is a synthetic dye, pH indicator in acid-base titrations and causes irritation incase of skin contact and eye contact (12). Another one methyl red is an azodye and used in acid base titrations as pH indicator. It is prepared by diazotization of anthranilic acid and followed by dimethyl aniline (13). Green synthesis method of nanoparticles involves plant extracts which is easy, first and less complicated handling procedure (5). The present study was carried out to synthesize silver nanoparticles using the leaf extract from *Cascabela thevetia* and *Wrightia tomentosa* belongs to Apocyanaceae family. The catalytic activity was screened on 4-Nitrophenol, Methylene blue, Methyl orange and Methyl red.

Materials and methods

Chemicals, reagents and plant source : The leaves of *Cascabela thevetia* were collected from Acharya Nagarjuna University campus, Guntur, India and the leaves of *Wrightia tomentosa* were collected from Tirumala hills, Tirupathi, India. The plants were taxonomically identified and authenticated by Prof. M. Vijayalakshmi, Department of Botany, Acharya Nagarjuna University, Guntur, Andhra Pradesh, India. The Silver nitrate ($AgNO_3$) with 99.5% purity, 4-Nitrophenol, Methylene blue, Methyl orange and Methyl red were purchased from Merck. Molecular grade water (Millipore, Milli Q) was used in this study.

Biosynthesis of AgNPs from the extracts of C.thevetia and W.tomentosa : The leaves of *C. thevetia* and *W. tomentosa* were washed thrice with distilled water, dried and coarsely powdered. The powder of *C. thevetia* and *W. tomentosa* leaf (3gms) dispensed into 100ml of distilled water, boiled at 100°C for 10 minutes and the extract was filtered through Whatman filter paper. The 10ml of aqueous plant extract was mixed with 190ml of already prepared 1mM silver nitrate solution. The suspension was stirred using a magnetic stirrer for 5 min and kept at incubation for 48h at room temperature. The change in color of the solution from light yellow to dark brown indicates the termination of the reaction and synthesis of AgNPs.

UV-Visible spectrophotometric analysis of the biosynthesized AgNPs

The formation and stability of silver nanoparticles was confirmed by UV-Visible spectroscopic studies after 48hrs using $AgNO_3$ solution as blank. Spectral analysis of the AgNPs was executed using UV-Visible Double beam spectrophotometer (Thermo Fischer) and the values were recorded between the range from 200 to 800 nm.

Evaluation of catalytic activity of AgNPs

The leaf extract mediated AgNPs of *Cascabela thevetia* and *Wrightia tomentosa* were utilised as catalysts seperately in the degradation and removal of 4-Nitrophenol, Methylene blue, Methyl orange and Methyl red by $NaBH_4$. The catalytic degradation of respective dye involves three reactions and carried out in a 3.5ml Quartz cuvette. The first reaction is prepared by adding 1.5ml of 1mM of synthetic chemical to 1.5ml of milli Q water. After UV-visible spectrophotometric analysis 1mg of solid $NaBH_4$ was added at first reaction for the preparation of second reaction. The third reaction is prepared by adding 20 micro litres of biosynthesized AgNPs to the second reaction. All three reactions were studied in Thermo scientific UV-Visible spectrophotometer using milli Q water as blank (10).

Results and Discussion

The aqueous leaf extracts of *C. thevetia* and *W. tomentosa* when mixed with $AgNO_3$ solution as seperate reactions, both the respective solutions showed pale yellow colour. However after 48 hours incubation, both the mixures turned in to deep reddish brown colour indicating the formation of AgNPs (14) (Fig1). UV-Vis analysis of the biosynthesized AgNPs of both the plants recorded and absorption maxima at 443.07nm and 440.05nm respectively due to surface plasmon resonance (15) and conforming the formation of AgNPs (Fig 2).

Catalytic activity of biosynthesized AgNPs: Reduction reactions of 4-Nitrophenol

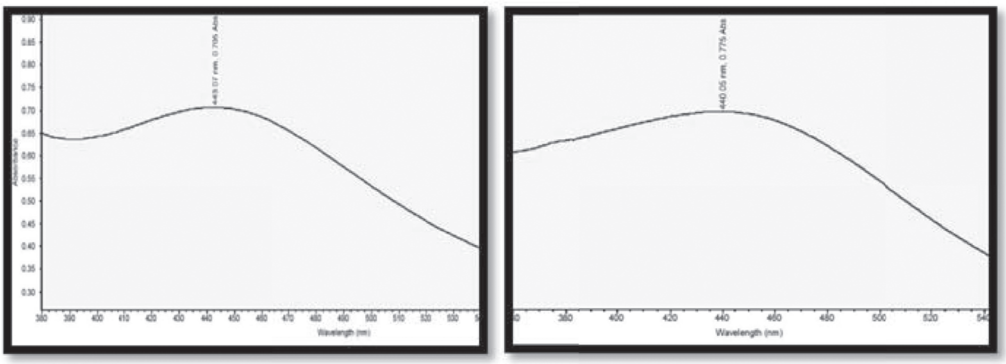
The dye degradation reactions were monitered and depicted in the following order 4-Nitrophenol, Methylene blue, Methyl orange and Methyl red. All reactions were analysed by UV-Visible spectrophotometer. Figure 3 has shown the UV-Visible analysis of dye degradation of the 4-Nitrophenol using $NaBH_4$ with AgNPs of *C. thevetia* and *W. tomentosa* as catalysts. The reaction of 4-Nitrophenol when monitered in spectrophotometer the absorption maximum 1.262 was observed at 318nm (16). In addition of $NaBH_4$ to first reaction the absorption maximum shifted to 400nm with the solution appeared bright yellow colour because of the formation of sodium phenolate and no change in the absorption maximum with respect to time was observed. With the addition of AgNPs the solution turned colourless and absorption maxima suddenly decreased from 1.262 to 0.822 in the case of AgNPs synthesized with the extract of *C.thevetia* and from 1.262 to 0.534 with the AgNPs synthesized from the extract of *W. tomentosa* indicating the complete degradation of 4-Nitrophenol (9, 17).

A B

Fig. 1: A) AgNPs of *C. thevetia* and B) AgNPs of *W.tomentosa*

Reduction reactions of Methylene blue

The degradation and removal of methylene blue by $NaBH_4$ in the presence of biosynthesized AgNPs as catalyst were analyzed. The results related to the reduction reactions of methylene blue by AgNPs are illustrated in figure 4. Methylene blue showed maximum absorption 2.33 at 664nm (18). After the addition of 1mg NaBH4 to the reaction mixture, the absorption maximum peak was shifted to 656.04nm. However the synthesize AgNPs of both the plants



A B

Fig. 2. UV- Visible analysis of A) *C. thevetia* AgNPs B) *W. tomentosa* AgNPs

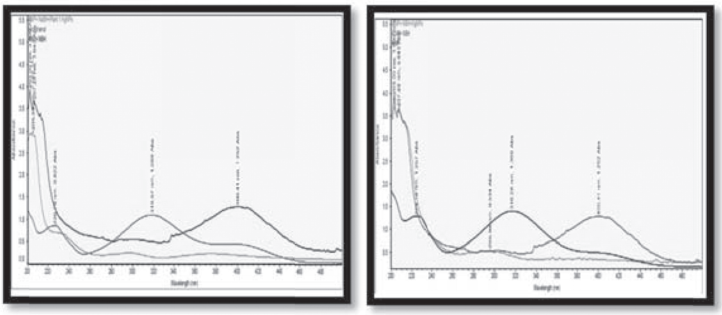


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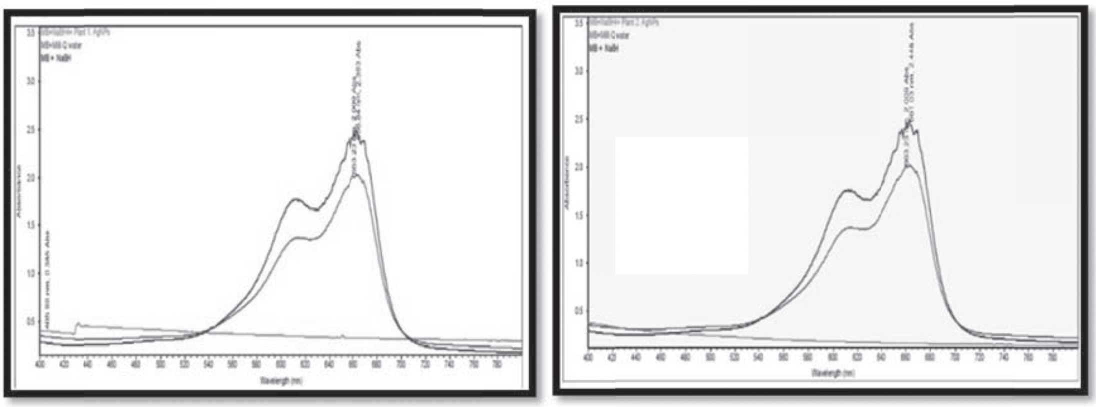
Fig. 3: Catalytic activity of A) *C. thevetia* AgNPs B) *W.tomentosa* AgNPs on 4-Nitrophenol



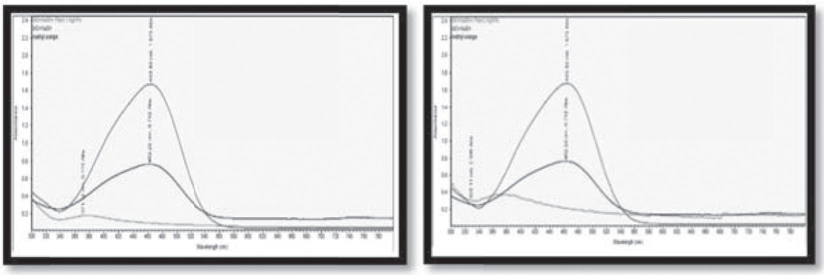
A B

Fig. 4: Catalytic activity of A)*C. thevetia* AgNPs B) *W.tomentosa* AgNPs on Methylene blue

in separate reactions turned the solution colourless and the absorption was decreased from 2.33 to 0.385 and from 2.33 to 0.284 for *C. thevetia* and *W.tomentosa* respectively indicating that methylene blue was completely degraded (19).

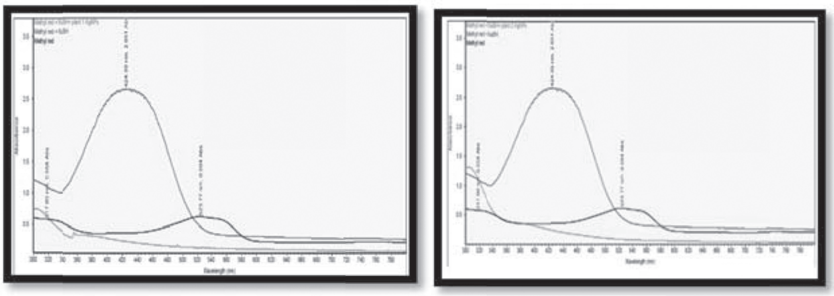
Reduction reactions of Methyl orange : The degradation and removal reactions of methyl orange by $NaBH_4$ in the presence of AgNPs were studied by UV-visible spectrophotometer (Figure 5). The absorption maximum was found to be 0.752 at 462.22nm (8) and addition of 1mg $NaBH_4$ the maximum absorption was observed at 463.89nm. After adding AgNPs of both the plants in separate reactions, the solution turned colorless with decrease in absorption maxima from 0.752 to 0.170 and 0.752 to 0.275 for *C. thevetia* and *W.tomentosa* respectively (20) indicating the reduction of methyl orange.

Reduction reactions of Methyl red : The UV-visible spectrophotometric analysis of the reduction reaction of methyl red by $NaBH_4$ in the presence of AgNPs as reducing agent is illustrated in figure 6. An absorption maximum of 2.651 was observed at 523.77nm (21). After addition of 1mg $NaBH_4$ the absorption maximum



A B

Fig. 5: Catalytic activity of A) *C. thevetia* AgNPs B) *W.tomentosa* AgNPs on Methyl orange



A B

Fig. 6: Catalytic activity of A) *C. thevetia* AgNPs B) *W.tomentosa* AgNPs on Methyl red

S.No	**Name of the Dye**	**Absorption Maxima of *C. thevetia***		**Absorption Maxima of *W.tomentosa***	
		Before to the addition of AgNPs	After the addition of AgNPs	Before to the addition of AgNPs	After the addition of AgNPs
1	4-Nitrophenol	1.262	0.822	1.262	0.534
2	Methylene blue	2.33	0.385	2.33	0.284
3	Methyl orange	0.752	0.170	0.752	0.275
4	Methyl red	2.651	0.558	2.651	0.558

Table : UV-Visible Absorption maxima of synthetic chemicals in catalytic activity analysis.

was recorded at 424.89nm. With the addition of AgNPs of both the plants in separate reactions the solution turned colorless and the absorption completely decreased from 2.651 to 0.558 in the case of both plants indicating the complete reduction of methyl red (22, 23).

Conclusion

AgNPs were synthesized using the aqueous leaf extract of *Cascabela thevetia* and *Wrightia tomentosa* in seperate reactions. The green synthesized AgNPs were used as catalysts in the reduction and degradation of 4-

Nitrophenol, Methylene blue, Methyl orange and Methyl red using $NaBH_4$. All four reactions of respective dyes were analysed by UV-Visible spectrophotometer. In the reduction process of four dyes the absorbation maxima of the four dyes decreased i) 4-Nitrophenol (from 1.262 to 0.822) with AgNPs of *C.thevetia* and (from 1.262 to 0.534) with AgNPs of *W. tomentosa*.ii) Methylene blue (from 2.33 to 0.385) with AgNPs of *C. thevetia* and (from 2.33 to 0.284) with the AgNPs of *W.tomentosa.* iii) Methyl orange (from 0.752 to 0.170) with the AgNPs of *C. thevetia* and (from 0.752 to 0.275) with the AgNPs of *W.tomentosa.* iv) Methyl red (2.651 to 0.558)with the AgNPs synthesized form both plants. From the above results it can be concluded that the AgNPs of both plants acted as catalyst in degradation of the above said dyes using $NaBH_4$.

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