PHOTO INDUCED GREEN SYNTHESIS OF SILVER NANOPARTICLES USING ANNONA RETICULA (CUSTARD APPLE) LEAF EXTRACT AND CATALYTIC REDUCTION OF CONGO RED

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Abstract: A simple, green method is described for the synthesis of silver nanoparticles ((AgNPs) from the leaf extract of *Annona reticula*, which acts as a reducing and capping agent. The synthesized AgNPs were characterized by UV-Vis spectroscopy, Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD).The produced AgNPs showed UV-Vis absorbance at 420 nm.The synthesized AgNPs were found to be crystalline and spherical with an average size of6±2 nm.These AgNPs were assessed for the catalytic reduction of Congo Red (CR). It was established that the reduction reaction follows the pseudo-first order kinetics with a reaction rate constant of 0.274 min^{-1} for CR. Thus, the synthesized AgNPs were found to show outstanding catalytic activity in the degradation of CR.

***Keywords*: Silver nanoparticles, *Annona reticula*, Congo red, TEM, XRD**

I. INTRODUCTION

In recent years nanomaterials plays a significant role in the science and technology due to the distinctive physicochemical properties like size, morphology and distribution [1]. Physical and chemical properties significantly differ from nanosized metal particles and those of the bulk materials [2]. Among the several metal nanoparticles AgNPs has become the attention of research due to their distinctive properties, electrical, optical and surface plasmon resonance absorption properties which are strongly depends to their interparticle distance, shape and size [3].

AgNPs is having wide range of applications in various fields such as catalysis, drug delivery, sensors and biomedical. Although a series of conventional procedures have been employed in preparation of AgNPs i.e. chemical reduction, laser ablation and electrochemical reduction etc. [4-6].All these synthesis methods have some drawbacks, i.e. use of toxic, hazardous chemicals and expensive, etc. which pose potent environmental and biological risks. Thus, there is an increasing demand in the direction of alternative procedures using green chemistry approach in synthesis of AgNPs. Green chemistry an ecofriendly approach which has numerous advantages such as cost effective, simplicity and reliability [7]. Several biological systems such as leaf extract, fungi, bacteria, plants and fruit extract can actively reduce and stabilize AgNPs in an ecofriendly manner [8-11].

The release of organic dye effluents from plastic, leather, textile and paper industries it leads to the environmental pollution that causes from their recalcitrance, high visibility, undesirability. For that reason, the control of industries released pollutant is an essential work which helps in the making of a clean and harmless environment [12].CR is a kind of azo dye with –N=N- bonds, highly soluble in aqueous solutions and it is anionic dye widely used in rubber, paper, textile, cosmetics, ceramics and plastic industries. CR is a metabolized to benzidine, a known human carcinogen and exposure to CR dye can cause allergic comprised [13-15].

The present study reports the synthesis of AgNPs using the *Annona reticula* leaf extract. This extract serves as both reducing and stabilizing agents. The characterization of AgNPs was carried out by UV–Visible spectroscopy, FTIR spectroscopy, XRD analysis and TEM. The AgNPs were explored with respect to their prospective catalytic applications.

II. MATERIAL AND METHODS

2.1 Preparation of leaf extract

Annona reticula leaves were freshly collected from the region of Mahabub Nagar, India. To remove the soil and other contaminants present on the surface of the fresh leaves were washed with double distilled water. After the wash, 5 grams of leaves were cut into small pieces and then soaked into 100 ml double distilled water. These leaves were continuously stirred at 55 °C for 15 min and filtered to get the extract [16].

2.2 Synthesis of AgNPs

Solutions were prepared with double distilled water. 4 ml of the aqueous AgNO3 solution was mixed with 4 ml of the aqueous AgNO3 solution was mixed with 4 ml ofaqueous extract solution. This reaction is carried out in the presence of sunlight at 40 °C temperature by 30 min time. The resulting solution was clear yellow colored, indicating the formation of AgNPs.

2.3 Characterization

UV-Vis spectra of AgNPs and CR were recorded using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu). FTIR analysis was carried out with an instrument IR Affinity-1 (Shimadzu) in the scanning range of 650-4000 cm^{-1}. The crystallinity of the AgNPs was studied by XRD (Rigaku, miniflex) analysis with CuKα radiation. The size and morphology were determined by TEM the measurements were done on JEOL 2000 FX-II TEM.

2.4 Catalytic reduction of CR dye

In typical reduction reactions, the reduction of CR was carried out in the presence of $NaBH_4$ and AgNPs used as a catalyst. In a typical procedure, 3 mL of 1 mM CR solution was mixed with 1 ml of 9 mM $NaBH_4$ and the reaction mixture was made up to 10 mL using DD water

and stirred for 5 min. 4 mL of these mixture were taken in a cuvette, sufficient quantities of AgNPs were added and UV-Vis spectra were recorded at different time intervals.

III. RESULTS AND DISCUSSION

3.1 UV-Vis spectroscopy

Formation of silver nanoparticles was confirmed by using UV–Vis spectral analysis. The color change is attributed to the SPR phenomenon. The UV–Visible absorption spectra recorded, showed a maximum peak in the wavelength range of around 420-430 nm as evident from Fig. 1, which is ascribed to the SPR band for AgNPs. The leaf extract concentrations were varied from 0.25% to 1 % with 2 mM concentration of silver nitrate experimented with the development of AgNPs. Fig.1 indicate that the sharpness in the absorption peak increases with an increase in the concentration of leaf extract, thus being sharper with a higher concentration. Fig.2 shows concentration of $AgNO_3$ changes from 0.5 to 2 mM with 1% leaf extract. The absorption maximum increases with an increase in the concentration of $AgNO_3$, mainly due to the formation of more AgNPs [15].

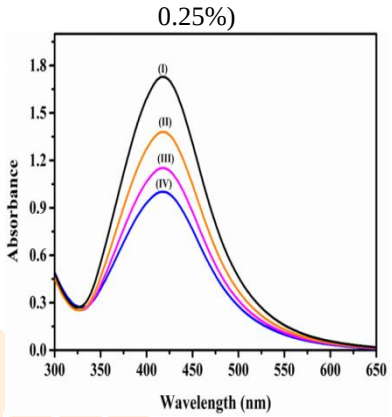

Fig.1 Absorption spectra of AgNPs systems synthesized different fruit extract concentrations (I-1%, II-0.75%, III: 0.5%, IV-

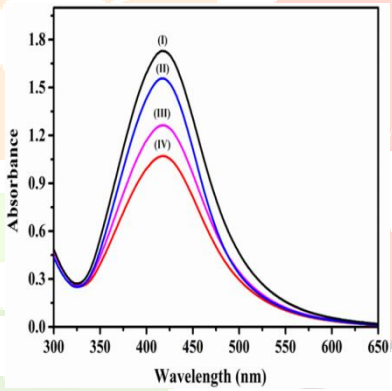

Fig. 2. Different concentrations of $AgNO_3$ (I-2mM, II-1.5 mM, III: 1 mM, IV-0.5 mM).

3.2 FTIR

Fig.3 shows the FTIR spectra of leaf extract and leaf extract capped AgNPs. The FTIR spectra of a leaf extract showed bonds at 3379, 1600, 1401, 1275 and 1037 cm^{-1}.The FTIR spectra of AgNPs showed characteristic bands at 3429, 1723, 1615, 1420, 1249 and 1043 cm^{-1}. In the FTIR spectrum of AgNPs showed prominent shifting in comparison with leaf extract peaks. The change in the peak positions was observed from 3379 to 3429, 1600 to1615, and 1401 to 1420cm^{-1}. This indicates the involvement of -OH, -NH, -C=O groups in AgNPs synthesis and stabilization process.

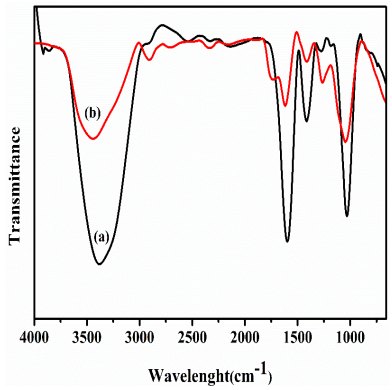

Fig. 3. FTIR spectra of the leaf extract and leaf extract capped AgNPs

3.3 XRD analysis

The X-ray diffraction pattern of synthesized AgNPs was recorded in the 2θ range of 20-30. The XRD spectrum was shown in the Fig 4, four main Bragg diffraction peaks were observed at 37.99°, 44.53°, 64.2° and 77.15°. All these diffraction peaks corresponded to (111), (200), (200) and (311) planes of face centered cubic structure of AgNPs. The diffraction peaks were matched with standard database joint committee

on powder diffraction standards (JCPDS file No 7440-22-4), this result indicating that synthesized AgNPs aware of pure crystalline nature [17].

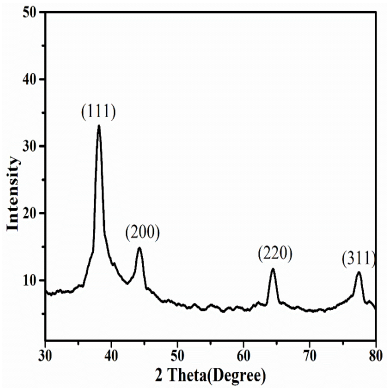

Fig.4. XRD pattern of synthesized AgNPs.

3.4 TEM

The shape, morphology and size distribution of the synthesized AgNPs were studied by TEM. The TEM image (Fig.5) shows that the AgNPs are spherical shape and the average size of the AgNPs are 6±2 nm.Fig.6presents a histogramof the particle size distribution of AgNPs. The selected area electron diffraction pattern (Fig.5) of AgNPs exhibit polycrystalline diffraction rings indicating that these nanoparticles are crystalline metallic nature.

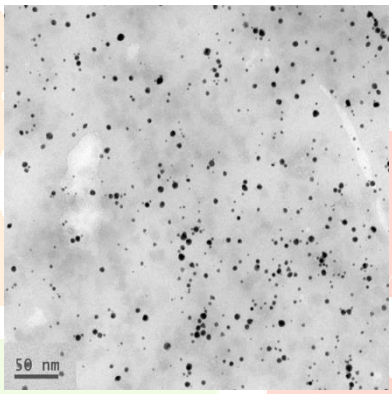

Fig. 5. TEM images of synthesized AgNPs

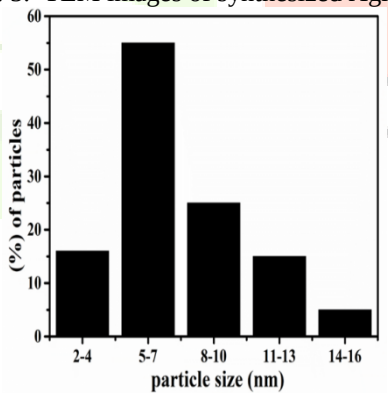

Fig.6.Particle size distribution histogram of AgNPs

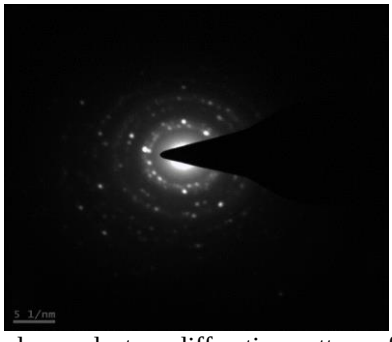

Fig.7.Selected area electron diffraction pattern of the AgNPs

3.5 Catalytic reduction of Congo red

In this part, the reduction of the CR dye in the presence of $NaBH_4$ was chosen to evaluate the catalytic activity of synthesized AgNPs. These reduction reactions were monitored by UV-Vis spectroscopy. In aqueous medium, CR shows the absorption peak at 350 nm and 498 nm [15]. 1.5 mL of 1 mM CR aqueous solution was mixed with 1.5 mL of 10 mM $NaBH_4$ and the mixture was makeup up to 10 mL suing

DD water and then stirred for 10 min. Fig.8 shows the UV-Vis spectra of CR with $NaBH_4$ in the absence of AgNPs recorded in 15 min interval for a period of 120 min at room temperature. Fig.8 shows a small decreasing tend of the absorption peak intensity was observed it indicates the reduction of CR, but in a slow process. The AgNPs was added to the mixture of CR and $NaBH_4$, the absorption intensity of CR rapidly decreased in the presence of AgNPs. The reduction reaction was completed within 8 min. Fig.9 shows a continuous decrease of CR absorption peak at 493 nm by increasing time could be observed it was indicated that the dye has been degraded slowly. Further, there was no peak appeared throughout the process. A linear relationship found between $\ln(A_t/A_0)$ versus reaction time (Fig. 10) indicates that the reduction of dyes follows a pseudo-firs-order kinetics with respect to dye as the concentration of $NaBH_4$(10 mm), was relatively higher than that of dye. The rate constant was found to be 0.274 min^{-1}.

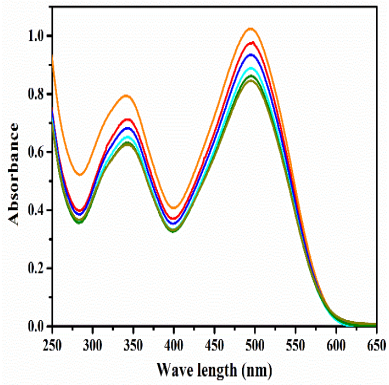

Fig. 8. Reduction of Congo red dye in the presence of $NaBH_4$ and absence of AgNPs

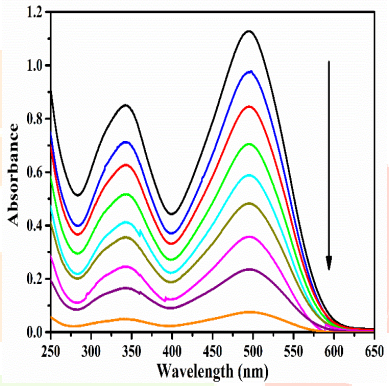

Fig.9. Time-dependent UV–Vis spectra for the catalytic reduction of Congo red by $NaBH_4$ in the presence of AgNPs

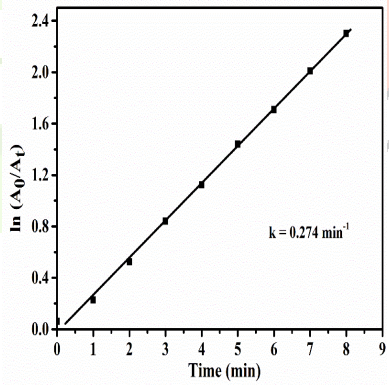

Fig.10. The plot of $\ln(A_0/A_t)$ versus time for the reduction of Congo red

IV. CONCLUSIONS

This work reports the successful synthesis of silver nanoparticles using *Annona reticula*leaf extract as a novel reducing and stabilizing agent of silver salts. Absorption spectra at 421 nm, confirm the presence of SPR of AgNPs. Analytical characterization like FTIR, XRD and TEM supports the particle reduction mechanism, size and structure. The synthesized AgNPs exhibited very good catalytic activity and the kinetics of the reaction was found to be pseudo first order with respect to the CR.

REFERENCES

[1] R.W. Murray, Nanoelectrochemistry: metal nanoparticles, nanoelectrodes, and nanopores., Chem Rev. 108 (2008) 2688–720.
[2] A.M. Abdel-Mohsen, R. Hrdina, L. Burgert, G. Krylova, R.M. Abdel-Rahman, A. Krejcova, Green synthesis of hyaluronanfibers with silver nanoparticles, Carbohydr. Polym. 89 (2012) 411-422
[3] V.J. Mohanraj, Y. Chen, Nanoparticles – A Review, Trop J Pharm Res, 5 (2006) 561–573.
[4] N.R. Jana, X. Peng Single-phase and gram-scale routes toward nearly monodisperse au and other noble metal nanocrystals. J Am Chem Soc 125(2003) 14280–14281
[5] L. Rodrı, L. Rodríguez-Sánchez, M.C. Blanco, L.C. Ferracin, Electrochemical Synthesis of Silver Nanoparticles, J Phys Chem B. 104 (2000) 9683–9688.

[6] Y.H. Chen, C.S. Yeh, Laser ablation method: Use of surfactants to form the dispersed Ag nanoparticles, Colloids Surfaces APhysicochemEng Asp. 197 (2002) 133–139.
[7] J. a. Dahl, B.L.S. Maddux, J.E. Hutchison, Toward greener nanosynthesis, Chem Rev. 107 (2007) 2228–2269.
[8] H. Joy Prabu, I. Johnson, Plant-mediated biosynthesis and characterization of silver nanoparticles by leaf extracts of Tragiainvolucrata, Cymbopogon citronella, Solanum verbascifolium and Tylophora ovata, Karbala Int J Mod Sci. 1 (2015) 237–246.
[9] R. Kumar, S.M. Roopan, A. Prabhakarn, V.G. Khanna, S. Chakroborty, Agricultural waste Annona squamosa peel extract: Biosynthesis of silver nanoparticles, Spectrochim Acta - Part A Mol BiomolSpectrosc. 90 (2012) 173–176.
[10] S.S.P. Ashish A. Rokade, Jong Hwa Kim, Se Ri Lim, Seong Il Yoo, Young EupJin, A Novel Green Synthesis of Silver Nanoparticles Using RubuscrataegifoliusBge Fruit Extract, J Clust Sci. 28 (2017) 2017–2026.
[11] D. Philip, Green synthesis of gold and silver nanoparticles using Hibiscus rosa sinensis, Physica E 42 (2010) 1417–1424
[12] M. Ghaedi, S. Ramazani, M. Roosta, Gold nanoparticle loaded activated carbon as novel adsorbent for the removal of Congo red, Indian Journal of Science and Technology 4 (2011) 1208–1217.
[13] F. Shojaeipoor, D. Elhamifar, B. Masoumi, D. Elhamifar, B. Barazesh, Ionic liquid based nanoporous organosilica supported propylamine as highly efficient adsorbent for removal of congo red from aqueous solution, Arab J Chem. (2016). doi:10.1016/j.arabjc.2016.05.001.
[14] J. Pal, M. Kanti, Efficient adsorption of Congo red dye from aqueous solution using green synthesized coinage nanoparticles coated activated carbon beads, (2013). doi:10.1007/s13204-013-0277-y.
[15] B. Reddy, G. Madhusudhan, A. Ramakrishna, Catalytic reduction of methylene blue and Congo red dyes using green synthesized gold nanoparticles capped by salmalia malabarica gum, Int Nano Lett. 5 (2015) 215–222.
[16] M. Gomathi, P.V. Rajkumar, A. Prakasam, K. Ravichandran, Green synthesis of silver nanoparticles using Datura stramonium leaf extract and assessment of their antibacterial activity, Resour Technol. 3 (2017) 280–284
[17] P. Subramanian, R. Periyannan, V. Gandhi, R. Ganesan, P.N. Marimuthu, Author ' s Accepted Manuscript A green route to synthesis silver nanoparticles using Sargassumpolycystum and its antioxidant and Reference : To appear in : Materials Letters, Mater Lett. (2016). doi:10.1016/j.matlet.2016.12.005.