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Study on Catalytic Reduction of Methylene Blue Using Silver Nanoparticles Synthesized via Green Route

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Abstract: We have synthesized silver nanoparticles using silver nitrate and *Azadirachta indica* (Neem) aqueous leaf extract at room temperature. The method used for synthesis is simple, rapid, environmental free and do not involve toxic chemicals. The terpenoids and flavonoids available in neem plant leaf extract act as both capping and reducing agents. The synthesized nanoparticles are characterized UV Visible spectroscopy, X ray diffraction analysis and fluorescence spectroscopy.

The synthesized AgNPs are used for study of the catalytic degradation of methylene blue by sodium borohydride (NaBH_4) in presence of AgNPs as catalyst. The 100% degradation of methylene blue was achieved by (NaBH_4 +AgNPs) in just 08 minutes which highlights the efficient catalytic activity of AgNPs.

Keywords: Silver nanoparticles, Characterization, *Azadirachta indica*, reduction, Methylene blue.

I. INTRODUCTION

In last few years different metal nanoparticles of various shapes, sizes and compositions have different catalytic applications. The metal nanoparticles of gold, silver, platinum is have significant applications in various field of catalysis and environmental science. One such important metal nanoparticle is silver nanoparticle and it can be prepared by different ways like chemical, electrochemical, radiation and photochemical¹. But with increasing focus on bio mediated preparation of metal nanoparticles is getting more attention.

There are number of methods for synthesis of AgNPs using different plant leaf extract as well as by using microorganisms such as bacteria, fungi and yeast for the synthesis.²⁻⁹ Several reports are available on the green synthesis of AgNPs using plant extract. Different functional groups which contain several and present in plant extract works as reducing agents and nanoparticle growth controlling agents.

Here we have reported the synthesis of AgNPs using the aqueous leaf extract of Neem plant¹⁰ and its application as a catalyst for the reduction of methylene blue (MB) dye using aqueous sodium borohydride (NaBH_4). The biosynthesized AgNPs using Neem leaf extract showed good catalytic activity for reduction of MB.

II. EXPERIMENTAL

The plant extract-mediated bio reduction involves mixing of aqueous plant extract with suitable amount of silver nitrate solution. The synthesis of silver nanoparticles occurs at room temperature and get completed in few minutes.

A. Materials and Methods

Silver nitrate (AgNO_3 , 99.0%), sodium borohydride (NaBH_4) and methylene blue of AR grade and purchased from SD fine chemicals and fresh Neem leaves are taken from college campus.

B. Preparation of Plant Extract

Fresh neem leaves were collected in summer season and in month of May and identified taxonomically. Leaves were washed carefully with double distilled water and cleaned properly About 20 grams of finely cut leaves were taken in 250 ml beaker containing distilled water and boiled for 15 min to get extract of leaves. The extract was then cooled and filtered by using Whatman filter paper. The filtered extract was then used as a reducing and capping agent for synthesis of AgNPs.

C. Green Synthesis of Silver Nanoparticles

The solution of silver nitrate ($1 \times 10^{-3} \text{M}$) is prepared using double distilled water (100 mL). Then 1,2,3 ml of neem extract was added separately to 10 mL solution of silver nitrate ($1 \times 10^{-3} \text{M}$). The set of solutions are kept in dark to avoid action of light on AgNO_3 solution. The reduction of Ag^+ to Ag^0 was confirmed by change in colour from light yellow to dark brown which confirms the reduction of Ag ions. Its formation was also confirmed by using UV-Visible spectroscopy.¹¹



Fig. 1 Synthesized silver nano particles with increasing concentration of Neem extract

D. Reduction of Methylene Blue

The catalytic efficiency of AgNPs - neem extract was studied for methylene blue reduction by NaBH_4 . To track this reaction 0.5ml of freshly prepared NaBH_4 solution (0.05M) was added to 5ml of methylene blue solution ($1 \times 10^{-3} \text{M}$) taken in quartz cell. The 0.5 ml of AgNPs - neem extract was added to start the reaction. The change in the concentration of methylene blue with time was monitored by UV Visible spectrophotometer.

III. RESULTS AND DISCUSSION

A. Characterization of Synthesized Silver Nanoparticles

UV-Visible spectral analysis was done by using Shimadzu UV-Visible spectrophotometer with a resolution of 1 nm between 300 and 700 nm. One milliliter of the sample was pipetted into a test tube and subsequently analyzed at room temperature. A sharp peak seen at wavelength at 414.15 nm. As the concentration of neem extract increases in colour intensity of the absorbance also increases (Fig.1). These bands are assigned to surface plasmon band that corresponds to the completely or roughly spherical shape of AgNPs. The UV spectra and visual observations revealed that formation of silver nanoparticles occurred rapidly within 15 min.

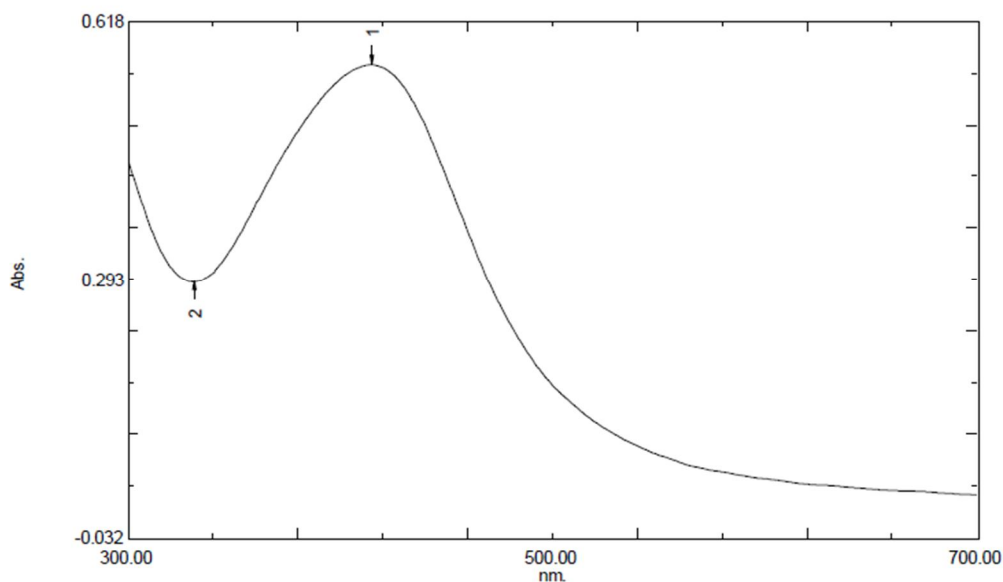


Fig.2 UV Visible spectrum of silver nanoparticles

B. FTIR Analysis

The plant extract plays dual role and it act as both reducing and capping agent. The presence of functional groups was confirmed by FTIR analysis of AgNPs. A broad band between 3421 cm^{-1} is due to the N-H stretching vibration of group NH_2 and OH the overlapping of the stretching vibration of attributed for water and A. indica leaf extract molecules. 2922.25 cm^{-1} (C-H stretching vibrations) the alkanes; 2343.59 cm^{-1} (C=N stretching vibrations) the nitriles; The band at 1649 cm^{-1} corresponds to amide C=O stretching of COOH group in neem extract. The observed peaks at 1157 cm^{-1} denote -C=O-C- linkages, or -C=O- bonds. The observed peaks are mainly attributed to flavonoids and terpenoids excessively present in plants 608.69 cm^{-1} (C-C stretching vibrations) the aromatics; 1448.59 cm^{-1} (C-H bend stretching vibration) the alkanes; 1238.34, 1157.33 and 1030.02 cm^{-1} (C-N stretching vibration) the aliphatic amines; 949.01 cm^{-1} (=C-H bend stretching vibration) the alkenes; These observations were comparable with the previous findings.¹²



Fig.3 IR spectrum of neem extract

C. Xray Diffraction studies

The synthesized of AgNPs showed four diffraction peaks at 2θ values of 38.4° , 44.51° , 64.6° , 77.40° which corresponds to the (111), (200), (220), (311) and the different peak intensity profile are characteristic of cubic structure of AgNPs. The peaks at 2θ values corresponding to the Bragg's reflections of planes conforms the FCC crystalline structure of silver. The relatively higher intensity of planes [111] [220] in FCC crystalline structure supports the stability of the green synthesized AgNPs. The XRD pattern study shows that AgNPs are crystalline in nature. The main crystalline phase was silver, and there were no obvious other phases as impurities were found in the XRD patterns.¹³

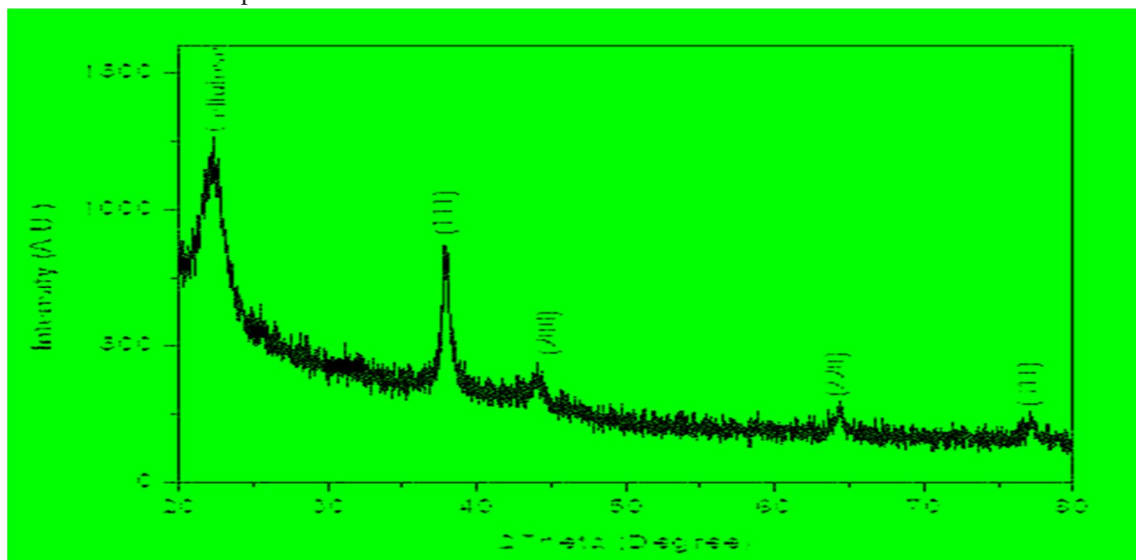


Fig.4 XRD spectrum of Silver nanoparticles

D. Fluorescence Emission Spectrum

Photoluminescence (PL) spectrum is one of the methods to estimate the optical property of silver nanoparticles as photonic materials. The PL of the synthesized bio-inspired AgNPs by Neem leaf extract is studied by fluorescence emission spectroscopy. The colloidal silver nanoparticles are dispersed in water and the PL emission spectra are recorded for the excitation wavelength at 350 nm. A broad emission is obtained at 397 nm. (Fig.5) The intensity of fluorescence emission peak is gradually increased up to 397 nm, after which it is slowly decreased up to 650 nm, slight broad emission at 447 nm may be due to presence of biochemical or antioxidants present in plant extract.¹⁴



Fig.5 Fluorescence emission spectrum of silver nanoparticles formed at excitation at 350 nm

E. Procedure for Degradation of Methylene Blue

In order to study the catalytic degradation of MB solution of volume 5 mL having concentration $1 \times 10^{-3} M$ mixed with 0.5ml of freshly prepared $NaBH_4$ solution (0.05M). Two different samples were prepared. The solution without AgNPs is a blank solution. In the second sample 0.5 ml of synthesized AgNPs solution was further added into the previously made mixture of MB (5mL) and $NaBH_4$ (0.5mL). The final volume of the reaction mixture was adjusted to 20 ml by adding double distilled water. The experiment was carried out at room temperature. The catalytic decomposition of methylene blue was studied by measuring different values of absorbance. As is evident from Fig.6, the UV-vis. spectrum of MB has absorptions at 663 nm 614 nm respectively. The absorbance of the peak at 663 nm was found to decrease with time. At the same time, a new peak appeared at 418 nm whose intensity increased with time. The new peak at 418 nm is may be due to reappearance of AgNPs in the solution after the successful reduction of MB. The reaction was completed in 08 min as was evident from almost zero absorption at 663 nm.¹⁵ Fig7

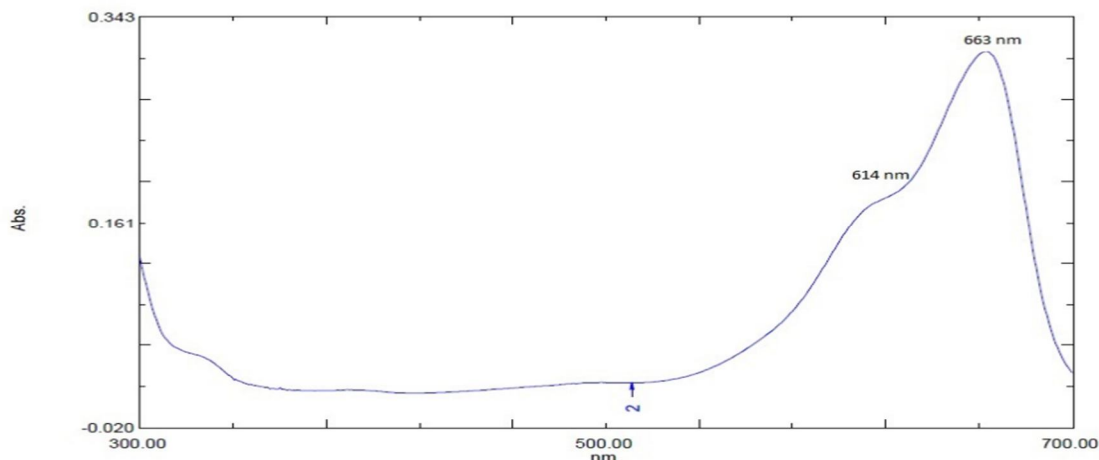


Fig.6 UV Visible spectrum of Methylene Blue

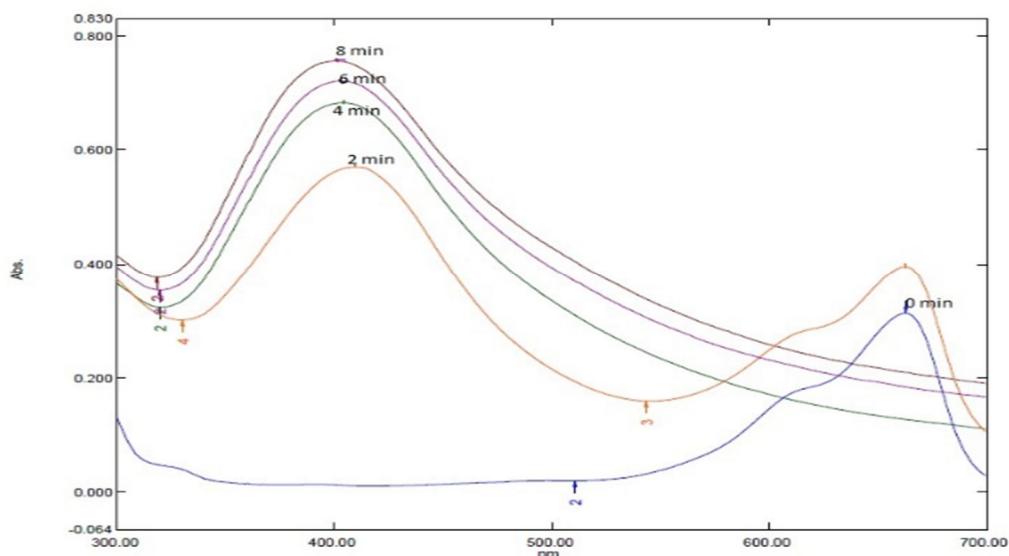


Fig.7 UV Visible spectrum of Methylene Blue degradation in presence of silver nanoparticles

The main steps involved in this catalytic reaction are includes the diffusion and adsorption of the electron donor borohydride ion and the electron acceptor methyl blue on the surface of AgNPs catalyst, then the electron transfer between them, and finally the diffusion of reaction products away from the surface of catalyst.

Since the amount of NaBH_4 used in this reaction is much higher than that of MB, its concentration remains practically constant during the reaction and hence the reaction may be considered to follow pseudo-first order kinetics. So, the rate equation may be written as $k = 1/t \ln [A_0]/[A]$, where 'k' is pseudo-first order rate constant, $[A_0]$ is the initial concentration of methyl blue dye and $[A]$ is the concentration at 't' time. Figure 8, shows the plots of $(1 + \log [A])$ versus time. As time increases the concentration of AgNPs reappearing after degradation increases. The good linear correlation between the variables reveals that the reaction strictly follows pseudo-first order kinetics and rate constant of reaction is 0.010725 per second.¹⁶

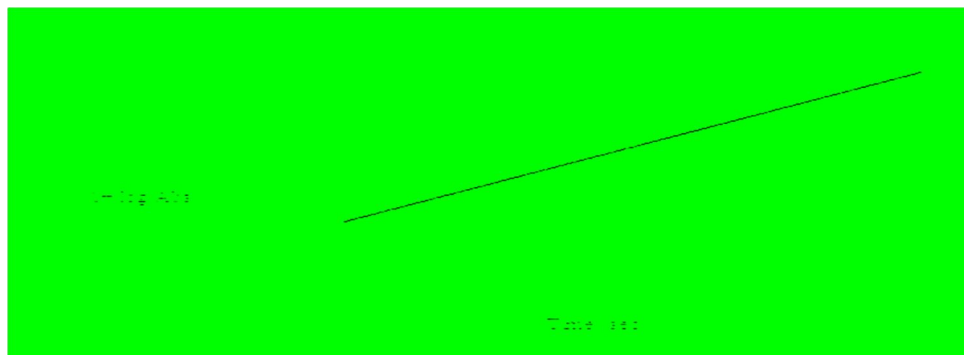


Fig.8 Graph for first order reaction for degradation of methylene blue

IV. CONCLUSIONS

In this work we synthesized silver nanoparticles by green method using *Azadirachta indica* leaf extract. There is no need to use of separate chemicals which act as reducing and capping agent for preparing nanoparticles. The silver nanoparticles are characterized by UV visible spectroscopy, X ray diffraction study, FTIR analysis and fluorescence emission spectroscopy. Synthesized silver nanoparticles act as catalyst for reduction of methylene blue using NaBH_4 as reducing agent. The 100% degradation of methylene blue was achieved by $(\text{NaBH}_4 + \text{AgNPs})$ in just 08 minutes which highlights the efficient catalytic activity of silver nanoparticles.

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