

Catalytic degradation Methylene blue dye by green synthesized silver nanoparticles

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Abstract: *In this study silver nano-particles were successfully synthesized by using Eucalyptus leaf extract. The aqueous leaf extract was added to silver nitrate solution and after incubation, pale yellow colour of reaction mixture was changed to brownish colour which indicates the reduction of silver ions to silver nanoparticles. The AgNPs were characterized by Ultraviolet–visible (UV–vis) spectrometer, FTIR, and Transmission electron microscopy (TEM). The XRD confirmed the crystalline nature and TEM showed spherical AgNPs. The degradation of methylene blue was carried out in the presence of silver nanoparticles in the visible region, using as a promising catalytic agent. The absorption spectrum showed the decreased peaks for methylene blue at different time intervals. Initially absorption peaks at 660nm for Methylene blue dye were decreased gradually with the increase of exposure time.*

Keywords: *Green Synthesis, Eucalyptus leaf extract, Silver nanoparticles, dye degradation.*

1. Introduction

It is well known that nano-biotechnology and nano-toxicology are the most dynamic inter disciplinary areas of research in contemporary material science where by plants and other natural recourses have a significant role in the synthesis of biogenic coated advanced nanoparticles. Nanomaterials have been receiving attention due to their unique physical and chemical properties compared with their larger-size counterparts[1]-[3]. The noble metal nanoparticles have been fabricated by chemical reduction with stabilising reagents (NaBH₄, citrate, or ascorbate) [4], thermal decomposition [5], and photo reduction in reverse micelles [6] etc. Many of these approaches are expensive, consume a lot of energy, result in low yields, and the chemicals used in their production are toxic and hazardous [7-8]. Currently green synthesis of metallic nanoparticles is an emerging science in the field of nanotechnology and nanomedicine. Due to its wide applicability in various fields, “green chemistry” has been evolved to a widespread scope. Traditionally, chemical reduction has been the most groundwork for synthesis of metallic nanoparticles which often involves use of toxic chemicals are utilized to involve in most of the synthetic protocols. In order to avoid the use of toxic chemicals, organic solvents, several researchers attempt to develop the metallic nanoparticles by environmental friendly and biological approaches. Green approach of nanoparticles synthesis by biological entities has been gaining great advantages which are environmental benign, less toxic, and time consuming; and also it is a single step process.

Currently, plant and plant derived materials are used for nanoparticles synthesis which is more compatible than the microbe-mediated nanoparticles synthesis process because they eliminate the culture maintenance and are easy to handle. Silver nanoparticles have also been fabricated using plant extracts as reducing and capping agents. The main advantages of using plant extracts are that the process is simple, cheap, scaling-up, eco-friendly, and safe [9-12]. Eucalyptus leaves (ELs) contain a wide range of active components and the research is still on the hunt for their potential uses as they are rich in polyphenols, including flavonoids and tannic acids,

organic acids and volatile oils. In this study, a novel approach for synthesis of Ag-NPs was developed using ELs extract, which is a simple, economical and environmentally benign method. Methylene Blue (MB) is traditionally used as a dye for materials such as silk, leather, and paper. It is highly toxic to mammalian cells, carcinogenic and can cause skin irritation. Therefore, removal of MB from effluent is essential to protect the environment. Conventional biological treatment in removing dyes from wastewaters is generally ineffective as the dyes are resistant to microorganisms. Moreover, the physico-chemical treatment methods are ineffective at higher effluent concentrations. In recent years, Nanotechnology has been extended to the wastewater treatments. Due to high surface area AgNPs exhibits an enhanced reactivity. To the best of our knowledge till date there is no study available on catalytic activity of AgNPs in reduction of MB dye using leaf extract of *Eucalyptus leaf extract*. Moreover, the catalytic degradation of synthetic dye Malachite green by aqueous leaf extract in presence of AgNPs was investigated.

2. Experimental

2.1. Materials and Chemicals

In this study, *Eucalyptus citriodora* (EC) are used as the biomass materials. These EL was collected on the campus of Jadavpur University in Jadavpur, India. After being washed thoroughly, EC was dried in 40 C, then smashed finely and the powder screened through 90-mesh sieve, finally stored for late use. Silver nitrate (AgNO₃) was used as the source of Ag ions, required for the synthesis of Ag-NPs. Deionized water is used in all experiments.

2.2. Synthesis of Ag-NPs

6 g EL powder was bathed with 150 ml deionized water at 50 C for 1 h, after that, the extract was filtered and stored at 4 C for further experiments. In a typical reaction procedure, 50 ml of EL extract was added to 25 ml 5m M aqueous AgNO₃ solution, with stirring at 30 C. The color of the solution changed immediately from light yellow to reddish brown after the extract was added. The obtained Ag-NPs were centrifuged at 10,000 rpm for 10 min, subsequently washed three times and dispersed in deionized water to eliminate the non-coordinated materials.

2.3. Catalytic Performance Test

Methylene blue purchased from CDH chemicals, India was used for this study. In order to assess the catalytic activity of synthesized AgNPs, two reactions were carried out and absorbance values were monitored using UV-visible spectrophotometer. The values of absorption maxima (max) at 664nm were compared, with that of methylene blue. The schematic representations of the two reactions are depicted in Fig. 1.

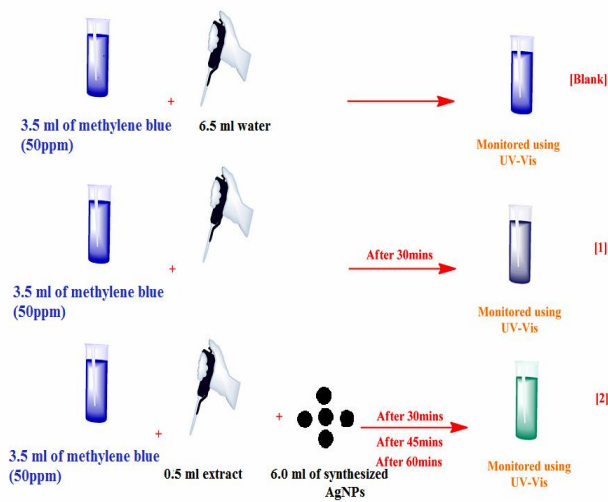


Fig. 1 Schematic representations of the reactions for evaluation of the effect of synthesized AgNPs on the reduction of methylene blue

3. Result and Discussion

The formation of Ag-NPs is relevant to the coherent oscillation of SPR at the surface of NPs [13] and scanned with a UV-vis spectrometer (Varian Cary 50Bio) in the wave-length region between 300 and 600 nm. Fig. 2 shows the UV-vis absorption spectra of the AgNPs synthesized with leaf extract obtained from EU shows peaks at at 440 nm.

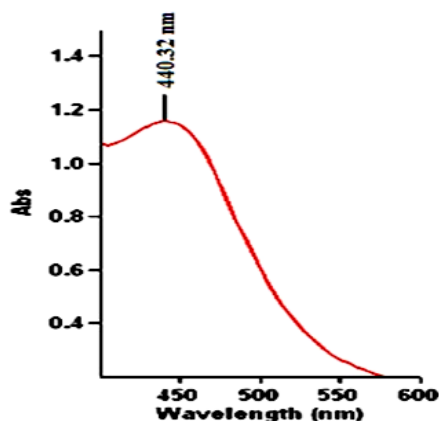


Fig.2 UV-visible absorption spectra of synthesized AgNPs.

Meanwhile, XRD of dry Ag-NPs powder was measured on an XRD (D/MAX-2500 V) operated under the condition of 40 kV and 50 mA with $\text{CuK}\alpha$ radiation ($\lambda=0.1542$ nm). The XRD patterns (Fig. 3) analysis of NPs indicate that synthesized Ag-NPs are crystalline and the four distinct diffraction peaks at 38.111, 44.301, 64.441 and 77.401 which could be assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face-centered cubic Ag-NPs respectively are in agreement with the database of Joint Committee on Powder Diffraction Standards (JCPDS No. 99-0094).

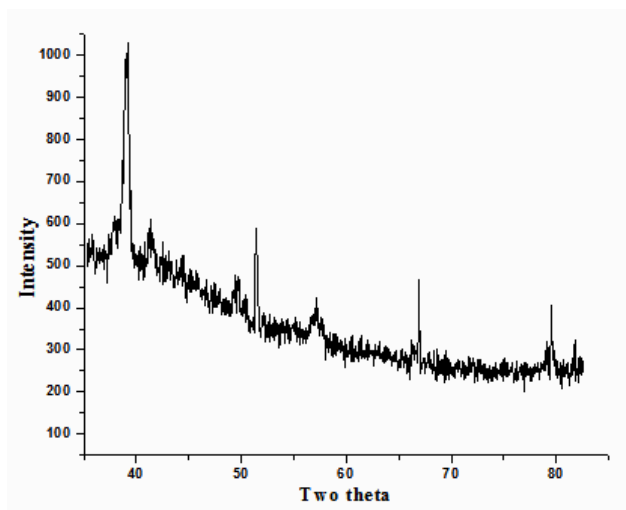


Fig. 3 XRD patterns of synthesized AgNPs.

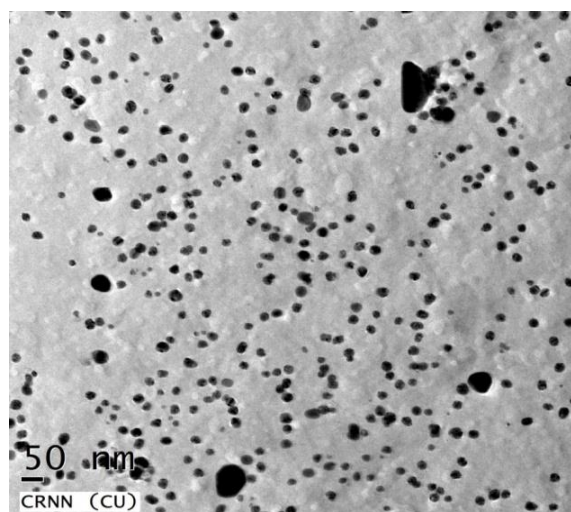


Fig. 4 HR-TEM images of synthesized AgNPs

The structure and morphology of the green synthesized Ag-NPs using the extract of EU were further confirmed by the HR-TEM (JEOL JEM 2100 High Resolution Transmission Electron Microscope operating in the range of 200 kV) micrograph images, showing at the scales of 100 and 10 nm (Fig. 4). The images depict

that the Ag-NPs are spherical in shape, with the particles size distribution between 10 to 40 nm and an average diameter of 25 nm, which is in fairly good consistency of the average crystallite size calculated from XRD analysis. The present study tried to use the FTIR spectra (Perkin Elmer spectrum 2), presented in Fig. 3 to identify the possible reducing and stabilizing biomolecules involved in the NPs synthesis. Shown in Fig. 5B, the bands at 2925.44 (C–H stretching vibration) and 1043.56 cm⁻¹ (C–O stretching) were observed, which are typical for O–H stretching of alcohols or phenols, and the band at 1623.24 cm⁻¹ is characteristic of aromatic C=C [7,18], respectively. After NPs synthesis in Fig. 5A, the bands at 2925.44, 1623.24 and 1043.56 cm⁻¹ shifted to 2929.28, 1633.08 and 1054.49 cm⁻¹, respectively, which could be assumed that the phenolic hydroxyl groups are involved in the synthesis as reducing agents.

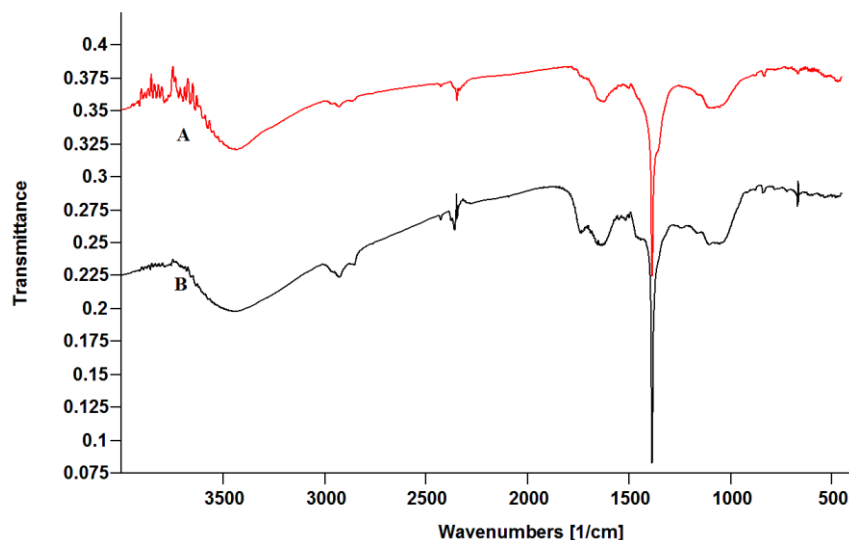


Fig. 5 FT-IR spectra of A) EC leaf powder and B) Synthesized AgNPs with capping of phytoconstituents

Catalytic activity of AgNPs on reduction of Methylene Blue: It is a well known fact that AgNPs and their composites show greater catalytic activity in the area of dye reduction and removal. Pure methylene blue has a max value of 664 nm. Thirty minutes after the addition of the extract to the dye, the absorbance is gradually decreased and is shifted to higher wavelength. The decrease of absorbance is indicative of the ability of phytoextract to degrade methylene blue [13-15]. System containing dye, AgNPs and the extract at the end of 30 min time interval showed a marked decrease in the absorbance of methylene blue and increase of SPR peak of AgNPs (Fig. 6).

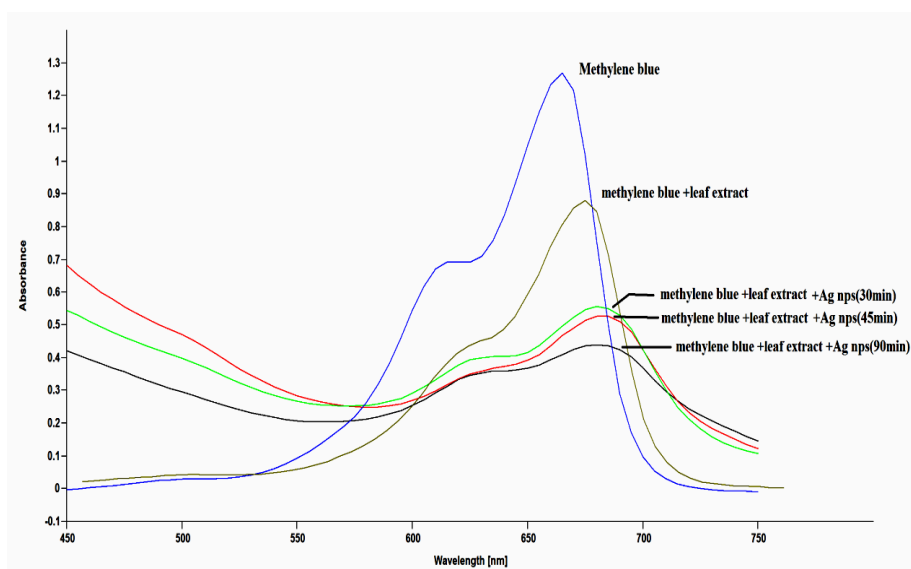


Fig.6 UV-visible spectra of methylene blue reduction by Eucalyptus leaves extract in the presence of AgNPs.

4. Conclusion

We report a simple and efficient way to synthesis stable spherical AgNPs using eucalyptus leave extract. The synthesized AgNPs were initially confirmed by using UV–vis spectroscopy and TEM study. Crystalline nature of AgNPs was evidenced through XRD studies and multifunctional nature of plant extract was confirmed by FTIR studies. The synthesized AgNPs showed excellent catalytic activity in the reduction/degradation of methylene blue. Hence this synthesis process may be the best substitute of both chemical and other physical methods used in industry for large scale production of NPs.

5. Acknowledgement

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6. Reference

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