RESEARCH ARTICLE

Methylene Blue Dye Degradation Using Silver Nanoparticles Synthesized From Andographis Paniculata Leaves Extract

ABSTRACT

Today, the ejection of hazardous dyes from textile industries in water reservoirs like rivers, lakes and groundwater has become a severe problem. To remove these pollutants is challenging by classical water treatment procedures. Thus, for effluent treatment, we need a more convenient method. Here, we describe use of green synthesized silver nanoparticles in the degradation of precarious dye like methylene blue. The silver nanoparticles synthesized from leaves extract of andographis paniculata which act as a nanocatalyst. The synthesis of silver nanoparticles (AgNPs) and the reduction of silver ions are studied using UV-Visible spectroscopy (Ultraviolet-Visible spectroscopy) and FT-IR spectroscopy (Fourier Transform Infrared spectroscopy) respectively. Organic compounds are responsible for the capping and reduction of silver nanoparticles, according to Fourier Transform infrared spectra. The report accentuate that the AgNPs examined to be an effective catalyst for reduction of precarious dyes nearly 84% at 16 hrs of exposure time.

Keywords: Green synthesis, AgNPs, FT-IR, Leaf extract, Dye degradation.

1. INTRODUCTION

One of the most important areas of modern material science research is nanoparticles (NPs). It attracted researchers in the field of electronics, industrial and biomedical fields (Prashant et.al., 2008). Various other techniques are available to synthesize nanoparticles like as physical, chemical, and biological methods. But comparatively the green approach is most suitable. In this, field, the rate of formation of metal nanoparticles has been faster, ecofriendly, and non - toxic.

Silver (Ag) has received a lot of attention among the Nobel metals because of its unique qualities such as optical behavior, catalytic activity, chemical stability, and electrical conductivity (Virendra et. al., 2009). The green synthesized silver nanoparticles (AgNPs) shows various medical applications as it possesses anticancer (Abolghasem et.al., 2014), antimicrobial (Veera et.al., 2012) and antioxidant activities (Sopan et.al., 2016). Silver nanoparticles were commercially used for wound dressing (Najmeh et.al., 2019), drug delivery (Kavitha et.al., 2013), cosmetics (Geovanna et.al., 2020) Animal feed (Muhammad, 2018), water purification (Surya, 2020), biomolecular detection and diagnostic studies (Suksu et.al., 2016).

Green chemistry opens on to the creation of chemical products from natural resources, which are non-toxic to society as well as the environment. The active biomolecules found in the plant extract may bind to the surface of the NPs and reduce the silver ions to silver nanoparticles, enhancing the antibacterial activity of silver nanoparticles.

Andographis paniculata is commonly known as the king of bitters or kalmegh. It is a branched, erect, attractive annual herb that grows to a height of half to one meter. It is a member of the Acanthaceae family and is native to India, Sri Lanka, and parts of China, America, the West Indies, Southeast Asia, and Christmas Island. A. paniculata contains labdane diterpenoid lactone, flavonoids, and other compounds, according to phytochemical studies. It shows pharmacological properties (Siddhartha et.al., 2007 and Khare, 2007). The plant is traditionally used to treat various ailments. It shows antidiabetic activity (Bu-Chin et.al., 2003), antibacterial activity (Pushpendra et.al., 2013), antioxidant activities (Nibha et.al., 2008). The andographis paniculata leaf was utilized as a reducing agent for silver ion reduction, resulting in silver nanoparticle formation. Freshwater resources are essential components of life because all life-supporting activities (eg: drinking, washing, and cultivation) are dependent on them (Bill, 2008). Synthetic organic dyes damage water resources because they are widely used in the textile sector. So, the removal of non-biodegradable dyes makes critical ecological problems. Recently nanoparticles are more effective to overcome this problem as multiple techniques are available.

The biogenesis of silver nanoparticles utilizing Andographis paniculata leaf extract was successfully described in this study. Under UV irradiation, synthesized silver nanoparticles were used to degrade dyes. Solar radiation typically contains 45 percent visible light (λ > 400 nm) and 5% ultraviolet light (λ< 400 nm) (Parashar et.al., 2009). Silver nanoparticles have a unique feature that allows them to absorb visible and ultraviolet light from solar radiation. This is due to the surface plasmon resonance phenomenon. As a result, they offer a significant potential to deal with toxic dyes via a photocatalytic approach. These preferable nanostructures based photocatalyst e.g. (AgNPs) are most effective and thus treat noxious organic pollutants.

Fig 1: Leaf of *Andographis paniculata*

2. Materials and Methods

Materials and chemical collection

Fresh *Andographis paniculata* leaves were taken and it is authenticated because we selected using statistical parameters (sampling and survey) and leaves were taken from botanical garden of Govt.V.Y.T.P.G.Autonomous college. Durg (Chhatisgarh) and is recorded in the Herbarium file of the Botany department. Silver nitrate-Merck (Delhi), Methylene Blue Sigma Aldrich, Bangalore, all of the materials were analytical grade, which meant they could be utilized right away without further purification. Throughout the experiment, double distilled water was utilized to make the aqueous solution.

2.2 Silver nanoparticle synthesis

Andographis paniculata leaf extract was used to make AgNPs. The plant's healthy leaves were plucked, washed properly, and dried in the shade. The powder was made by finely grinding the dried leaves. 5 g of fine powder was diluted in 100 ml sterile distilled water, boiled for 10 min at 60 ° C, and filtered using Whatman filter paper. The filtrate was kept at 40°C until it was needed. The filtrate solution was used as a source extract for the synthesis of AgNPs and further used in the subsequent procedure.

At room temperature, 10 ml of leaf extract was used to reduce 90 ml of an aqueous solution of 1mM silver nitrate. The reaction mixture was kept at room temperature in the dark, yielding a reddish-brown solution suggesting the production of green AgNPs. A control was also maintained when including leaf extract into the silver nitrate solution. The resulting AgNPs solution was purified by centrifugation three times at 9000 rpm for 15 minutes. To remove contaminants, the supernatant was removed and the particle was washed three times with sterile water

Fig 2: Pictures show the visual identification Of AgNPs synthesis by A.paniculata leaf extract.

2.3 Photocatalytic degradation of methylene blue dye

A stock solution of 10 mg of methylene blue dye was introduced to 1000 ml of double-distilled water in a typical assay. In 30 ml of methylene blue dye solution, 3 mg of biosynthesized AgNPs was added and properly mixed. A control and a test solution were exposed in the sunlight and monitored. The color variation was observed at regular intervals, and the dye's absorption spectrum was measured using UV- Vis spectrophotometry at various wavelengths. The appearance of dark brown color in the reaction mixture revealed the synthesis of silver nanoparticles. The dye concentration during degradation was determined using the absorbance value at 665 nm. The percentage of dye degradation was calculated using the formula below.

Degradation in percent (%) = $[C_0 - C)]/ C_0]$ 100

Where C_0 is the initial dye solution concentration and C is the dye solution concentration after photocatalytic degradation. (Mahendran et.al., 2014)

2.4 Green Silver NPs Characterization (Andographis paniculate - AgNPs)

The silver nanoparticles were identified visually as the color of the solution changed from green to reddish-brown, confirming the synthesis of NPs. The UV-Spectrophotometer (UV-Vis carry 5000 double beam) was used to characterize the synthesized NPs at a resolution of one nm in the 300-700 nm band. The nanopowder formed was dissolved in de-ionized water and was diluted 10 times. The de-ionized water was taken as a reference for absorbance and thus determine lambda max. The Origin Pro 8 was used to re-plot the absorption values. FT-IR analysis was carried out using a BRUKER Germany FT-IR Spectrophotometer model ALPHAII ECO in ATR mode. FTIR spectra were obtained using KBr pellet method in the 4000-400cm range with a resolution of 4cm-1. The crystalline nature of the nanoparticles was measured using X-ray diffraction (XRD) (Brucker AXS D8 Advance).

3. Result and Discussion

3.1 UV-Visible spectrophotometry: The plant extract is environmentally friendly, cheap, and inefficient for the production of NPs. The current study is concerned with the synthesis of AgNPs using Kalmegh (Andographis paniculata). The synthesis of AgNPs with leaf extract was confirmed by the fact that nano metallic Ag presents a distinct peak at 465 nm and that the following color changes were reddish-brown, but no color changes were achieved in the absence of plant extract. Due to surface plasmon resonance (SPR), metal nanoparticles exhibit a significant absorption of electromagnetic waves in the visible range. A characteristic fluorescence peak of AgNPs in the water phase was previously reported at 465 nm (Jiang et.al., 2005).

The concentration of various groups and molecules present influences reduction and stability. Similar findings have been reported in the case of the stabilizing effect of the biological extract on metal NPs formation (Sankar et. al., 2015). One of the reports, also stated that color changes occur during the reduction of silver ions from silver nitrate when exposed to plant extract (Edison, 2012).

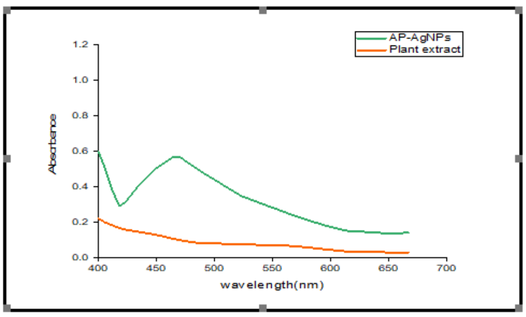

Fig 3: UV-Vis spectra of A.paniculata (red line) and silver nanoparticles (green line) synthesized by A. paniculata leaf extract.

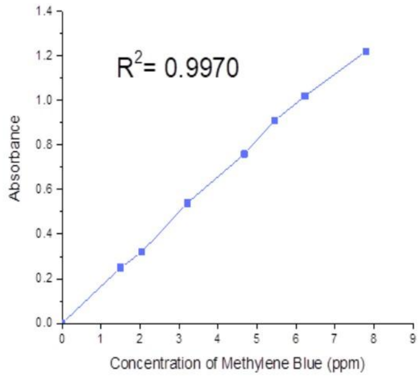

Fig. 4: Calibaration curve for methylene blue dye

3.2 FT-IR (Fourier Transform Infrared Spectrophotometry):
The functional group components of the synthesized AgNPs were determined using FTIR analysis. The FTIR spectrum of plant extract before and after nanoparticle preparation is shown in Fig. 5. 3500-3000, 2500-2200, and 1600-1650 cm^{-1} were found to have distinctive FTIR peaks. Peaks observed between 3500-3300 cm^{-1} are generally assigned to the phenolic hydroxyl group in the structure, which mainly substantiate the presence of diterpenoid lactone of the plant, andrographolide, according to literature studies. The existence of flavanoids and compounds having an unsaturated C=C structure in the aromatic ring structure was established by the peaks in the 2500-2200 cm^{-1} range. Similarly, stretch bending vibrations were assigned strong absorbance intensities in the range of 1600 to 1650 cm-1. As a result, non-bonding chemical interactions between extract and AgNPs have been evidenced in the spectrum. The primary component of A. paniculata leaf extract is andrographolide (Parashar, 2009). The interaction between silver ions and functional groups contained in Andographis paniculata is measured using FTIR. As compared to the other parts of the plant, mature leaves contain more amount of andrographolide and diterpenoids. Andrographolide shows antidiabetic, hepatoprotective, proapoptotic, and anti-inflammatory capabilities. The FT-IR bands of silver NPs were deduced at 965, 1638, 2168, 3351. The peak at 965 may correspond to the C=C bonding of alkene. The peak at 1638 can be attributable to amide carbonyl stretch and may be related to proteins that are encapsulated (Udhayaraj, 2013). The peak at 2168 can be correlated to alkynes. The peak 3351 can be correlated to O-H group shows a group present in the andrographolide which is a highly reactive

group and is responsible for H_2O adsorption (Maria, 2018). As a result, it is possible to deduce that andrographolides are responsible for capping and efficient stabilization.

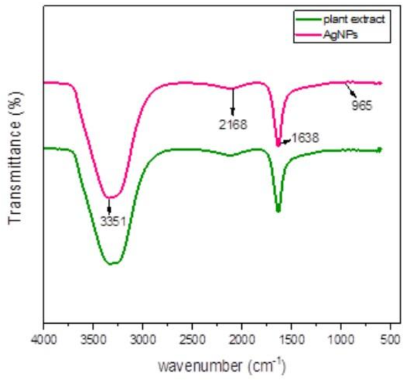

Fig 5: FTIR Spectra of silver nanoparticles synthesized by treating A.paniculata leaf extract.

3.3 XRD Analysis:

An XRD pattern was used to determine the crystallinity of synthesized AgNPs. The diffraction peaks are located at 2θ = 35.34°, 38.39°, 43.65°, and 64.47°. The sharp bands in the XRD data could be due to proteins in the plant extract acting as reducing agents and stabilizing the nanoparticles that were synthesized. As demonstrated in fig 6, AgNPs exhibit diffraction peaks typical of a metallic face-centered cube. This is a typical XRD pattern of AgNPs produced through green synthesis. The presence of AgNPs was confirmed by the Bragg reflections at 2θ = 38.39°, which can be indexed to the (111) orientations. These findings demonstrated that the nanoparticles are made of extremely crystalline Ag (Singh et.al., 2019). These results indicated that the nanoparticles are composed of highly crystalline Ag. The crystal parameters of Ag NPs were calculated based on the Scherer equation :

$$D = K\lambda / \beta\cos\theta$$

where D is the mean crystal size (nm), l is the X-ray wavelength (1.54 Å), β is the full width of the half maxima (FWHM), k is the shape factor (0.9) and θ is the angle of X-ray diffraction peak. The crystalline size of as-prepared Ag particles was 85 nm.

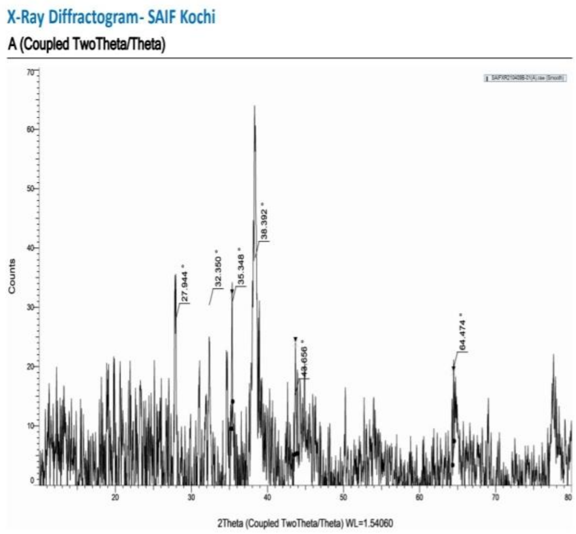

Fig:6 XRD pattern of silver nanoparticles synthesized from andographis paniculata.

3.4 Visual observation of methylene blue dye degaradation:

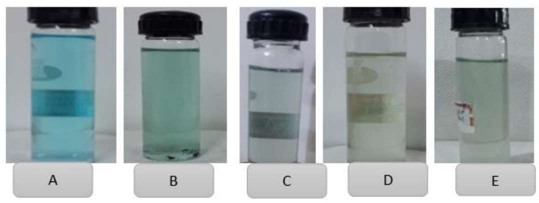

Fig 7: Colour variations from blue to colourless indicate methylene blue degradation at different time intervals (a) initial (0hr) (b) 2 hours (c) 6 hours (d) 12 hours (e) 16 hours

Photocatalytic degradation of methylene blue (Fig. 7) using green synthesized AgNPs was primarily identified by color change. Initially, the color of dye shows blue color changed to light blue, after 2 hours of incubation with AgNPs while exposed to sunlight. Thereafter the light blue color changed to faint blue after 6 hours. Finally, the degradation process was completed at 16 hrs and was identified by the color change to colorless.

3.4.1 Mechanism:

In the presence of visible and UV range of sunlight irradiation, biosynthesized AgNPs shows surface plasmon resonance property and interband transition to degrade toxic dyes by photocatalysis process. When active photons collide with the surface of AgNPs, the AgNPs' bands electrons absorb this visible light, causing the electrons to excite to a higher energy state. (Jayanta, 2017). Afterward, plasmon release energy, and thus heating of electrons gas occurred. These higher energy or high-temperature electrons interact with the environmental oxygen molecules resulting in the formation of oxygen free radicals (O_2*). Thus, the degradation of dye molecules proceeds due to the interaction of generated free radicals with dye molecules. Additionally, the holes generated in the 5 sp orbital accepts electrons from dye molecules results in the improvement of degradation of dye. Moreover, in the presence of UV- light, interband excitation of electrons from the 4d orbital to the 5sp orbital occurs, resulting in electron excitation to a higher energy state. These highly powerful electrons react with the 0_2 and OH- to form (0_2*) and hydroxyl radicals (OH*), respectively. These free radicals are responsible for dye degradation. (Jagpreet et.al., 2019)

3.4.2 UV-Visible Spectrophotometer:
The dye methylene blue was used to explain the photocatalytic activity of AgNPs on dye degradation. The presence of AgNPs in the visible region at different times resulted in the degradation of methylene blue dye. At different time intervals, the absorption spectrums of methylene blue dye decrease with the continuous exposure time, the initial absorption peak at 665 nm for methylene blue dye were decreased steadily and as a result, the photocatalytic degradation reaction of methylene blue continues. At 465nm, the absorption peak of methylene blue was reduced while the absorption band of silver nanoparticles was increased. The steadily decreasing absorbance value of dye approaching the baseline and the increased peak for AgNPs indicate that the photocatalytic degradation of the dyes has been completed. The percentage of degradation efficiency of AgNPs was calculated as 84% at 16 hrs exposure. As the exposure time of dye is increased the degradation percent was increased of dye AgNPs complex in sunlight (fig. 8 & 9). The absorption peak for methylene blue was centralized at 665 nm in the visible area, which gradually declined and disappeared as the reaction time increased, signifying that the dye had been degraded (table 1).

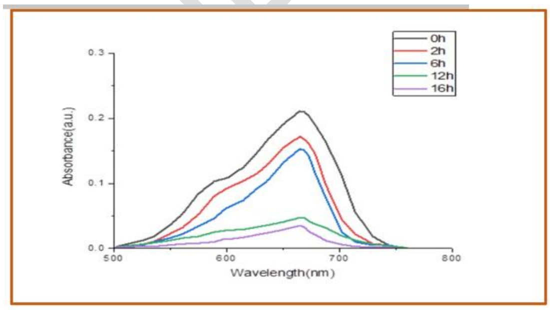

Fig 9: At various time intervals, the absorption spectra of methylene blue solution treated with silver nanoparticles (AgNPs) were recorded.

Table 1: The percentage of methylene blue degraded by biosynthesized AgNPs.

S.No.	Exposure Time(hours)	Absorbance at 665nm	The concentration of dye solution (ppm)	% Degradation
1.	0	0.211	10	0%
2.	2	0.172	8.1	19%
3.	6	0.153	7.2	28%
4.	12	0.0473	2.03	79.7%
5.	16	0.0357	1.6	84%

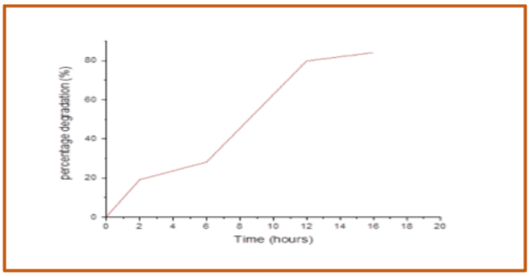

Fig 8: Graph between time and percentage degradation of dye

4. Conclusion and future aspects

In this study, the economic, eco-friendly compatible method is developed for the synthesis of silver nanoparticles. Thus, no need for any special conditions such as vacuum conditions, catalysts, and sophisticated instruments. Herein, the AgNPs were synthesized using A.paniculata leaf extract at room temperature. FTIR supports the presence of functional groups of phytochemical molecules capped on the prepared AgNPs. Methylene blue dye was used to test the photocatalytic activity of green synthesized AgNPs. With increasing time, the major absorption peak at 665nm declined steadily, showing photocatalytic degradation of methylene blue dye. The utilization of a natural, sustainable, and environmentally friendly reducing agent for the synthesis of silver nanoparticles was reported in this study. It has strong photocatalytic activity against dye molecules and can be used to purify water as well as treat dye effluent

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. COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly used products in our area of research and country. There is no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by the personal efforts of the authors.

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