Review Article

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

ABSTRACT

Today, ejection of hazardous dyes from textile industries in water reservoirs like river, lakes and ground water has become a severe problem. To remove these pollutants are challengable by classical water treatment procedure. Thus, for effluent treatment we need more convenient method. Here, we describe use of green synthesized silver nanoparticles in degradation of precarious dye like methylene blue. The silver nanoparticles synthesized from leaves extract of andographis paniculata which act as nano catalyst. The synthesis of AgNPs (Silver nano-particles) 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 hr 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 the 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 ~~these~~ 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 behaviour, catalytic activity, chemical stability and electrical conductivity (Virendra et. al., 2009).The green synthesized silver nanoparticles (AgNPs) shows various medical applications as it possess 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 the 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 are commonly known as king of bitters or kalmegh. It is a branched, erect, attractive annual herb that grows to a height of half to one metre. 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. Fresh water resources are essential components of life because all the life supporting activity (eg: drinking, washing and cultivation) are depended (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 degraded dyes. Solar radiation typically contains 45 percent visible light (λ > 400 nm) and 5% ultraviolet light (λ< 400 nm) [19]. 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 ~~procedures~~

Materials and chemical collection

Fresh Andographis paniculata leaves were taken from the Govt.V.Y.T.P.G. College~~'s~~ garden in Durg, Chhattisgarh. Silver nitrate-Merck (Delhi), methylene blue sigma Alderich, 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

A. 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. After being heated at 60°C for 15 minutes, 5 grammes of fine powder were diluted in 100 ml of double distilled water and filtered using Whatman filter paper No.1. The filtrate was kept at 40°C until it was needed. The filtrate solution was used as a source extract for the manufacture of AgNPs and was used in the following technique.

At room temperature, 10 ml of leaf extract was used to reduce 90 ml of an aqueous solution of 1m~~m~~ M 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.

The formation of dark brown colour revealed the formation of silver nanoparticles in the reaction mixture.

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 colour 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 colour 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 (%) = [C0 - C)]/ C0] 100

Where C0 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 (AP-AgNPs)

The silver nanoparticles were identified visually as the colour 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. FT-IR analysis was carried out using a BRUKER Germany FT-IR Spectrophotometer model ALPHAII ECO in ATR mode. FTIR spectra were obtained in the 4000-400cm range with a resolution of 4cm-1.

3. Result and Discussion

3.1 UV-Visible spectrophotometry: The plant extract is environmentally friendly, cheap and inefficient for production of NPs. The current study is concerned with the synthesis of AgNPs using Kalmegh (A. paniculata). The synthesis of AgNPs with leaf extract was confirmed by the fact that nanometallic Ag presents a distinct peak at 465 nm and that following colour changes were dark brown, but no colour 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.

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 biological extract on metal NPs formation (Sankar, 2015). In one of the reports, also stated that colour changes occur during the reduction of silver ion from silver nitrate when exposed to plant extract (Edison, 2012).

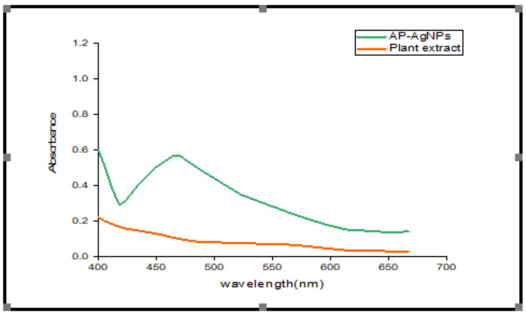

Fig 3: UV-Vis spectra of A.paniculata (red line) and silver nanoparticles (green line) synthesised by A. paniculata leaf extract.

3.2 FT-IR (Fourier Transform Infrared Spectrophotometry):
The primary component of A. paniculata leaf extract is andrographolide (Parashar, 2009). The interaction between silver ions and functional groups contained in A. 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 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 corelated to alkynes. The peak 3351 can be corelated to O-H group shows a group present in the andrographolide which are highly reactive group and are responsible for H_2O adsorption (Maria, 2018). As a result, it is possible to deduce that andrographolides responsible for capping and efficient stabilization.

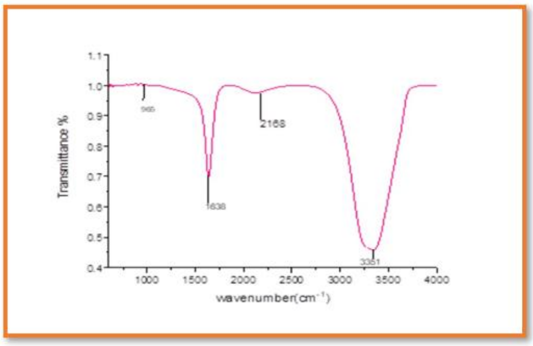

Fig 4: FTIR Spectra of silver nanoparticles synthesised by treating A.paniculata leaf extract.

3.3 Visual observation of methylene blue dye degaradation :

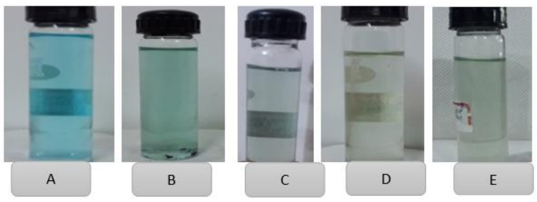

Fig 5: Colour variations from blue to colourless indicate methylene blue degradation at different time intervals (a) initial (0hr) (b) 2 hours (c) 6 hours (d) 12 hours (e) 16 hours

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

3.3.1 Mechanism:

In the presence of visible and UV range of sunlight irradiation, biosynthesised 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). Afterwards, 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 (O2*). 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 02 and OH- to form (02*) and hydroxyl radicals (OH*), respectively. These free radicals are responsible for dye degradation. (Jagpreet et.al., 2019)

3.3.2 UV-Visible Spectrophotometer:

The dye methylene blue was used to explain the photocatalytic activity of AgNPs on dye degradation's. The presence of AgNPs in the visible region at different times resulted in the degradation of methylene blue dye. At the different time interval, 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 base line 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: - 5). The absorption peak for methylene blue was centralized at 665 nm in the visible area, which gradually declined and disappeared as reaction time increased, signifying that the dye had been degraded.

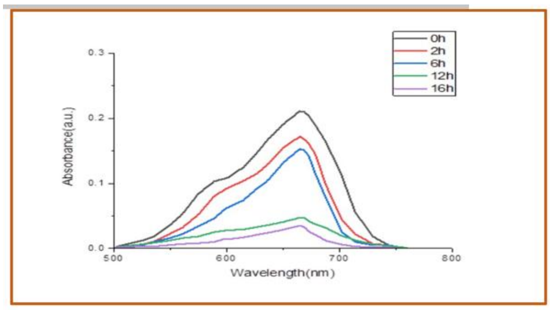

Fig 6: At various time intervals, the absorption spectra of methylene blue solution treated with silver nanoparticles (AgNPs) were recorded.

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

S.No.	Exposure Time(hours)	Absorbance at 665nm	Concentration of dye solution (ppm)	% Degra
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%

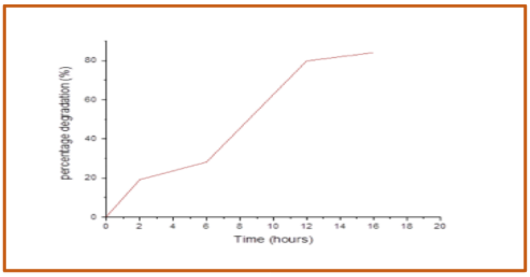

Fig 7: Graph between time and percentage degradation of dye

4. Conclusion and future aspects

In this study, 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. Here in, 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 synthesised AgNPs. With increasing time, the major absorption peak at 665nm declined steadily, showing photocatalytic degradation of methylene blue dye. The utilisation 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 use products in our area of research and country. There is absolutely 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 for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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