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Eco-friendly Synthesized Silver Nanoparticles for Photocatalytic Degradation of Methylene Blue Dye

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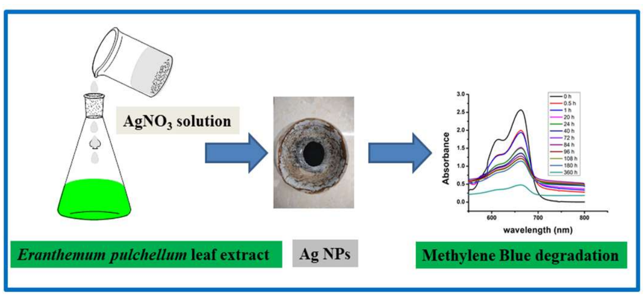
ABSTRACT

A bio-mediated Synthesis of the silver nanoparticles (Ag NPs) by using aqueous leaves extract (PE) of plant Eranthemum pulchellum (blue sage) and its assessment for the photocatalytic degradation of methylene blue dye is reported here. These prepared Ag NPs were characterized by fourier transforms infrared spectroscopy (FTIR), ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM) and high resolution-transmission electron microscopy (HR-TEM). These synthesized Ag NPs have shown its potential towards photocatalytic degradation of harmful synthetic organic methylene blue dye up to 81.3 %.

Graphical abstract:



Bio-mediated Ag NPs synthesis and methylene blue dye degradation.

Keywords: Silver nanoparticles, Photocatalysis, Methylene blue dye, Bio-mediated, Reducing agents.

INTRODUCTION

Dyes are inorganic or organic materials that are responsible for colour of a particular substance. These dyes produce colour either by chemical or physical interaction with different substances. These dyes emit or absorb UV-Visible light in the range of 400-700 nm. Dyes can be obtained directly from nature or these can be synthesized by various chemical procedures. Natural dyes are produced mainly from plants. Some natural dyes are also obtained from lower invertebrates as well as minerals. Some of the oldest known synthetic dyes are Han Blue ($BaCuSi_4O_{10}$), Egyptian Blue ($CaCuSi_4O_{10}$), and Lirple ($BaCuSi_2O_4$) [1]. Commercial journey of the modern synthetic organic dyes started from the discovery of Mauve by Perkin [2, 3]. Since then an enormous number of commercially viable organic dyes have been produced. Worldwide around 100000 synthetic dyes are available in the market with annual production near to 100000 tons [4]. Synthetic dyes are immensely utilized in various industries like textile, leather, printing, pharmaceutical, cosmetics and food [5, 6]. During application of the synthetic dyes a measurable fraction remains unutilized. These unutilized dyes become the part of water bodies and leads to the severe contamination. Water pollution due to these dyes creates severe health hazard and disrupts aquatic ecosystem because of their extreme toxicity, longer lifespan and least tendency for biodegradation. These dyes alleviate sunlight in aquatic ecosystems leading to interruption of photosynthesis which ultimately lowers dissolved oxygen. This lowering harm flora and fauna of these ecosystems and damages food chain system. Further these synthetic dyes percolates underground and pollutes ground water [7, 8].

Therefore, for environmental concerns it has become mandatory to treat these harmful unutilized dyes to fewer toxic substances prior to discharge in aquatic ecosystems. Conventional methods for treatment of these synthetic dyes consists of different chemical (oxidation, anaerobic treatment, coagulation and flocculation) and physical (ion exchange, membrane filtration and adsorption) processes. But the major limitations associated with these processes are high energy demand and formation of other pollutants during the process [7, 9, 10]. The major advantages associated with bio-mediated approaches are that it requires less toxic and inexpensive chemicals as well as these approaches are safer for environment [11]. Metal nanoparticles synthesized via these approaches have been utilized in the different areas of medicine, catalysis, drug delivery, electronics, optics and different sensors [12, 13]. Recently there are several reports have been found where metal nanoparticles have been found to be a potential candidate for the degradation of the organic synthetic dyes [14, 15]. Extensive literature survey reveals that silver nanoparticles have been successfully used for the degradation of different unsafe organic synthetic dyes such as Methyl Orange, Congo red, Auramine O, Rhodamine B, Acriflavine, Phloxine B, and Thymol Blue dyes etc., [16-18].

Present study depicts a photocatalytic degradation of toxic methylene blue dye by an eco-friendly and bio-mediated method synthesized silver nanoparticles utilizing leaf extract of *Eranthemum pulchellum* (blue sage).

MATERIALS AND METHODS

Chemicals: Silver nitrate ($AgNO_3$) was obtained from Merck Chemicals. Methylene blue was obtained from Fisher Scientific, India. All the chemicals were directly utilized without purification. Preparation of the Ag NPs and all the photocatalytic experiments were accomplished in triple distilled water.

Biosynthesis and Instrumentation techniques of silver nanoparticles: Detailed procedures of plant extract preparation, synthesis of Ag NPs and instrumentation techniques have been adopted from our previous publication [13].

Photocatalytic Degradation of Methylene Blue dye: Synthesized silver nanoparticles were utilized for the photocatalytic degradation study of the methylene blue dye. 100 mL solution of 3×10^{-5} M methylene blue dye was taken in a round bottom flask. To this stirred solution 5 mg of Ag NPs were added at room temperature. Progress of the reaction was monitored at different time interval by Systronics double beam spectrophotometer. Progress of the reaction was monitored up to 360 h. For the estimation of the degradation percentage of the methylene blue dye following formula was used

$$\text{Degradation (\%)} = [(A_0\text{-}At)/A0] \times 100$$

Where, A_0 = Initial absorbance of the methylene blue dye and At = Absorbance of the methylene blue dye at different time t.

RESULTS AND DISCUSSION

All the requisite characterization data and related discussion for the formation of Ag NPs can be seen in our previous publication [13].

Photocatalytic Degradation of Methylene Blue dye: During the course of reaction initial dark blue color of methylene blue dye fades to the light blue color with addition of Ag NPs catalyst infers the degradation of methylene blue dye with the passage of time (Figure 1).

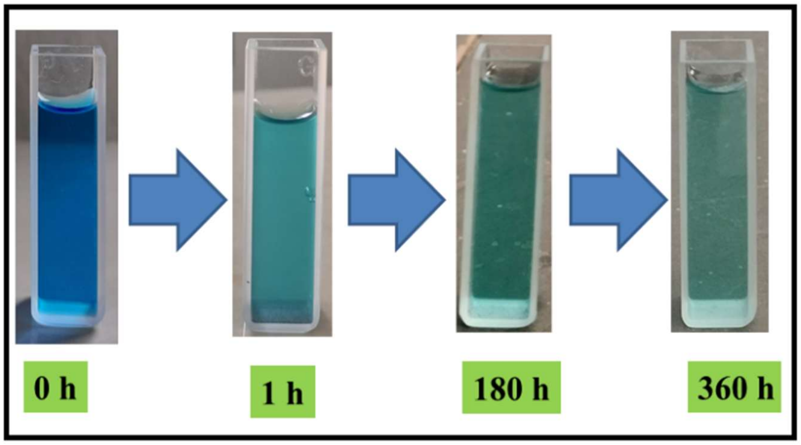


Figure 1. Color of methylene blue dye at different time intervals after photocatalytic degradation.

Further the progress of the catalytic degradation of methylene blue was monitored by UV-Vis spectrophotometer (Figure 2). Initially the catalytic degradation of methylene blue dye was fast and it took only half an hour to achieve the 22% degradation of dye. After that degradation rate became slow and it took 84 hours to achieve the 50% dye degradation. Reaction was monitored upto 360 hours and after this time nearly 81% dye was degraded. Percentage photocatalytic degradation of methylene blue dye with passage of time using Ag NPs is shown in figure 3.

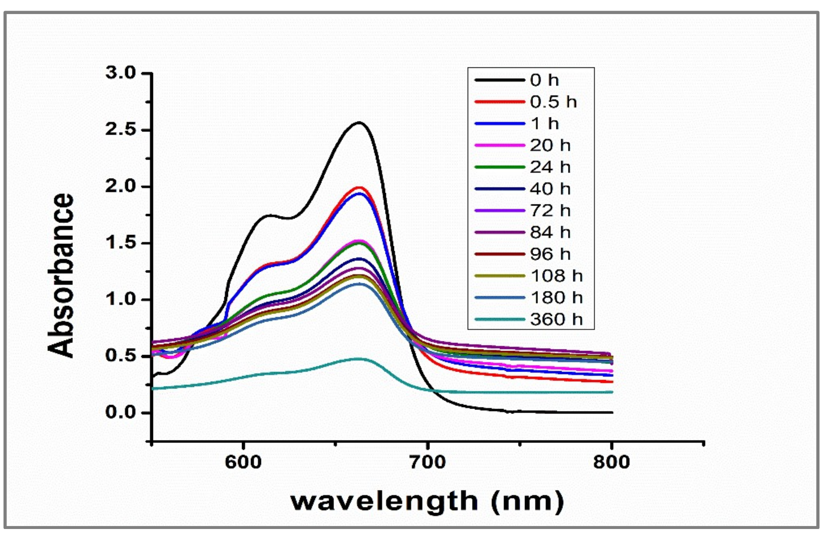


Figure 2. Progress of photocatalytic degradation of methylene blue dye at different time intervals.

Some of the comparative literature reports related to the photocatalytic degradation of methylene blue dye using different bio-mediated synthesized silver nanoparticles are shown in the table 1. This comparison shows that our synthesized Ag NPs having better potential for photocatalytic degradation of methylene blue dye as compared to some of the earlier reports such as Ag NPs synthesized by *Albizia procera*, *Crataegus pentagyna* and Jasmine.

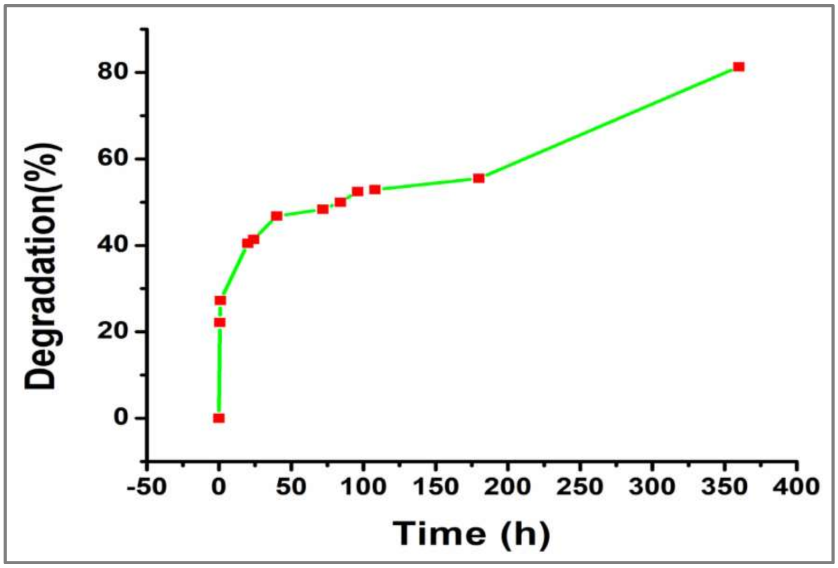


Figure 3. Percentage photocatalytic degradation of methylene blue dye at different time intervals.

Table 1. Photocatalytic degradation of methylene blue dye using different bio-mediated synthesized silver nanoparticles

S No.	Source	% degradation	Time	Reference
1.	Honey	92	72 h	19
2.	*Morinda tinctoria*	95	72 h	20
3.	*Sophora mollis*	88	160 min	21
4.	*Albizia procera*	51.5	70 min	22
5.	*Gymnema sylvestre*	Nearly completion	7 h	23
6.	*Disporopsis longifolia*	100	240 min	24
7.	*Crataegus pentagyna*	78	90 min	25
8.	Jasmine	72	72 min	26
9.	Cauliflower	97.6	150 min	27
10.	*Eranthemum pulchellum*	81.3	360 h	This work

Plausible Mechanism for Photocatalytic Degradation of Methylene Blue dye: Mechanism for the photocatalysis of methylene blue has been depicted in figure 4. Here photocatalyst Ag NPs behave as semiconductor that is having valence band electrons. These valence band electrons are excited to the conduction band by illuminating with sun light having suitable energy to overcome the band gap energy barrier. This transfer of valence band electrons creates holes in the valence band. These electron hole pairs generate highly reactive superoxide($^{\cdot}O^{-}_2$) and hydroxyl radicals ($^{\cdot}OH$). These highly reactive radicals react with methylene blue dye and furnish carbon dioxide (CO_2), water (H_2O) along with other degraded products [28, 29].

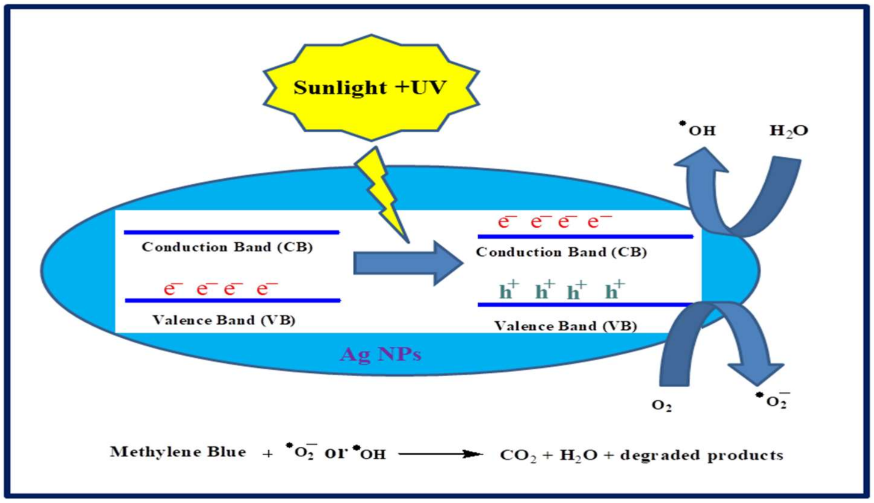


Figure 4. Plausible mechanism for photocatalytic degradation of methylene blue dye.

APPLICATION

Methylene blue is hazardous synthetic dye which is heavily used in textile industries. Unutilized methylene blue dye goes to the water bodies as industrial effluent which pollutes to the aquatic environment. This incidence directly and indirectly (via food chain) becomes the cause of many health issues. Therefore, its treatment is utmost important after its application. In this regard, our research provides an environment friendly approach via Ag NPs for the efficient treatment of toxic methylene blue dye.

CONCLUSION

This research work consists of a simple, commercially viable and an environment friendly method for the synthesis of Ag NPs utilizing leaves extract of plant *Eranthemum pulchellum*. Different biomolecules existing in aqueous leaves extract display a very important part by acting as reducing agent for silver ions and stabilizing Ag NPs via capping to these molecules. These synthesized Ag NPs are characterized by UV-vis spectroscopy, FTIR, HR-TEM, SEM, and XRD. Since the methylene blue dye released in water bodies as industrial effluent is hazardous for human health, environment and aquatic ecosystem, therefore its proper treatment is an urgent need of the hour. Present study provides an alternate bio-mediated Ag NPs with high potential to degrade toxic methylene blue dye in aqueous media.

Conflict of interest: The authors declare no competing interests.

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