

Original Research Article

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Degradation of Malachite Green (Dye) by using Photo-Catalytic Biogenic Silver Nanoparticles Synthesized using Red Algae (*Gracilaria corticata*) Aqueous Extract

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ABSTRACT

Keywords

Gracilaria corticata, Silver nanoparticles, Malachite green dye, Photo-catalytic activity.

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In this paper, we report on biosynthesis of silver nanoparticles using *Gracilaria corticata* (Red seaweed) at room temperature along with photo-catalytic degradation of Malachite green dye. UV spectral analysis showed peak at 380 nm with special reference to the excitation of surfaces plasmon vibration by silver nanoparticles. The morphology of silver nanoparticles was found to be spherical and ranges about 100 nm as confirmed by HR-SEM. Positive zeta potential value of 7.7mV suggests that the nanoparticles are moderately stable in colloidal solution. Further, photo-catalytic degradation of malachite was measured spectrophotometrically by using silver as nano-catalyst under visible light illumination. The results revealed that biosynthesized silver nanoparticles using *Gracilaria corticata* was found to be impressive in degrading malachite green.

Introduction

Nanotechnology deals with the synthesis of nanoparticles with controlled size, shape, and dispersity of materials at the nanometer scale length and their potential use for human well-being. Nanometer sized materials have a high surface area; and a high fraction of surface atoms have been studied because of their exclusive properties such as optic, electronic, and catalytic. Among all nanoparticles noble metal nanoparticles have enormous applications in diverse areas such as bio-imaging, sensor, diagnosis, and novel therapeutic in biomedical field (Salata, 2004). Metallic silver and silver nanoparticles were recently applied as antimicrobial agents in

various products such as cosmetics (Kokura *et al.*, 2010), animal feed (Hojberg *et al.*, 2005), Coating of catheters (Roe *et al.*, 2008), wound dressing (Fernandez *et al.*, 2008), and water purification (Choi *et al.*, 2008) with a minimal risk of toxicity in humans. Nowadays the biological systems were eagerly used for nanoscale material synthesis and assembly is an alternative method of physical and chemical process. 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. Nanoparticles synthesis by medicinal plants shows more benefit; they may enhance the antibacterial activity of silver nanoparticles, because the medicinally valuable active biomolecule present in the plants may bind on the surface of the nanoparticles and reduce the silver ions to silver nanoparticles.

Malachite green (MG) has numerous industrial applications (dyeing of silk, leather, plastics and paper). Their appearance is harmful for humans and animals following inhalation and/or ingestion, produces toxicity to respiratory system and reduces fertility in humans. The triphenylmethane dyes biodegradation due to presence of nitrogen in their back bone (generate carcinogenic, genotoxic, mutagenic and teratogenic problems) is a difficult task (Papinutti *et al.*, 2006). MG has high resistance to light and oxidizing agents, while its removal based on biological treatment and chemical precipitation has low efficiency (Dogan Uluozlu *et al.*, 2008). It is now established that Ag is considered a promising semiconductor that is extensively involved in removal of several toxic organic contaminants through both adsorption and photo-catalytic process due to the stability of its chemical structure, biocompatibility, strong oxidizing power, non-toxicity and low cost of the metal precursors. Ag can be only triggered by UV radiation that encompasses only about 4% - 5% of natural solar radiation due to its wide band gap energy (3.2 eV). This defect limits the industrialization of this powder. Moreover, the mineralization processes through various redox reactions are encountered by the rapid recombination of the charge carriers. Another major defect in the preparation of nano titanium oxide through

sol-gel route is the rapid hydrolysis of titanium alkoxide salts that lead to irregular condensation of hydroxide particles into amorphous solid (Ismail, 2012). This random condensation of particles is the primary cause for obtaining irregular particle and pore structure.

The synthesis of AgNPs using plant extracts is simple, economical and requires less reaction time. Moreover, the microorganisms generate nanoparticles at a much slower rate than the plant extracts. Leaf extracts of *Ficus benghalensis* (Saxena *et al.*, 2012), *Crossandra infundibuliformis* (Kaviya *et al.*, 2012) have been shown to produce AgNPs with good stability. Other parts of plants such as tuber, bark and buds have also been reported in AgNPs synthesis. In this study, we successfully reported the biosynthesis of silver nanoparticles using *Gracilaria corticata* aqueous extract. Synthesized silver nanoparticles were applied to dye degradation under sunlight irradiation

Materials and Methods

Materials

Silver nitrate (>99% pure) was purchased from Sigma Aldrich, India. Potato dextrose broth, Potato dextrose agar, Nutrient broth, Nutrient agar plate, was supplied by Himedia, India.

Sample collection and preparation (*Gracilaria corticata*)

The red algae (*Gracilaria corticata*) were collected from the Rameshwaram sea coast area, Tamilnadu, India and were brought to the nanotechnology laboratory and washed with distilled water several times to remove the impurities. The clean algae were dried at room temperature in the shade for a week and powdered using a mortar and pestle.

Preparation of *Gracilaria corticata* (red algae) extract

Dried powdered *Gracilaria corticata* (5g) was mixed with 100ml distilled water then the solution was kept for continues heating at 80°C for 1hour at room temperature with frequent shaking. After that the extract were filtered by using Whatmann No1 filter paper. The extract was collected and stored at 4°C for further use.

Synthesis of silver nanoparticles from *Gracilaria corticata*

10 ml of the aqueous extract of *Gracilaria corticata* was added into 90ml of aqueous solution of 1mM Silver nitrate. The mixture was exposed to a range of controlled temperatures for 24h. Appearance of brown color in solution indicated the formation of AgNPs. The solution was then kept in dark for further analysis collected and stored at 4°C for further use.

Photo-catalytic malachite green dye degradation

The photo-catalytic degradation of malachite green was evaluated by biosynthesized Ag nanoparticles. All the experiments were performed outdoor with sun as the main source of light (Li *et al.*, 2005). Prior to the experiment, a suspension was prepared by adding 20 mg of Ag nanoparticles to 50 ml of methyl orange solution (Fisher Scientific). Later, the mixture was allowed to stir constantly for about 30 min in darkness to ensure constant equilibrium of Ag nanoparticles in the organic solution.

During the reaction, the mixture was kept under sunlight within a Pyrex glass beaker and stirred constantly. The mean temperature was found to be 30°C with 10 h mean shine duration, A control was prepared in similar

manner without addition of silver nanoparticles. The absorption spectrum of the suspension mixture was measured periodically using a UV-visible spectrophotometer (Shimadzu, UV-2450, Japan) after centrifugation to ensure the degradation of malachite green solution.

Characterization of Ag nanoparticles

UV – Visible spectrum for synthesized nanoparticles

The nanoparticles were monitored by UV-visible spectrum at various time intervals. The UV – Visible spectra of this solution was recorded in spectra 50 ANALYTIKJENA Spectrophotometer, from 250 to 400nm.

Particle Size and Zeta potential analyzer for synthesized nanoparticles

The aqueous suspension of the synthesized nanoparticles was filtered through a 0.22 µm syringe driven filter unit and the size of the distributed nanoparticles were measured by using the principle of Dynamic Light Scattering (DLS) technique made in a Nanopartica (HORIBA, SZ-100) compact scattering spectrometer.

High Resolution Scanning Electron Microscope (HR-SEM)

The structural morphological characteristics of the bacterial sample were observed under scanning electron microscope (HR-SEM) Hitachi's SU6600 at magnification ranging from 10X to 600,000X operated at accelerating voltage of 30 kv.

Results and Discussion

It is well know that seaweeds are extremely different from terrestrial plants with the ability to reduce silver ions. However, when

1mM AgNO₃ solution was added to the aqueous seaweed broth (ASB), no reaction occurred. Instead, after 24h of incubation at room temperature, the color of the solution intensified to brown indicating the formation of Ag nanoparticles as shown in (Fig. 1) inset. The characteristic color change obtained may perhaps be due to the excitation of surface plasmon resonance (SPR) and reduction of AgNO₃.

UV-Visible spectral analysis

It is well-known that silver nanoparticles exhibit brown color, which arises due to excitation of surface Plasmon vibrations of the silver nanoparticles. After addition of 1mM silver nitrate solution to the aqueous extract, the colour of the composition has been changed to dark brown colour. The maximum absorbance peak is observed at 380nm for *Gracilaria corticata* (Fig. 2). The overall observations suggest that the bio reduction of (silver ions) Ag⁺ to Ag⁽⁰⁾ was confirmed by UV-Visible spectroscopy.

Dynamic light scattering analysis

The particle size distribution spectra for the silver nanoparticles were recorded as diameter (nm) verses frequency (%/nm) spectra with diameter (nm) on x-axis and frequency (%/nm) on y-axis. The zeta potential spectra for the silver nanoparticles were recorded zeta potential verses intensity spectra with zeta potential (mV) on x-axis and intensity (a.u) on y-axis. Dynamic light scattering technique has been used to measure hydrodynamic diameter of the hydrosol (particle suspension). *Gracilaria corticata* AgNPs was found to be 96.5nm (Fig. 3a) the recorded value of zeta potential of the silver nanoparticles was 7.7mV (Fig. 3b) which resulted in the agglomerated state of the formed AgNPs

Scanning Electron Microscopy analysis

The surface morphology, size and shape of *Gracilaria corticata* silver nanoparticles were characterized from the SEM micrograph, it is evident that AgNPs were spherical in shape and were poly-dispersed. The measured average size of AgNPs was 100nm and the nanoparticles range from 100-500nm occasional agglomeration of the AgNPs has been observed. The electrostatic interactions and hydrogen bond between the bioorganic capping molecules bond are responsible for the synthesis of silver nanoparticles using *Gracilaria corticata* extract (Fig. 4). In this study, small AgNPs were attached to the surface of large bio-molecules. The aggregation of the nanoparticles indicates that they were in the direct contact, but stabilized by a capping agent, It is evident from the micrograph that individual silver nanoparticles as well as a number of aggregates are present and they are spherical in shape

Photo-catalytic degradation studies

Photo-catalytic degradation of malachite green dye was investigated using biometrically synthesized silver nano particles by solar irradiation technique at different time intervals as shown in (Fig. 5). The characteristic absorption peak of malachite green for *Gracilaria corticata* solution was found to be 380 nm. Degradation of malachite green was visualized by decrease in peak intensity within 6 h of incubation time.

There is no considerable shift in peak position for malachite green solution without exposure to Ag nano-catalysts. Kansal *et al.* (2008) have reported that compared to other irradiation techniques, solar light was found to be faster in decolorizing malachite green in the presence of metal nanoparticles as catalyst.

Fig.1 *Gracilaria corticata*



Fig.2 UV-visible spectroscopy showing *Gracilaria corticata* mediated synthesized silver nanoparticles

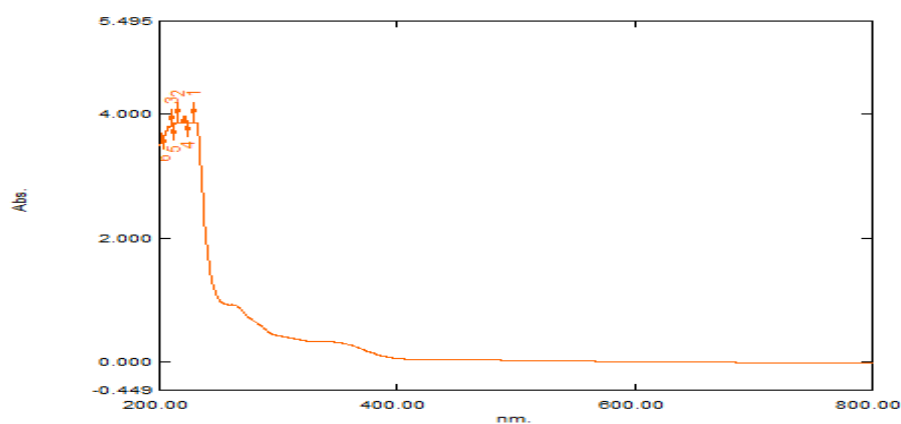


Fig.3 DLS analysis showing a) Particle size b) Zeta potential *Gracilaria corticata* mediated synthesized silver nanoparticles

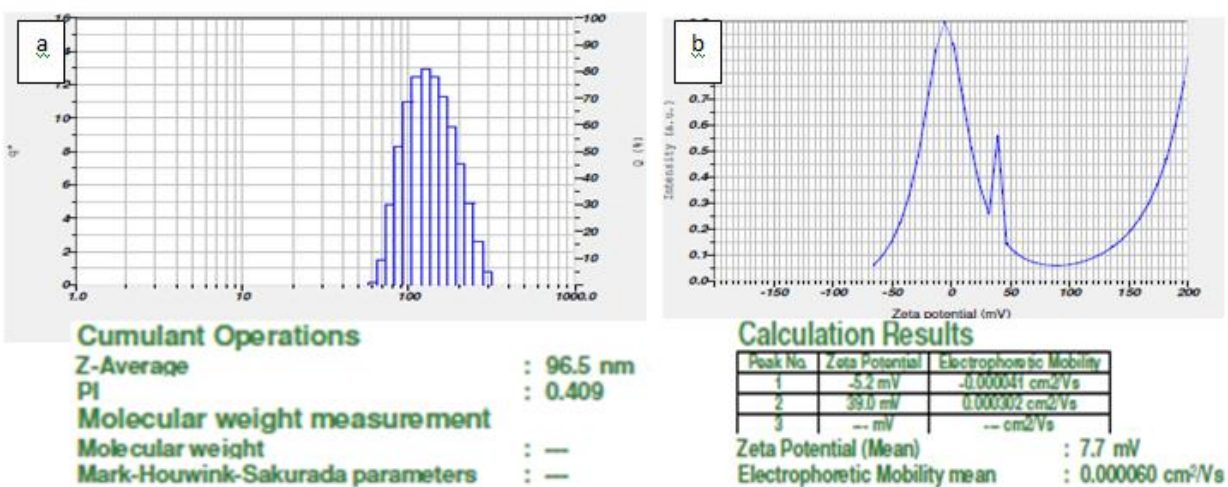


Fig.4 Showing SEM images of *Gracilaria corticata* mediated synthesis of silver nanoparticles

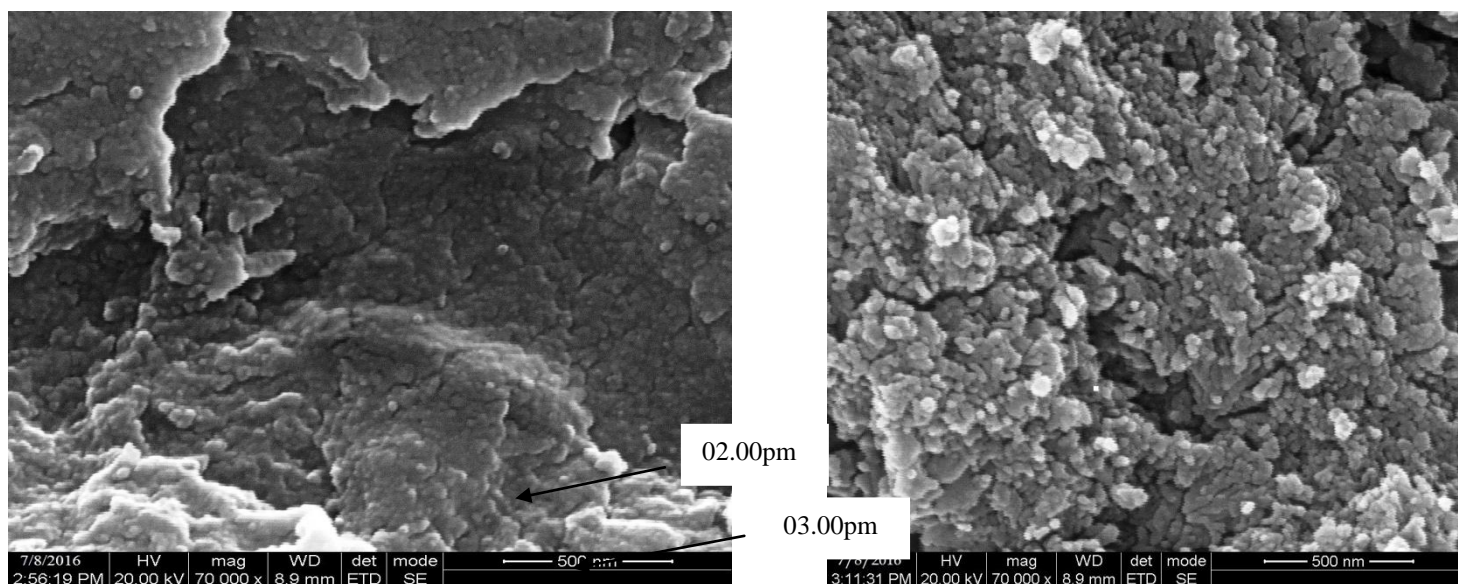
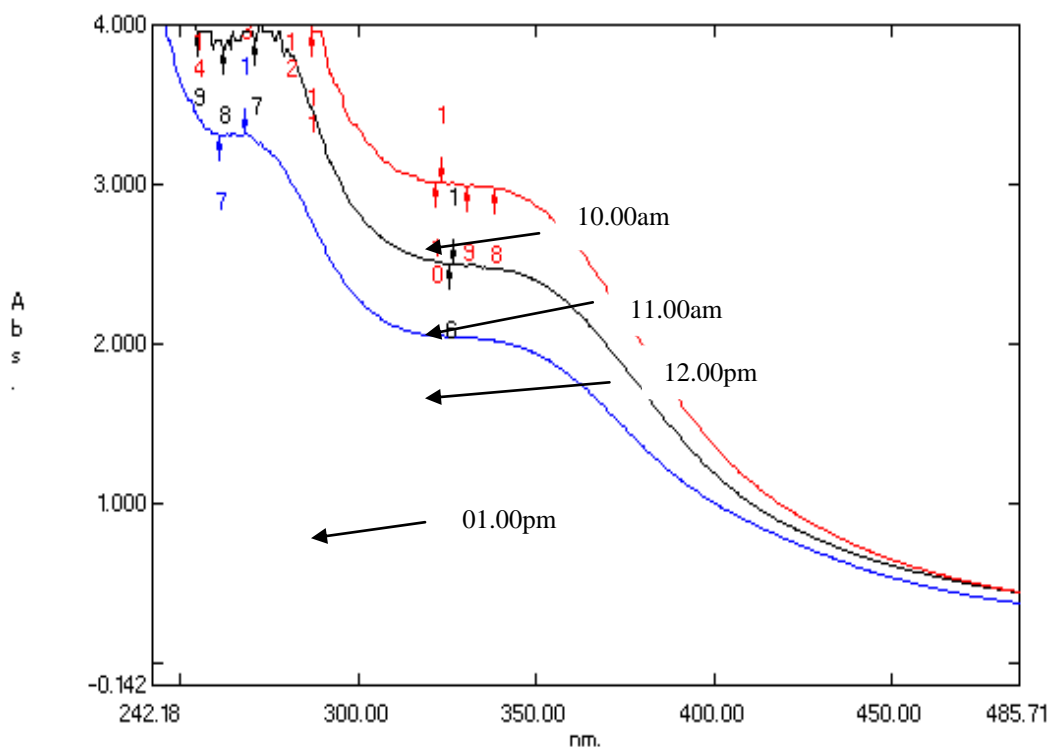
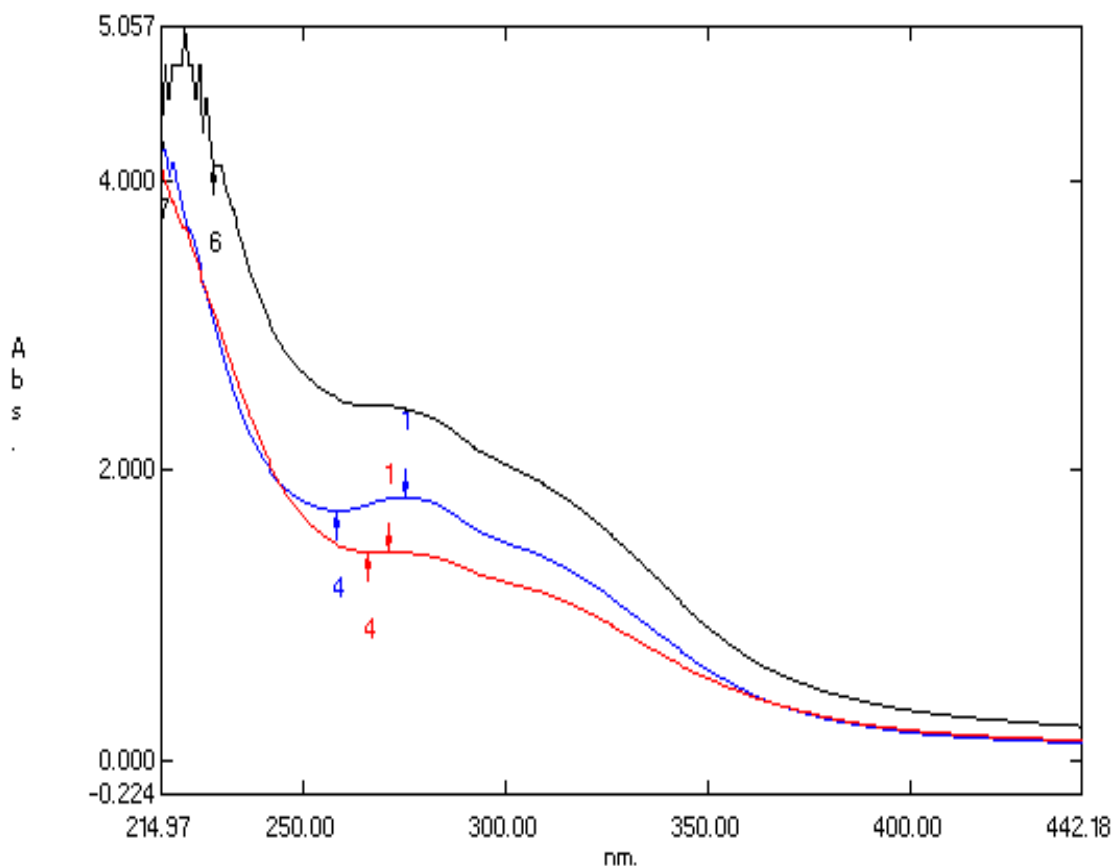


Fig.5 Showing Dye degradation of Malachite green by *Gracilaria corticata* mediated synthesis of silver nanoparticles





The adsorption of Ag nanoparticles on to the malachite green solution was initially low and further increased with constant increase in time. Altogether, the photo-catalytic properties of Ag nanoparticles in visible light may well be due to excitation of SPR, which is nothing but oscillation of charge density that can propagate at the interface between metal and dielectric medium. Guo *et al.*, (2008) stated that, Ag nanoparticles are good, highly efficient and stable photo-catalysts under ambient temperature with visible light illumination for degrading organic compounds and dyes. The nanoparticles were found to be active in degrading malachite green solution with visible light illumination. These findings suggests that, silver nanoparticles synthesized by facile method from *Gracilaria corticata* can able to degrade dyes in the presence of visible light and paves way for environmental bioremediation very effective dye degradation towards malachite green.

The mechanism of sunlight irradiation strategy has been explained that the solar photons hit the nanoparticles present in the reaction mixture during exposure in sunlight, the electrons at the particle surface are excited and reacts with dissolved oxygen molecules in the reacting medium and converted into oxygen anion radicals. These radicals break the organic dye into simpler organic molecules leading to the rapid degradation of the dye. Therefore, the phyto-synthesized silver nanoparticles may act as a stable and efficient photo-catalyst for degradation of malachite green under visible light irradiation

In general, the greater the amount of the photo-catalyst, the higher rate of reaction due to increased active sites of the photo-catalyst would be. However, at the same time more photo-catalyst would also have induced greater aggregation, which resulted in the decrease in the surface area of the photo-catalyst, making a significant fraction of the

catalyst to be inaccessible to adsorbing the dye. Besides this, the degradation rate constant decreased after an optimum value for the photo-catalyst loading as in the concentration of dye, the opacity of dye solution also increased and UV radiation got scattered reducing the optical path. In these conditions, the penetration depth of the photon was decreased and fewer catalyst nanoparticles could be activated.

Degradation of methyl orange was visualized by decrease in peak intensity within 6h of incubation time. There is no considerable shift in peak position for malachite green solution without exposure to Ag nano-catalysts.

In conclusion, silver nanoparticles from *Gracilaria corticata* were synthesized biometrically in room temperature within 24h of incubation time. The formation of silver nanoparticles was confirmed by UV spectra, FE-SEM, and zeta potential measurements studies. The nanoparticles were found to be active in degrading malachite green solution with visible light illumination. These findings suggests that, silver nanoparticles synthesized by facile method from *Gracilaria corticata* can able to degrade dyes in the presence of visible light and paves way for environmental bioremediation.

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