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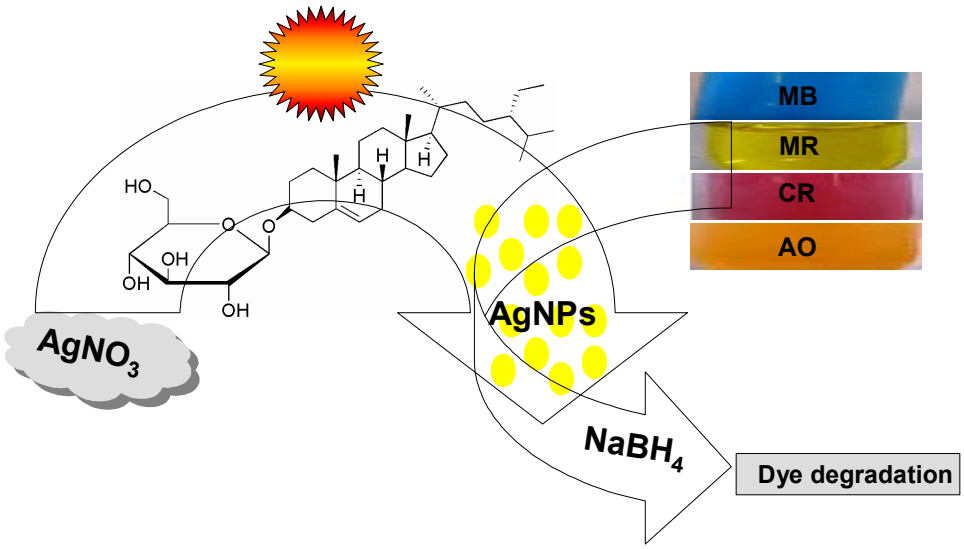
Graphical Abstract



A sunlight-induced synthesis of silver nanopartilces using β-sitosterol-D-glucopyranoside, a bio-surfactant isolated from the Indian sacred grass, *Desmostachya bipinnata*.

Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

β-sitosterol-D-glucopyranoside isolated from *Desmostachya bipinnata* mediate photoinduced rapid green synthesis of silver nanoparticles

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

In this work, we report an completely green chemistry approach to synthesize silver nanoparticles (AgNPs) using the compound β-sitosterol-D-glucopyranoside (BS) isolated from the Indian sacred grass *Desmostachya bipinnata*, using natural sunlight as the initiator. BS synthesizes the AgNPs, in a free radical exchange process involving reactive oxygen species. The possible mechanism of BS on the reduction and stabilization of AgNPs is also discussed. The optical properties, morphology of the AgNPs were characterized by absorption spectroscopy and transmission electron microscopy. These bio inspired AgNPs exhibited good catalytic activity during the catalytic degradation of environmental hazardous organic dyes like methylene blue, methyl red, congo red and acridine orange, in aqueous media.

1. Introduction

Silver nanoparticles (AgNPs) are of great interest and importance for the application in optical, electronics, catalysis, sensors, surface-enhanced Raman scattering and health care[1]. Due to the wide range of application of AgNPs, various methods have been developed to synthesis metal nanoparticles. Among these methods, the most preferred synthetic route is the wet chemical reduction of metals salts in their liquid phase in presence of a stabilizer and reducing agents[2]. The negative impact caused by hazardous chemicals used in the wet chemical reduction method lead to the development of green nanotechnology that employees naturally occurring materials, such as plant extracts, bacteria, fungus and bio-derived chemicals, in synthesizing stable nanomaterials[3]. Among other bio-inspired process of synthesizing NPs, plant extracts mediated synthesis have been considered more advantageous over the other environmentally benign biological process, because it eliminates the elaborate process of maintenance[4]. Moreover, it is eco-friendly, cost-effective and very easy to scale up for large-scale production. Despite its advantages, the use of plant extract suffers from the uncertainty about the chemical components responsible for synthesis and function of the nanoparticles. Because of this, it is difficult to predict the formation mechanism of nanoparticle using plant extract. Howevere, there are studies reports the involvement of polyphenols, flavonoids in the synthesis of AgNPs[4]. To get more detail insight into the plant extract mediated nanoparticles syntheses, it is imperative to identify the exact phyto constituents responsible for nanoparticle formation.

An essential criterion for any green nanotechnology is an environmentally non-hazardous solvent system and synthetic producer. Solar energy is believed to be the largest source of carbon neutral renewable energy. Moreover, sunlight is a non-toxic and non-polluting[5]. Recently, Zarchi and co-workers reported the sun-light induced synthesis of silver nanoparticles using ethanol extract of *Andrachnea chordifolia*. It was shown that the toxicity of AgNPs was considerably reduced when it is prepared by sunlight[6]. Gold nanostructure prepared using sunlight irradiation has been reported as a selective sensor for lead ion[7]. Sunlight induced synthesis of silver nanoparticles on *Citrus limetta* aqueous extract has been reported as a selective sensor for mercury ion[8]. Bimetallic silver-gold nanostructures synthesized via sunlight irradiation on DNA template were found application in TNT/tumor maker detection[9].

Herein, we report the sunlight mediated synthesis of silver nanoparticles using the aqueous extract of *Desmostachya bipinnata*. *D bipinnata* is one of the sacrificial grasses used in Indian vedic rituals and ceremonies and its medicinal properties has been well reported[10]. It is also used as a fodder crop in semi-arid regions[11]. We have isolated a sterol glycoside, β-sitosterol-D-glucopyranoside (BS) from its aqueous extract. This particular compound, BS, has been shown to reduce Ag^{+} to Ag^{0} under the influence of sunlight, indicating that the BS contained in the aqueous extract, is responsible for the formation of AgNPs. The possible mechanism of BS on the reduction and stabilization of AgNPs are also discussed. The possible application of AgNPs obtained with *D. bipinnata* aqueous extract in catalytic degradation of various organic dyes was explored, in aqueous medium.

2. Materials and Methods

2.1. *Collection and processing of plant*

The plants *Desmostachya bipinnata* were obtained along the river beds of River Cauvery, in Thanjavur District, Tamil Nadu, India. The plant was authenticated by Dr. Jayendran, Department of

Botany, Government Arts College, Ootacamund, India. All voucher specimens after matching with the authenticated herbarium sample in the RAPINAT Herbarium, Trichy, India, was deposited in Government Arts College, Ootacamund, India.

2.2. Preparation of Plant aqueous extract

The shade dried leaves and aerial parts were ground to fine powder and used for extraction. The aqueous extract was prepared by soaking 1 kg of plant material in Millipore water at 30ºC for 24 h and filtered through Whatman No.1 filter paper. The extraction was done three times and pooled up, and then was concentrated under vacuum with a Rotary evaporator (Buchi® Rotavap R-210).

2.3. Typical Synthesis of silver nanoparticles from the plant aqueous extract

In a typical procedure, 50 mg of lyophilized aqueous extract of *D bipinnata* was mixed with 50 ml of deionized water and filtered through Whatman filter paper No. 41. To this extract, 1mM $AgNO_3$ aqueous solution is added with stirring at room temperature. *D bipinnata* extract produces colour change with $AgNO_3$ solution after keeping for 48 h at room light. However, upon exposure to sunlight, the colourless silver nitrate solution was converted into pale yellow colour within a minute and drastically deepened to yellow colour in 5 min. AgNPs can also be prepared by irradiating the *D bipinnata* extract with 1 mM $AgNO_3$ under UV-light.

2.4. Isolation of β-sitosterol-D-glucopyranoside *(BS)*

The aqueous extract of *D. pinnata* (30g) was taken for column chromatography with silica gel (60-120 mesh) packed in a glass column of 4 x 45 cm with bed height of 30 cm was eluted with chloroform with increasing concentration of MeOH. The column elution was monitored by TLC and fractions were pooled based on similar TLC profiles. Fraction 6 and 7 were combined together and subjected to column chromatography with silica gel (230-400 mesh) and eluted with chloroform, chloroform-methanol (2, 4, 8, 10 and 20 %) and methanol successively. The compound, BS was obtained from this column chromatography. The structure of the compound was confirmed by various spectroscopic techniques.

2.5. Characterization

UV-vis spectra of the silver nanoparticle solutions were recorded on a Thermo Scientific Evolution 201 spectrophotometer operated at a resolution of 1 nm. The size, morphology and crystallinity of AgNPs were also characterized using high-resolution transmission electron microscopy (HR-TEM) with an accelerated voltage of 200 kV. Samples of TEM measurements were prepared by placing a drop of NP solution on the graphite grid and drying it in vacuum. The concentration of the formed AgNPs was determined by atomic absorption spectroscopy. About 98 µg/mL of colloidal silver was present in the solution, which corresponds to 0.92 mM.

2.6. Reactive oxygen species and free radical assays

The presence of reactive oxygen species (ROS) in the solution were measured by dichlorofluorescein diacetae (DCFH-DA). Briefly, 1 mg/mL of *D. bipinnata* aqueous extract or BS was incubated with DCFH-DA and exposed to room light and sunlight. DCFH-DA dissolved in water is used a control. After 10 min, fluorescence was measured on a Jasco FP-8200 spectrofluorimeter operating at a slit width of 2.5 nm. The excitation and emission wavelength was set at 485 and 528 nm, respectively.

The generation of free radical by *D. bipinnata* aqueous extract after exposing to sunlight was measured by diphenyl picrylhydryl (DPPH) assay. Briefly, 10 µL of 0.1 mM DPPH (dissolved in ethanol) was added to different concentration of *D. bipinnata* aqueous extract and exposed in room light and sunlight for 10 min. The reduction of the DPPH free radical was measured by reading the absorbance at 517 nm. Ascorbic acid was used as the positive control. The lower absorbance of the reaction mixture indicated a higher percentage of scavenging activity. The inhibition ratio was calculated from the following equation

$$\% \text{ scavenging} = [(\text{control absorbance} - \text{sample absorbance})/(\text{control absorbance})] \times 100$$

2.7. Catalytic activity

Dye degradation activities of AgNPs were investigated using the discolouration of methylene blue (MB). Briefly, 15 µM of MB solution were mixed with $NaBH_4$ (50 mM) and 50 µL of AgNPs (1 mM) and the absorption spectra were recorded immediately. The change in absorption at 664 nm was used for kinetic analysis.

Since the concentration of $NaBH_4$ was much higher than that of organic dyes, the degradation kinetics can be described by first-order rate law[12]. Therefore, the reaction kinetics can be described as $\ln(C_t/C_0) = -kt$, where k is the apparent first-order rate constant, t is the reaction time. C_t and C_0 are the concentrations of substrate at time t and 0, respectively. The rate constant, k was obtained directly from the slope of the linear part of the kinetic trace.

3. Results and Discussion

3.1. Silver nanoparticles preparation and characterization

Biogenic AgNPs are usually obtained by incubating $AgNO_3$ solution with aqueous plant extracts[4]. Addition of a 1 mM $AgNO_3$ solution into *D. bipinnata* aqueous extract produced a colour change from colourless to yellow (Fig. 1) after 48 h of incubation and showed a surface plasmon resonance (SPR) absorption peak at 450 nm, characteristics of a AgNPs[13]. Irradiating the mixture of *D. bipinnata* aqueous extract and 1 mM $AgNO_3$ by sunlight produces an intense yellow colour within 5 min and showed SPR absorption peak at 445 nm. This indicates the formation of nanosized silver. In order to confirm the complete reduction of Ag^+ to Ag^0, sodium borohydride was added to the performed AgNPs. No changes were observed in UV-Vis spectra, confirms the complete reduction process. Both, room light and sunlight irradiated preparation showed broad SPR band, which is an indicative of polydispersed NPs formation in the aqueous solution[14].

Since sunlight is also a source of UV radiation, we performed experiments at constant concentration of $AgNO_3$ and *D. bipinnata* aqueous extract under ambient conditions in the lab using UV light. The exposure to UV light for 3 h produces a colour change from colourless to brown colour and showed a very broad SPR peak at 485 nm. The position, width of the

absorption peak and intensity of the peak depends on the particle size, shape and dielectric constant of the surrounding medium[15]. All these experiments clearly indicate the involvement of light in the reduction of Ag^+ to Ag^0. These results also suggest that the phytomolecules present in the extract are responsible for the photochemical reduction of Ag^+ ions.

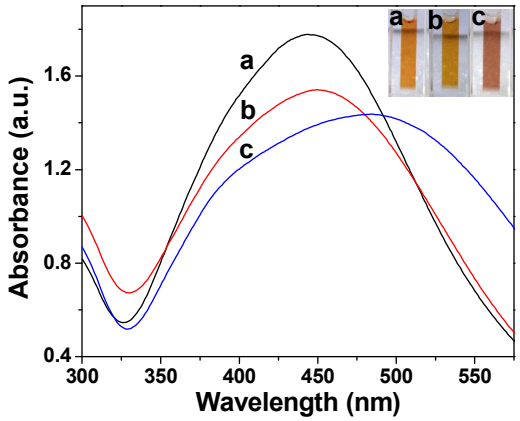


Fig.1: (A) UV-Visible spectra of AgNPs prepared from aqueous extract of *D. pinnata* mediated by (a) sunlight (b) room light and (c) UV light. Inset corresponds to photographs of the AgNPs solution formed at different conditions.

The dispersity of AgNPs prepared by room light, sun-light and UV-light was evaluated by comparing the full width at half-maximum (FWHM) from the UV-Vis spectra[16]. The FWHM calculated for AgNPs synthesized at sunlight, room light and UV light are 146 nm, 155 nm and 183 nm, respectively. These analyses suggest that AgNPs synthesized by different light sources are highly polydispersed. The stability of the synthesized AgNPs was determined by measuring their intensities at the peak maximum over a period of 7 days and no significant changes in the intensity were observed.

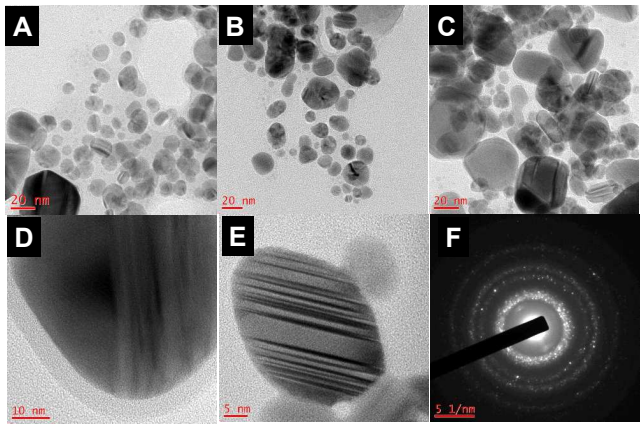


Fig. 2: TEM images of AgNPs prepared from aqueous extract of *D. pinnata* mediated by (A) sunlight, (B) room light, (C) UV light, (D) & (E) HRTEM and (F) SAED pattern.

As inferred from TEM images (Fig. 2), the formed AgNPs are highly polydispersed with diverse shapes, supporting the absorption spectral characteristics. The size of the particles measured from TEM images for the AgNPs prepared at sunlight, room light and UV light are in the range of 10-35 nm, 8-40 nm and 15-70nm, respectively. About 4 nm thickness of the capping agent stabilizing the NPs was detectable in Fig. 2D, indicating that the phytoconstituents present in *D.bipinnata* protect the AgNPs from aggolomerization. FTIR analysis further confirmed the presence of phytoconstituents around the nanoparticles (Fig. S1). The observed fringes pattern in HR-TEM (Fig. 2E) and selected area electron diffraction (SAED) pattern supports the crystalline nature of the as-prepared AgNPs (Fig. 2F).

3.2. Phytochemical analysis and isolation of BS

In order to identify the compound responsible for the photochemical reduction, we performed column chromatography on the *D.bipinnata* aqueous extract. The fractions converted the $AgNO_3$ into AgNPs under the sunlight was carefully collected and subjected to further chromatography steps. A compound (BS) was isolated as a white crystalline solid and had a molecular formula of $C_{35}H_{60}O_6$. It responded positively to the Liebermann-Burchard test for steroids[17]. Its IR absorption spectrum showed peaks at 3340cm^{-1} corresponding to hydroxyl (-OH) stretching, at 1720 cm^{-1} (corresponding to >C=O stretching) and absorption bands at 2900-2850cm^{-1} indicating the presence of possible methylene and methine groups. The EIMS spectrum had a molecular ion at m/z 414[M-sugar]$^+$ corresponding to the aglycone- steroid[18].

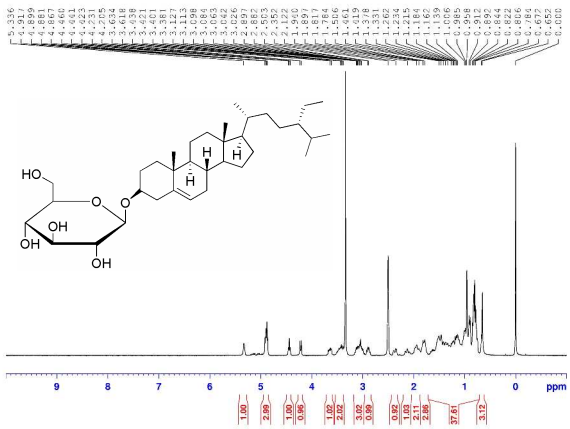


Fig. 3: (A) ^{1}H NMR spectrum of β-sitosterol-D-glucopyranoside

The ^{1}H NMR spectrum (Fig. 3) showed the presence of an olefinic signal (δ_H 5.08), indicating a >C=C< system in the ring. A one proton broad multiplet at δ_H 4.44 showed a cross peak with C2 protons and C4 proton in HETCOR and this signal was assigned to C3 methine proton. A plethora of multiplets found in the range δ_H 1.1- 2.14 and these were informative on the presence of different methylene and methine protons of the steroidal structure. The other proton resonances were allocated to the glucopyranoside. Further evidence was also provided by the ^{13}C-NMR that showed resonances for 35 carbon atoms. The C3 carbon resonated at 71.73 ppm. The anomeric and the oxygenated methylene carbons of the sugar appeared at 100 and 61 ppm respectively (Fig. S4). Thus on the basis of the spectral data, the structure of the compound was elucidated as stigmast-5-en—3-O-β-D-glucopyranoside (β sitosterol glucoside). All the spectral data were in complete concurrence with the literature[19].

3.3. Role of BS on the synthesis of AgNPs

The fraction containing the compound BS produced the AgNPs and exhibited significant SPR and so did the isolated compound, BS. At constant concentration of $AgNO_3$ and BS under ambient conditions in the lab, sunlight and UV light exposure produces AgNPs with characteristic SPR peak at 430, 460 and 455 nm, respectively (Fig 4). It was observed that the sunlight mediated formation of AgNPs occurred in 5 min, whereas the room light and UV light irradiation took 48 h and 3 h, respectively to produce AgNPs. The FWHM calculated for AgNPs synthesized by BS in sunlight, room light and UV light are 137 nm, 168 nm and 174 nm, respectively. Similar observations were made with the aqueous extract of *D. bipinnata* (Fig 1). This study confirms that BS present in the aqueous extract is most likely involved in the formation of AgNPs. To further substantiate the involvement of BS in the formation of AgNPs, we isolated BS from the other sacred grasses, *Imperata cylindrica* and *Cynodon dactylon* and subjected to AgNPs synthesis. Interestingly, BS isolated from *I. clindrica* and *C. dactylon* also produced AgNPs (unpublished observation).

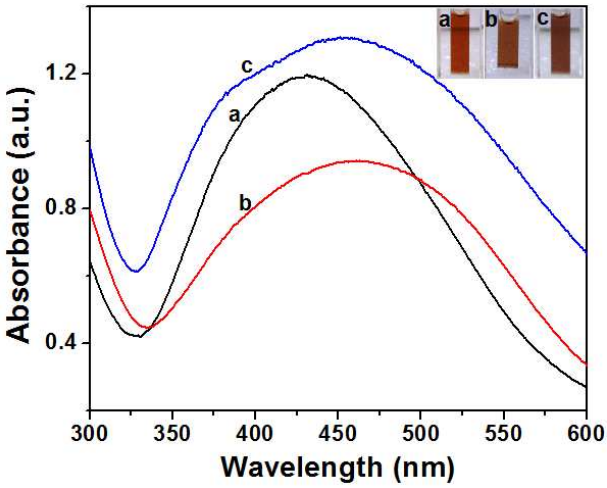


Fig. 4: (A) UV-Visible spectra of AgNPs prepared using β sitosterol glucoside mediated by (a) sunlight (b) room light and (c) UV light. Inset corresponds to photographs of the AgNPs solution formed at different conditions.

The microscopic structure of the BS mediated silver nanoparticles was investigated by HR-TEM (Fig S2). TEM images confirm the formation of silver nanoparticles with the size range between 8 and 60 nm. SAED pattern supports the formation of polycrystalline silver nanoparticles (Fig. S2). The size-distribution of nanoparticles was further determined by particle-size analyzer. The average particle size for BS and *D. bipinnata* aqueous extract stabilized AgNPs was found to be 149 and 183 nm, respectively (Fig. S5). These values are higher than the values obtained from HRTEM. The difference in size estimated is due to the differences in the techniques. The particle size analyzer measures the size of the cluster rather than the individual particles. However, the observed higher values can also attributed to the presence of phytoconsituents around the AgNPs. Zeta potential estimated for BS and *D. bipinnata* aqueous extract stabilized AgNPs was found to be -15.9 and -12.5 mV [16]. These values indicate that the AgNPs are stable due to the electrostatic repulsion (Fig. S6).

3.4. Possible mechanism of AgNPs formation

From the above data, it is clear that a photochemical reaction is involved in the reduction of Ag^+ to Ag^0. The major requirement of any photochemical electron transfer reaction is the generation of highly reactive species by light. To confirm the production of reactive species (if any) by light, we embarked on a fluorimetric detection of it. The fluorescent probe 2',7'-dichlorodihydrofluorescein diacetate (DCFH-DA) is widely used as an oxidant-sensitizer and is non fluorescent, and switches to a highly fluorescent DCF, when oxidized by ROS and other peroxides[20]. The addition of DCFH-DA to the *D. bipinnata* extract and BS showed highest fluorescence intensity in the sunlight irradiated samples compared to samples kept at room light, plausibly due to a higher generation of ROS after sunlight irradiation (Fig. 5A and 5B). Next, we examined the presence of free radical using the known free radical scavenger DPPH[21]. The samples irradiated with sunlight showed highest free radical scavenging activity, consistent with the generation of ROS (Fig. 5C). BS alone also exhibited the same profiles with DCFH-DA and DPPH.

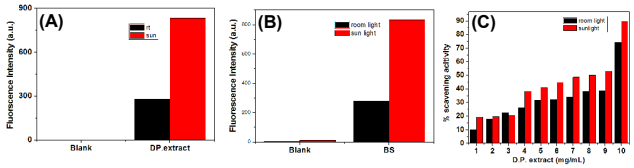
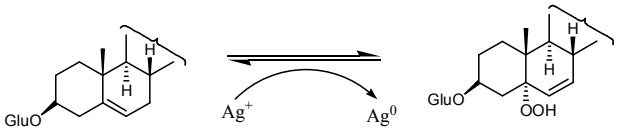


Fig. 5: Reactive oxygen species assay, (A) *D. bipinnata* aqueous extract and (B) β sitosterol glucoside. (C) Free radical scavenging assay.

Based on this result, we hypothesized the involvement of redox reaction in the formation of nanoparticles. Phytosterols are susceptible to photoxidation[22] with light through a formation of a transient endoperoxide. While forming the transient endoperoxide, BS releases the electrons for the formation of AgNPs (Scheme 1). This endoperoxide are presumably present in equilibrium under the light. To support the proposed mechanism, we investigated the structure of isolated BS after exposing to sunlight as well as with UV light. ^1H NMR and ^{13}C NMR clearly showed unaltered structure (Fig. S7 and S8), indicating that the BS is only mediating the sunlight induced reduction of silver ion to silver nanoparticles by undergoing transient transformation. However, the amphiphilic property of BS might play important role in preventing the nanoparticles agglomeration.



Scheme 1: BS mediated formation mechanism of AgNPs.

3.5. Application of DpAgNPs in dye degradation

Organic dyes releases from the industries are severely affecting the environment by contaminating the soil and water bodies[23]. The removal of these pollutants requires expensive procedures, which are not affordable by the small scale industries[24]. Of late there is a considerable interest in employing noble metal nanoparticles in degrading the organic dyes[25]. Recently, green synthesized AgNPs from plant extracts have been shown to

degrade methyl red dye under UV light[26]. Nevertheless, the sunlight induced synthesized AgNPs from plant extracts that offer an eco-friendly system, have never been explored in detail for degrading toxic organic dyes. Methylene blue (MB) has been widely used as a model dye to investigate the degradation of basic dyes[27]. MB is widely used in textile industry for dyeing cotton, wool, silk and acrylic fibers[28]. The previous reports on the degradation of MB has been based on hydrogen peroxide, ascorbic acid, photodecompostion on TiO_2, photocatalytic degradation on Ag^+ doped TiO_2[27], while the present study reports the catalytic degradation of MB using biogenic AgNPs and $NaBH_4$.

In aqueous medium MB shows an absorption maximum at 664 nm accompanied with a shoulder at 614 nm. Addition of *D. bipinnata* AgNPs and reducing agent, $NaBH_4$ to the MB solution gradually diminishes the blue colour (Fig 6A). As shown in Fig. 6A, the MB absorption peak decreases in a time dependent manner. In absence of *D. bipinnata* AgNPs or in the presence of $NaBH_4$, the peak at 664 nm remains undisturbed for more than 10 min. The discolourization and complete loss of MB absorption peak signify the importance of *D. bipinnata* AgNPs in degrading the organic dye, methylene blue. In order to follow the rate of degradation, time dependent change in the intensity at 664 nm was monitored using UV-Vis spectrophotometer (Fig S9). The linear correlation between ln (A_t/A_0) and the reaction time indicate the degradation is a *pseudo* first order reaction. The rate constant is calculated from its slope and is found to be 0.05 s^{-1} for the degradation of MB assisted by the *D.bipinnata* AgNPs. Noteworthy that BS-AgNPs also exhibit similar effect in degrading MB. This study clearly indicates that the bio-inspired AgNPs reported in this study has the potential to degrade hazardous organic dye releases from the industry.

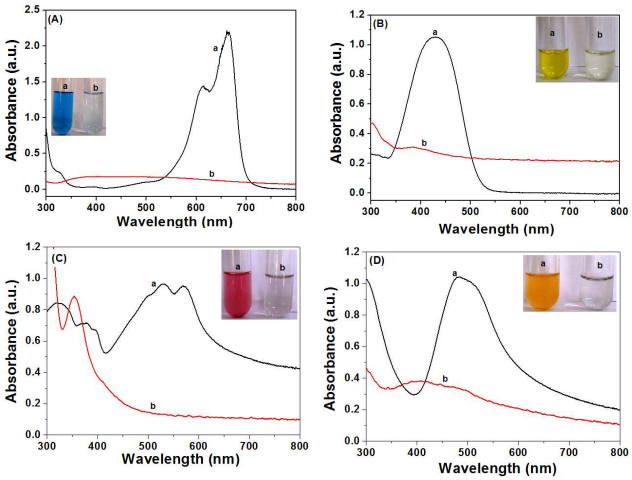


Fig. 6: Catalytic dye degradation. (A) Methylene blue, (B) Methyl red, (C) Congo red and (D) Acridine orange. In each panel (a) corresponds to the UV-Visible spectra of organic dye and (b) corresponds to its reduced product. AgNPs act as a catalyst and $NaBH_4$ act as a reducing agent. Insets correspond to the photograph of organic dye (a) and its reduced product (b).

As a proof of concept, we further evaluated the *D. bipinnata* AgNPs mediated degradation of other organic dyes, methyl red, congo red and acridine orange (Fig.6). Irrespective of the dye nature, addition of *D. bipinnata* AgNPs and $NaBH_4$ gradually diminishes the original colour of the dye to colourless. The discolouration happens in a time dependent manner. To obtain the rate of degradation, we monitored the change in the intensity with respect to time using UV-Vis spectrophotometer (Fig S9).

Table 1: Rate constant obtained for dye degradation by *D. bipinnata* AgNPs

Dye	Rate constant (s^{-1})
Methylene blue	0.057 ± 0.007
Methyl red	0.038 ± 0.004
Congo red	0.030 ± 0.003
Acridine orange	0.025 ± 0.006

The rate constant for the dye degradation were calculated as detailed in material and methods. Noteworthy that the $NaBH_4$ alone can decolourize the tested organic dyes, but it requires 5 h, 7 h, 8 h and 12 h to decolourize methylene blue, methyl red, congo red and acridine orange, respectively. Nevertheless, the kinetic analysis reported in Table 1 clearly indicates that the presence of *D. bipinnata* AgNPs accelerates the rate of degradation and almost all the tested dyes are degraded in less than 2 min. These results clearly indicate the catalytic role of *D. bipinnata* AgNPs in degrading the organic dyes and a significant improvement in degrading the organic dyes in shorter time interval.

4. Conclusion

D. bipinnata has been considered as a sacred plant in Indian mythology. For the first time, we reported the preparation of AgNPs using the aqueous extract of *D. bipinnata* under sunlight irradition. The use of natural light source, one-pot process, less reaction time, cost-effective, longer stability and reproducibility, renders this method more advantageous over the other available methods. The identification of bio surfactant—glycosides in the aqueous extract further delineated the role of surfactant like phytomolecules in the formation of AgNPs. The as-prepared *D. bipinnata* AgNPs exhibited a good catalytic activity during the catalytic degradation of environmental hazardous organic dyes, methylene blue, methyl red, congo red and acridine orange, in aqueous solution. Further testing their dye degrading ability on more number of hazardous dyes and industrial dye effluent would help in recommendations of these AgNPs for industrial use.

Author contributions

KBAA and S.S performed research and analyzed data. S.A designed research and characterized *D.bipinnata* and isolated BS, analyzed data, wrote the manuscript. V.A designed research and characterized AgNPs, analyzed data, wrote the manuscript.

Acknowledgment

KBAA and SS earnestly acknowledge the teaching assistantship from SASTRA University. VA acknowledges the financial support from Department of Science and Technology, Government of India (SB/FT/LS-217/2012). SA earnestly acknowledges the funding source from Department of Science and Technology, Government of India (SR/FT/CS-10/2011) and the TRR fund.

Notes and references

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Electronic Supplementary Information (ESI) available: kinetics data, ^{1}H-NMR spectra. See DOI: 10.1039/b000000x

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