Catalytic Reduction of Acid Blue 113 Dye by Silver Nanoparticles Synthesized Using *Tabebuia Aurea* Leaf Extract

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Abstract

The noble metal nanoparticles are of particular interest due to their wide applications in different fields. Among them silver nanoparticles may provide solution to technological and environmental problems in the area of wastewater treatment. silver nanoparticles are conventionally fabricated using chemical methods with toxic chemicals. We report here rapid green synthesis of stable silver nanomaterials employing *Tabebuia aurea* leaf extract. UV–vis spectrum displayed surface plasmon resonance at 410 nm which affirmed the synthesis. The SEM image showed the nano-size and spherical morphology of the synthesized nanoparticles. EDX analysis established the formation of elemental silver. XRD pattern of nanoparticles pertaining to (101) plane, shows that the fcc crystallinity. DLS confirmed the colloidal stability of nanoparticles with zeta potential value of −26.7 mV. FTIR analysis suggests that the presence of various functional moieties of the leaf extract accountable for the formation and capping of nanoparticle synthesis. The efficiency of synthesized silver nanoparticles as a potential catalyst in the reduction of the acid blue 113 by $NaBH_4$ is established in the present study. The process followed pseudo-first order model with degradation rate constant of 0.1335 min^{-1}.

Keywords: *Tabebuia aurea* ; Acid blue 113; Silver nanoparticles; Catalytic reduction; Green synthesis.

1. Introduction

The textile processing industry requires huge quantity of good quality water and discharges large volumes of wastewater with a variety of pollutants. Among them, the dye containing wastewater is notoriously hard to treat, thus limiting its reusability. Azo dyes are widely employed in textile industries for dyeing fabrics. It constitutes 60-70% of all synthetic dye stuffs. The remedial dye concentration of the effluent is reported to be 10-200 mg/L (Nautiyal & Shukla, 2018). Acid Blue 113, most popular azo dye, used for the coloration of silk, wool, leather and other fabric materials can cause numerous ecological issues and health risks for living beings including humans, due to the presence of benzene rings in their structures (Mariselvam, Ranjitsingh, Thamaraiselvi, & S.J., 2019). Therefore, it is important to eliminate these pollutants before being discharged directly into the environment. Processes like adsorption,

membrane filtration, electrochemical methods and microbial degradation have been conventionally used in the treatment of effluent dye. However, it is hard to eliminate the said dyes from wastewater, owing to its aromatic structure. Advanced oxidation processes are gaining importance for the effective reduction of azo dyes and cost effectiveness. Nanocatalysis has emerged as potential agents for the synthetic dye reduction (Saha, Begum, Mukherjee, & Kumar, 2017).

Recently, silver nanoparticles (SNP) are of particular interest among the researchers working in diverse applications in the field of medicine, catalysis, antimicrobial activity and wastewater treatment. The SNP possess higher surface to volume ratio and relatively small sizes attributed to their distinctive chemical, optical and physical properties compared to bulk materials(Junejo, Baykal, & Sirajuddin, 2014).Conventionally the SNP are synthesized by various chemical and physical with the use of toxic chemicals which causes serious environmental problems and requires high energy. Therefore, it is desirable to develop a environmentally friendly method which would not involve the toxic chemicals. Green synthetic approaches of SNP with plant extracts have emerged as a promising method as they are rapid, simple, less expensive and environmentally benign(Hamedi, Shojaosadati, & Mohammadi, 2017). Various studies exist on green synthesis of SNP using various plants such as *Convolvulus arvensis* (Hamedi et al., 2017), *Psidium guajava* (Wang, Wu, Xie, Wu, & Wu, 2018), *Nigella arvensis* (Chahardoli, Karimi, & Fattahi, 2018) and *Bridelia retusa* (Vinayagam, Varadavenkatesan, & Selvaraj, 2018).

The present work aims to study the reduction of Acid Blue 113 dye by $NaBH_4$ along with SNP as the catalyst. The SNP are synthesized by a green approach, using an extracted derived from *Tabebuia aurea* leaf as a dual bio-reductant and stabilizer. The SNP are characterized with a variety of suitable techniques.

2. Materials and Methods

2.1 Materials

Silver nitrate ($AgNO_3$) and acid blue 113 dye solutions were procured from Merck. $NaBH_4$ was obtained from SRL, India. Double-distilled water (DDW) was employed throughout the procedures.

2.2 Preparation of *Tabebuia aurea* leaf extract

Fresh leaves of *Tabebuia aurea* were sourced from in and around the region of Manipal, Karnataka, India. The leaves were thoroughly rinsed with tap water and then subsequently washed with double distilled water. The leaves were then sliced into tiny pieces and air dried by spreading it on blotting paper. The mixture of 10 g of leaves and 100 cc double distilled water was incubated in a water bath preset at 80°C, 20 min. After bringing to ambient conditions, the clear extract was obtained by processing through Whatman No. 1 filter paper and refrigerated at 4°C, until further use.

2.3 Formation of silver nanoparticles (TA–SNP)

In a typical procedure for SNP fabrication, a volume of 10 mL leaf extract of *T.aurea* was mixed with 90 cc of 1 mM $AgNO_3$ solution in a 250 cc Erlenmeyer flask. In order to achieve the Ag^+ ions reduction, the mixture was incubated in a preset water bath temperature of 80°C for a duration of 10 min. The observed color transformation was to confirm the formation of *T. aurea*-mediated silver nanoparticles (TA-SNP).

2.4 Characterization of TA–SNP

SEM analysis (Carl Zeiss, EVOMA18) was performed to analyze the surface morphology. The elemental constituents of TA-SNP mixture were determined using Oxford Instruments Energy-Dispersive Spectroscopy. XRD analysis was performed using a X-Ray diffractometer (Rigaku, Miniflex 600) with operating conditions of 40 kV and 15 mA employing Cu Kα radiation. The functional moieties of the TA-SNP solution was recognized using FTIR spectrophotometry, operated in the wavenumber range between 4,000 and 400 cm^{-1}. To estimate the hydrodynamic size distribution and net charge of the synthesized TA-SNP, DLS analysis was performed using photon correlation spectrometer (Malvern, Zetasizer Nano).

2.5. Catalytic reduction of acid blue 113 dye

To determine the catalytic efficiency of TA-SNP, two set of reactions were conducted using a clean quartz cuvette at ambient conditions. Initially, 3 mL of diluted acid blue 113 dye solution reacted with 0.1 mL stable TA-SNP along with 0.1 mL of fresh 0.1 M $NaBH_4$. Further, the control reaction proceeded using the same composition, but, in the absence of TA-SNP. The UV–vis spectrophotometer was used for the periodic monitoring of the progress of both the reactions.

3. Results and Discussions

Chapter 1 The mixing of the leaf extract of *Tabebuia aurea* with aqueous silver nitrate solution and the subsequent heating of the resultant mixture lead to a visible color transformation of the originally transparent solution to yellowish brown (Fig. 1). The color change indicates the formation of zero-valent TA-SNP with the help of active moieties on the *T. aurea* leaf extract. The size, shape and agglomeration state of the SNP influences its optical properties. Therefore, UV–vis spectroscopy stages a crucial role for the identification and characterization of SNP(Edison, Lee, & Sethuraman, 2016). UV–vis spectra of the synthesized TA-SNP is depicted in Fig. 2A. The discrete peak observed at 410 nm corresponds to the surface plasmon resonance (SPR) of the SNP. A similar SPR value has been reported by other researchers using the green approach (Narenkumar et al., 2018; T Varadavenkatesan, Selvaraj, & Vinayagam, 2019). In general, SNP exhibit a absorbance maxima in the 400-500 nm range, depending on the size and morphology of the SNP (Kumar, Smita, Cumbal, & Debut, 2014). In general, the absorption peaks between 410 and 420 nm confirms the spherical shape of the SNP (T Varadavenkatesan et al., 2019).

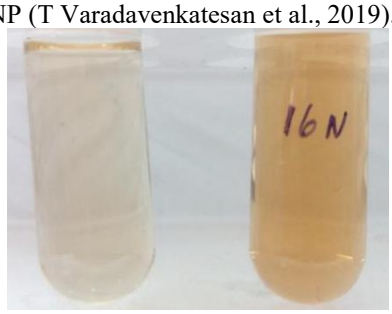

Fig.1. Color change of silver nitrate to silver nanoparticles (yellowish brown, right) by the addition of *Tabebuia aurea* leaf extract (pale yellow, left)

The size and surface morphology of the TA-SNP are analyzed by SEM (Fig. 2B). The SEM micrographs revealed the spheroidal shape and crystallinity with the particle size in the nanoscale (Fig. 2B). The TA-SNP are distributed uniformly in the absence of rough surface and aggregates.EDX analysis shows the profile of metallic elements

present in the reaction mixture. The absorption band is evidenced at approximately 3 keV, that is characteristic of the absorption band, corresponding to zerovalent silver (Saware & Venkataraman, 2014). This may be clearly seen in the graphical representation shown by the EDX analysis (Fig. 2C) in support of UV–Vis results, that proved the conversion of silver ions to its zerovalent form. The appearance of elemental peak of calcium is because of the glass slide, holding the TA-SNP. The crystallinity of TA-SNP was identified by XRD spectra with 2Θ values covering the 20° to 80° range. XRD analysis displayed the intense peak at 2Θ value of 32.8° (Fig. 2D). XRD pattern of TA-SNP reveals, the occurrence of peak correspond to (101) plane of fcc structure (JCPDS no. 04–0783) (Yadav, Manjunath, & Selvaraj, 2019).

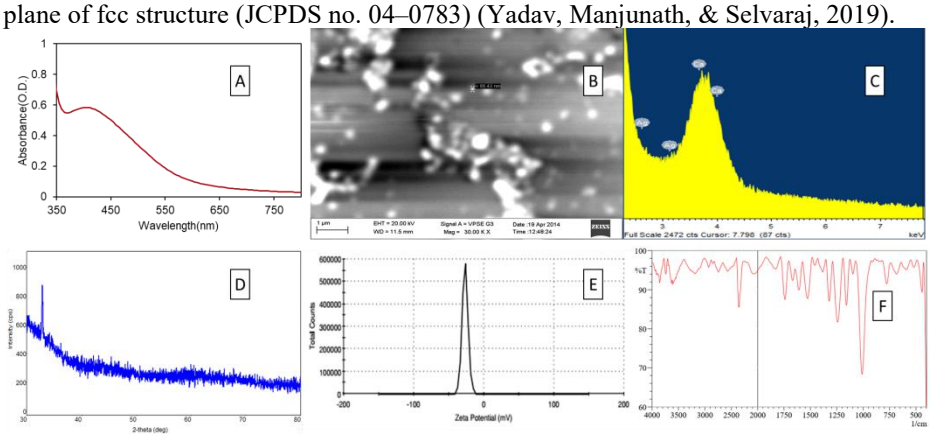

Fig. 2. (A) UV-vis spectra, (B) SEM image, (C) EDX profile, (D)XRD pattern, (E) Zeta potential and (F) FTIR spectra of the TA-SNP.

The measurement involving zeta potential verified the stability of the synthesized TA-SNP. The standard value of zeta potential for the stable nano suspension is ± 30 mV(Padalia, Moteriya, & Chanda, 2015). The zeta potential of − 26.9 mV (Fig. 2E) indicated that the surface of the TA-SNP was negative charged and electrostatic repulsion between them responsible for the dispersion in the medium. The DLS measurement also provides the particle mean size and its distribution data. The DLS pattern reveals that TA-SNP have a zeta mean diameter of 104 nm with PDI of 0.278. The average size of the TA-SNP measured by DLS method is slightly higher compared to the particle size estimated by SEM analysis because it measures the hydrodynamic radius (Singhal & Bhavesh, 2011).

The FTIR measurement helps in finding out the possible functional moieties, responsible for reduction cum capping effect, responsible for the effective stabilization of TA-SNP. FTIR spectra of TA-SNP nanoparticles (Fig. 2F) exhibited sharp peaks at 3855, 3739, 3629, 2354, 1741, 1608, 1527, 1323, 1242, 1159, 1010 and 777 cm^{-1}suggesting the presence of primary and secondary amines, flavonoids, carboxyl, amino, phenolic and secondary alcoholic groups (Kumar, Smita, Cumbal, & Debut, 2017; Thivaharan Varadavenkatesan, Selvaraj, & Vinayagam, 2019) leading to the reduction, capping and effective stabilization of TA-SNP.

The present study investigated the catalytic efficacy of TA-SNP nanocatalyst towards the reduction of Acid blue 113 with $NaBH_4$. The reduction reaction occurred at ambient temperature and the reaction was examined using UV–vis spectra. As can be observed in Fig. 3, the absorption peak at 566 nm (λ_{max} of Acid blue 113) considerably reduced within 20 min and other peaks appeared at 430 and 270 nm belonging to the degraded products. For the control reaction, i.e., in the absence of nanocatalyst (TA-

SNP), absorbance of Acid blue 113 (566 nm) decreased slowly and meager changes were noticed after several hours. The action of reduction occurred as electron transfer from the donor $NaBH_4$ to the acceptor Acid blue 113 after both of them get adsorbed onto the surface of TA-SNP (T Varadavenkatesan et al., 2019).

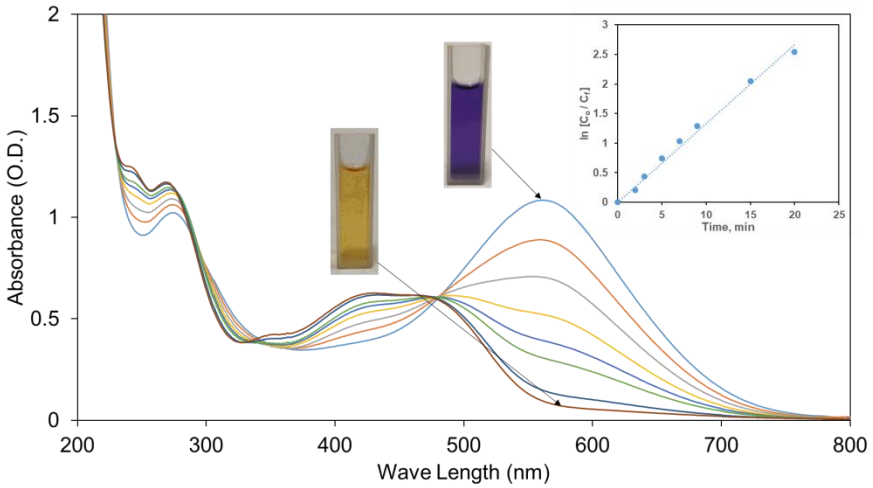

Fig. 3. Reduction of Acid blue 113 by $NaBH_4$ with TA-SNP.

Consequently, by a pseudo-first order mechanism, the kinetic data was fitted. The reaction kinetics is defined by $\ln[C_0/C_t] = kt$, where k is the apparent first-order rate constant (min^{-1}), t, the reaction duration. C_0 and C_t denote the absorbance of Acid blue 113 at time 0 and t, respectively. A linear correlation between reaction duration and $\ln[C_0/C_t]$ could be achieved in the reduction catalyzed by nanocatalyst of TA-SNP (inset of Fig. 3), and the constant rate of k is calculated to be 0.1335 min^{-1}. The complete disappearance of Acid blue 113 absorption peak signifies the catalytic efficacy of TA-SNP for the reduction Acid blue 113. The reduction process required relatively shorter time as compared to the photocatalytic degradation of Acid blue 113 with other metal nanocatalyst (Sathishkumar et al., 2014; Talebi, Chaibakhsh, & Moradi-Shoeili, 2017).

4. Conclusions

Due to the prevailing drawbacks of physico-chemical approaches for synthesis of SNP, there is a necessity to follow an easier, less expensive and environmentally benign procedures. The study has demonstrated that green synthesis of stable spherical SNP in a single step with the leaf extract of *T. aurea* without use of toxic chemicals. The phytochemicals in the leaf extract of *T. aurea* play a dual role of reductants-cum-stabilizers for the formation of TA-SNP as evident from the FTIR study. SEM and DLS studies verified the formation of well-dispersed and spherical shape nanoparticles. EDX and XRD studies confirmed the formation crystalline silver nanoparticles. In comparison with other methods reported in the literature, the green synthesized TA-SNP exhibited very good catalytic activity while being employed for the reduction of Acid blue 113 by $NaBH_4$ at room temperature. Thus, the present study would bring a new scope for removing the Acid blue 113 in the environment.

5. References

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