Green Synthesis, Characterization and Catalytic Degradation Ability of Silver Nanoparticles Synthesized Using *Thunbergia Grandiflora* Leaf Extract

Thivaharan Varadavenkatesan[a], Ramesh Vinayagam[b] and Raja Selvaraj[b]*

[a]*Department of Biotechnology, Manipal Institute of Technology (MIT), Manipal Academy of Higher Education (MAHE), Manipal, Karnataka- 576104, India*
[b]*Department of Chemical Engineering, Manipal Institute of Technology (MIT), Manipal Academy of Higher Education (MAHE), Manipal, Karnataka- 576104, India, E-mail:* raja.s@manipal.edu

Abstract

Now-a-days, green-synthesis methods for the preparation of nanomaterials have gained attention due to the simple and low-cost procedures involved and eco-friendliness. The formation of nanoparticles by employing various plant products is one among them. In the current investigation, silver nanoparticles (SNPs) have been synthesized by using the leaf extract of *Thunbergia grandiflora* and characterized by various methods. The formation of SNP was first visually affirmed by the color transformation of the leaf extract to brown, upon addition of silver nitrate while heating. The UV-vis image portrayed a distinctive peak at 431 nm. The SEM image revealed spherical nanoparticles with few agglomerations while the EDS confirmed the presence elemental silver. The XRD spectrum portrayed the crystalline structure with (1 1 1) plane of fcc structure. The stability of the nanoparticles was ascertained by the surface potential charge of –18.2 mV. The capping action of biomolecules present in the leaf extract was verified from the distinct bands observed in FTIR data. The catalytic activity of the SNP to degrade an industrial dye, Acid red 88, using sodium borohydride as reducing was demonstrated and it was observed that the degradation kinetics followed first order reaction. Hence, the outcome of this study may play a significant role in the nanoremediation of dye-laden wastewater.

Keywords: Thunbergia grandiflora; silver nanoparticles; green synthesis; dye degradation; acid red 88 dye

1. Introduction

In the recent past, nanoparticles have garnered attention because of their enhanced characteristics (mechanical, chemical, thermal, electrical and biological) when compared to their native bulk state. Silver nanoparticles, one of the noble metal nanoparticles have been extensively used for the various environmental applications such as wastewater treatment, bioremediation and biosensing (Kumar, Vizuete, Sharma, Debut, & Cumbal, 2019).

Conventionally, various synthesis methods namely chemical reduction, electrochemical, microwave and ultrasonic irradiation are available for the silver nanoparticle synthesis. However, these methods are either costly or make use of

harmful chemicals and thus they are not sustainable. In contrast to this, an upcoming method – "green nanotechnology (GT)" eliminates the use of harmful chemicals and employs a simple/benign method. Few examples of GT methods include the use of plant extracts and microorganisms for the synthesis. In particular, GT method based on the plant extracts is popular due to the simplest procedures involved and the process is rapid. The plant components present in the extract such as poly-phenols, proteins, vitamins and saccharides aid the formation and stabilization of SNPs (Ahmed, Ahmad, Swami, & Ikram, 2016).

Thunbergia grandiflora, is a climber which belongs to Acanthaceae family. *T.grandiflora* yields blue flowers and the plant leaf has many phytochemicals (Antonisamy, Aparna, Jeeva, Sukumaran, & Anantham, 2012). According to the literature, the leaf extract of this plant has been used to synthesize silver nanoparticles and antibacterial effect has been demonstrated (Mathew & Thomas, 2019). However, the catalytic activity of the silver nanoparticles has not been explored yet. Hence, an azo dye – acid red 88 (widely used in textile industries for dyeing various materials and is carcinogenic in nature)(Konicki, Sibera, & Narkiewicz, 2017) has been chosen in the present study and the catalytic degradation of this acid red 88 by SNPs in the presence of $NaBH_4$ has been studied.

Herein, the objectives of this study are to synthesize the SNPs by employing the leaf extract of *T. grandiflora*, characterize and explore the catalytic ability of the SNPs for the degradation of acid red 88.

2. Materials and Methods

2.1. Materials

Silver nitrate ($AgNO_3$) and acid red (AR) 88 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 Thunbergia Grandiflora Leaf extract (TGLE)

10 g of clean-chopped leaves were blended with 100 ml DDW and kept in a thermostat for 45 min at 85°C. which yielded a pale yellow extract. After cooling the contents, a filtrate was obtained and named as *Thunbergia grandiflora* leaf extract (TGLE) which was kept in a fridge for further use.

2.3. Synthesis of SNPs (TG–SNPs)

Defined amount of TGLE (10 cc) was added to 1 mmol/m^3 $AgNO_3$ (90 cc) and kept in a water-bath at 85°C for half an hour. An occurrence of brown color designated the TG–SNPs synthesis.

2.4. Characterization

The change in color and absorbance of the TG–SNPs were documented using UV-Visible Spectrophotometer. The morphological nature and individual elements present in TG–SNPs were examined by SEM and EDS respectively. The crystallinity of the sample was recorded using X-Ray diffractometer (XRD). Existence of various functional groups were analyzed by Fourier Transform Infrared (FTIR) spectroscopy. The size and the stability of the TG–SNPs suspension were examined by dynamic light scattering (DLS) method.

2.5. Catalytic Degradation of AR 88 Dye

The catalytic ability of the TG– SNPs has been examined by the degradation of AR 88 in the presence of $NaBH_4$. All the reactions were carried out in a cuvette. At first, the absorbance of 3mL of AR 88 was recorded. 200µL of TG–SNPs was mixed with the dye solution. Immediately, 200 µL of 50 mM $NaBH_4$ was also added and the change in the absorbance with respect to regular time intervals at 505 nm was documented.

3. Results and Discussions

The color changes of the TGLE extract and $AgNO_3$ while synthesis process were first visually monitored. The pale yellow TGLE changed to brown color when adding colorless $AgNO_3$ while heating at 80°C for half an hour (Fig. 1A inset). As per the literature, SNPs show a characteristic peak between 400 and 500 nm (Sastry, Mayya, & Bandyopadhyay, 1997). Herein, a strong peak at 431 nm can be witnessed (Fig. 1A) which is in accordance with the reported value for the SNPs synthesized using *T.grandiflora* (Mathew & Thomas, 2019).

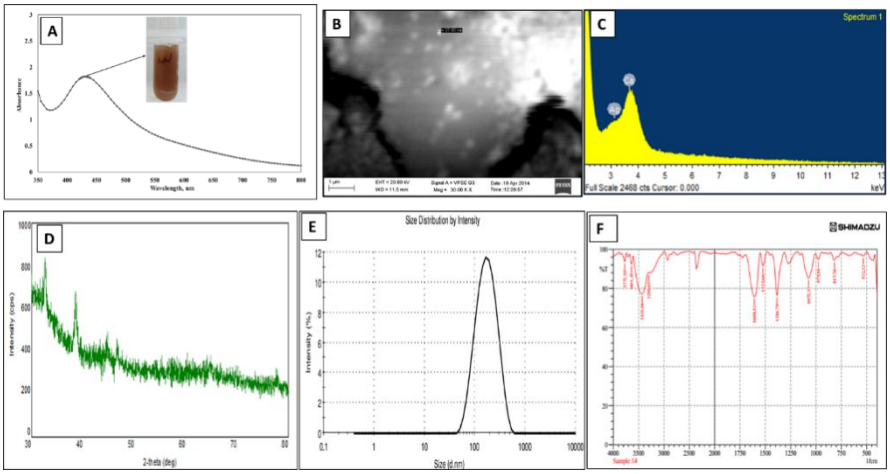

Fig. 1 (A) UV-vis spectra, (B) SEM image, (C) EDS image, (D)XRD spectra, (E) Particle size distribution by DLS and (F) FTIR spectra of the synthesized TG–SNPs.

Few aggregates with spherical morphology can be seen in SEM image (Fig. 1B). The aggregates of the nanoparticles might be due to the sample preparation methods involved or biomolecules existing in the TGLE (Devi & Joshi, 2015).

A peak for silver element around 3 keV can be witnessed (Fig. 1C) which is a characteristic feature for elemental silver. The existence of calcium peak possibly as a result of glass slide which held the nanoparticles (MubarakAli, Thajuddin, Jeganathan, & Gunasekaran, 2011).

The XRD image (Fig. 1D) indicated peaks at 2Θ (°) value of 32.58, 38.62 and 44.84 which corresponded to (1 0 1), (1 1 1) and (2 0 0) planes of the fcc crystalline structure which was in-line with the literature (Ramar et al., 2015).

The Z-average size of TG–SNPs was determined as 143.6nm by DLS (Fig. 1E). The PDI value was obtained as 0.218 which confirmed the mono-dispersion of the colloidal suspension. A negative surface potential charge (– 18.2 mV) substantiated the stability of the TG–SNPs (Almeida et al., 2010).

The FTIR image (Fig. 1F) displayed the bands (cm^{-1}) at 3433, 1524, 2950, 1384, 1072 and 1608 which denoted to the stretching of –OH, N-O, C=O, C-H, C-O and –NH bending respectively. In addition, the strong band at 2350 belonged to the S-H vibration of amino acids(de Matos & Courrol, 2014). The existence of these functional groups confirmed the stabilization of TG–SNPs by the phyto-components of TGLE.

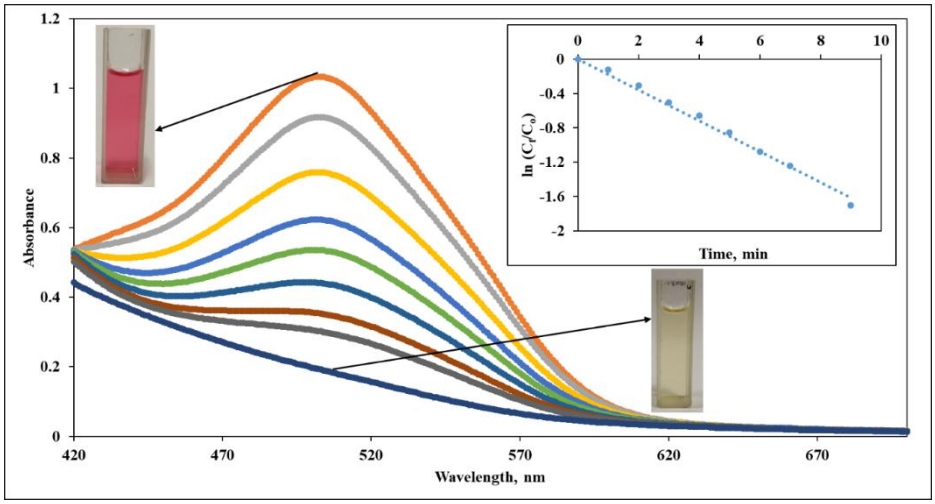

Fig. 2 Catalytic degradation of AR 88 dye in the presence of TG–SNPs and $NaBH_4$.

The catalytic degradation of AR 88 dye by TG–SNPs in the presence sodium borohydride is represented (Fig. 2). It is clear that the characteristic peak of dye at 505 nm starts declining as the time progresses during the process. The complete degradation happened within 9 min. The degradation process followed a first order model and a perfect straight line was obtained between ln [C_f/C_o] and "t" (Fig. 2 inset). The degradation constant has been calculated as 0.18 /min. TG–SNPs assisted the e^- movement from the borohydride anion to AR 88 dye for the degradation process (Ganapuram et al., 2015). Thus, the green-synthesized TG – SNPs generates a new scope of developing novel nanocatalysts for the degradation dyes in wastewater.

4. Conclusions

In the present investigation, SNPs have been successfully synthesized using the leaf extract of *Thunbergia grandiflora* and characterized by many methods. The catalytic ability of TG–SNPs for the degradation of AR 88 dye has been demonstrated in the presence of a reducing agent NaBH4. The first order degradation constant was estimated as 0.18 min^{-1}. The method reported here is very simple, environmentally benign and the nanoparticles formed in this process can be used for the degradation various dyes in wastewater.

5. References

Ahmed, S., Ahmad, M., Swami, B. L., & Ikram, S. (2016). A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: A green expertise. *Journal of Advanced Research*, *7*(1), 17–28.

Almeida, J. S., Lima, F., Da Ros, S., Bulhoes, L. O. S., de Carvalho, L. M., & Beck, R. C. R. (2010). Nanostructured systems containing rutin: in vitro antioxidant activity and photostability studies. *Nanoscale Research Letters*, *5*(10), 1603.

Antonisamy, J. M. @, Aparna, J. S., Jeeva, S., Sukumaran, S., & Anantham, B. (2012). Preliminary phytochemical studies on the methanolic flower extracts of some selected medicinal plants from India. *Asian Pacific Journal of Tropical Biomedicine*, *2*(1, Supplement), S79–S82.

de Matos, R. A., & Courrol, L. C. (2014). Saliva and light as templates for the green synthesis of silver nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *441*, 539–543.

Devi, L. S., & Joshi, S. R. (2015). Ultrastructures of silver nanoparticles biosynthesized using endophytic fungi. *Journal of Microscopy and Ultrastructure*, *3*(1), 29–37.

Ganapuram, B. R., Alle, M., Dadigala, R., Dasari, A., Maragoni, V., & Guttena, V. (2015). Catalytic reduction of methylene blue and Congo red dyes using green synthesized gold nanoparticles capped by salmalia malabarica gum. *International Nano Letters*, *5*(4), 215–222.

Konicki, W., Sibera, D., & Narkiewicz, U. (2017). Adsorption of Acid Red 88 Anionic Dye from Aqueous Solution onto $ZnO/ZnMn_2O_4$ Nanocomposite: Equilibrium, Kinetics, and Thermodynamics. *Polish Journal of Environmental Studies*, *26*(6), 2585–2593.

Kumar, B., Vizuete, K. S., Sharma, V., Debut, A., & Cumbal, L. (2019). Ecofriendly synthesis of monodispersed silver nanoparticles using Andean Mortiño berry as reductant and its photocatalytic activity. *Vacuum*, *160*, 272–278.

Mathew, A., & Thomas, S. (2019). Green Synthesis, Characterization and Applications of Silver Nanoparticles using Thunbergia grandiflora Roxb. *Journal of Nanoscience and Technology*, 669–672.

MubarakAli, D., Thajuddin, N., Jeganathan, K., & Gunasekaran, M. (2011). Plant extract mediated synthesis of silver and gold nanoparticles and its antibacterial activity against clinically isolated pathogens. *Colloids and Surfaces B: Biointerfaces*, *85*(2), 360–365.

Ramar, M., Manikandan, B., Marimuthu, P. N., Raman, T., Mahalingam, A., Subramanian, P., … Munusamy, A. (2015). Synthesis of silver nanoparticles using Solanum trilobatum fruits extract and its antibacterial, cytotoxic activity against human breast cancer cell line MCF 7. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *140*, 223–228.

Sastry, M., Mayya, K. S., & Bandyopadhyay, K. (1997). pH Dependent changes in the optical properties of carboxylic acid derivatized silver colloidal particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *127*(1–3), 221–228.