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Impact of Spherical Gold Nanoparticles from *Phyllanthus emblica* (Indian Gooseberry) Fruit Extract on the Photocatalytic Reduction of Methylene Blue Dye

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In present study, gold nanoparticles are synthesized using the aqueous fruit extract of *Phyllanthus emblica* (Indian gooseberry) *via* the green synthesis route. The biomolecules such as phenols, ascorbic acid, flavanols and tannins play an important role in the reduction of the metal ions as investigated by FT-IR studies. The UV-visible spectroscopy studies confirm the surface plasmon resonance peaks in the range of 532-550 nm and is characteristic of the colour change from pale yellow to pinkish-purple. The TEM analysis exhibits the spherical gold nanoparticles in the range of 10-50 nm. The zeta potential observed value is found to be -9.92 mV indicating a good stability and highly dependent on the shape and the interparticle interaction of metal nanoparticles in the medium. The particle size obtained by the dynamic light scattering method is in agreement with the TEM analysis. Gold nanoparticles act as a potential catalyst under mercury light illumination and shows 92.4 % degradation of methylene blue from the contaminated water.

Keywords: *Phyllanthus emblica*, Gold nanoparticles, Zeta potential, Transmission Electron Microscopy

INTRODUCTION

Nanoscience is the study of phenomena of materials less than 100 nm is size and have different optical, electrical, catalytic and photothermal properties when compared to larger particle size dimensions [1]. Gold nanoparticles (AuNPs) have a property of not losing its unique shining even on air or moisture exposure and hence has drawn scientific attention for tremendous applications like electronics, photodynamic therapy, effective catalysts for chemical reactions, medical diagnostics, biochemical sensing and novel optoelectronic devices [2]. The optical and electronic properties of AuNPs have been subjected to many changes by evaporation-condensation methods, microemulsion techniques, laser ablation, UV photoreduction and electrochemical synthetic methods making it suitable for the generation of metal nanoparticles [3]. Since metal nanoparticles have been increasingly employed in diverse fields, a need for a cost-effective approach to minimize health risks and non-toxicity is highly suggested for future applications. The green synthesis approach employs biological techniques wherein microorganisms or plant extracts can transform inorganic metal ions into active metal nanoparticles [4]. This synthesis procedure can offer flexible control over the particle size, pH value, reaction speed and time, incubation temperature and facilitates easy purification.

Textile industries are important for social and economic development in any country as it provides shelter, jobs and revenue to a major part of the population. With all the advantages linked with these industries, a few certain disadvantages need to be highly contemplated. For example, the pollutants released by the global textile, leather and paper industries are continuously creating a health hazard to marine systems [5]. Twenty percent of freshwater pollution is accountable to textile dyeing, manufacturing, colour application and treatment of raw materials. These industries discharge millions of gallons of toxic wastes like formaldehyde based dye fixing agents, nitrates, hydrocarbon based softeners, chromium compounds and non-biodegradable dyeing chemicals in freshwater [6]. To overcome this problem, several purification methods have been earlier adopted like ultrafiltration, reverse osmosis, desalination, bioremediation and *in situ* chemical oxidation [7].

Gold nanoparticles strongly absorb both ultraviolet and visible light and can also catalyze chemical reactions in the presence of sunlight [8]. Photocatalysis approach involving the use of metal nanoparticles is a more appropriate emerging method for water treatment due to its low cost, sample reusability and complete degradation of organic pollutants present in contaminated freshwater [9]. The catalytic degradation of synthetic dyes using metal nanoparticles with plant extracts like *Morinda tinctoria* [10], *Gmelina arborea* [11], *Salicornia brachiate* [12], *Pogestemon benghalensis* [13], *Eucommia ulmoides* [14], *etc*. have already been investigated.

In continuation of study on green synthesis, we wish to report the influence of gold nanoparticles synthesized using the fruit extract of *Phyllanthus emblica* (Indian gooseberry or Amla). This tree is a deciduous one found commonly in India and Nepal offering many therapeutic and antioxidant properties. The fruit has a rich source of vitamin C, quercetin, terpenoids, phyllaemblic compounds, gallic acid, tannins, flavonoids, pectin and various polyphenolic compounds. The *Phyllanthus emblica* fruit is known for its ability in reducing cell damage, increasing diuretic activity, relieving asthma and bronchitis, reducing blood sugar and risk of heart disease [15,16]. The as-synthesized gold nanoparticles offer an excellent catalytic function for the reduction of methylene blue to leuco methylene blue. To the best of our knowledge, the photocatalytic activity of gold nanoparticles synthesized by *Phyllanthus emblica* fruit extract has not been reported till date.

EXPERIMENTAL

Chloroauric acid ($HAuCl_4{\cdot}xH_2O$) was obtained from Loba Chemie Pvt. Ltd., Mumbai, India. Deionised milli quarter water was used to prepare all the solutions. All glassware used for the experimental work was cleaned, washed and well-dried before use.

Preparation of aqueous fruit extract: *Phyllanthus emblica* fruit extract was prepared by soaking 2.5 g of fruit in 50 mL of double distilled water. The mixture was then kept under magnetic stirring for 1 h at room temperature and then extracted using an electric blender. The extract was filtered using Whatmann filter paper (Grade 1) and this filtrate was used for the synthesis of AuNPs.

Green synthesis of gold nanoparticles: In a conical flask, 0.3 mL of aqueous extract of *Phyllanthus emblica* fruit was added to 50 mL of 10^{-3} $HAuCl_4{\cdot}xH_2O$ solution at room temperature. Within 5 min, a colour change from pale yellow to pinkish-purple was obtained indicating the preliminary formation of AuNPs. The fruit contains high amounts of ascorbic acid upto 445 mg/100 g [17] and this acid is mainly responsible to reduce and neutralize oxygen species forming an abscorate radical and an electron [18]. This free electron formed reduces the Au^+ ions to Au^0.

Catalytic studies: The photocatalytic studies of AuNPs was performed using Heber Visible Annular Photo Reactor using mercury light. In the typical experiment, 2 mL of $NaBH_4$, 50 mL aqueous solution of methylene blue and 0.5 mL of as-synthesized AuNPs were effectively mixed in the sample tubes of photoreactor and constantly stirred for a 2 min time duration. To check the degradation of dye, 5 mL of the proposed mixture was withdrawn and measured for 5 trials in a time span of 10 min.

Characterization: The reduction of AuNPs was confirmed by using Cary 5000 UV-Vis Spectrophotometer in the range of 300 to 1000 nm. Transmission Electron Microscope JEM 2100 was used at a voltage of 200 kV to investigate the size and morphology of AuNPs. The FT-IR spectra was measured using Bruker Avance III, 400 MHz to recognize the possible functional grouos responsible for the reduction and stabilization of AuNPs. Dynamic light scattering (DLS) and zeta potential techniques were recorded using Malvern instruments.

RESULTS AND DISCUSSION

UV-Visible studies: The reduction of aqueous Au^{0+} ions from $AuCl_4^-$ due to the interaction with *Phyllanthus emblica* fruit can be easily followed with UV-visible spectroscopy. The visual inspection of pinkish-purple colour is due to the excitation of surface plasmon vibrations of AuNPs and attributed to various factors like particle size, shape and chemical surroundings of the medium [19]. Few trials were performed by varying the concentration of *Phyllanthus emblica* fruit extract (0.1-0.7 mL) and the absorbance peaks were measured, respectively. When 0.1 and 0.2 mL of *Phyllanthus emblica* extract was added to 50 mL of 10^{-3} M $HAuCl_4$ solution, no visible colour change was observed. There was no synthesis of colloidal gold in this trial due to the non-availability of reducing agents in the fruit extract proportion. When 0.3 mL of *Phyllanthus emblica* extract was added to the solution at pH 7, a colour change from pale yellow to pinkish-purple was observed within 5 min of the reaction time. The result shows a strong absorbance peak at 533 nm representing the characteristic surface plasmon resonance (SPR) peak of spherical AuNPs formed (Fig. 1). There is no significant change in the absorbance peak value with lapse of time. In this study, we have tried to investigate the influence of only the fruit extract on the colloidal gold solution. Plant or fruit extract synthesis has several advantages over microorganism methods since the reaction rate is faster and there is no required rigid control. No microorganisms like yeast, bacteria and fungi have been used for this study as earlier reported [20] in the synthesis of AuNPs using *Phyllanthus emblica* fruit extract.

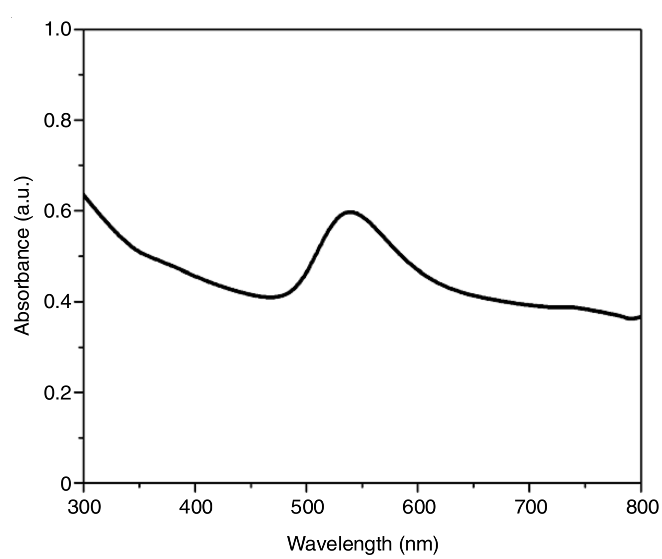

Fig. 1. UV-visible spectra of as-synthesized AuNPs

On increasing the concentration of *Phyllanthus emblica* extract to 0.5-1 mL, a darker purple colour was obtained when compared to 0.3 mL trial. The broadening of peak between 543-553 nm shows the formation of large size AuNPs with the stability decreasing after 24 h. The purple colour appeared colourless after 96 h due to the disturbance in equilibrium between the surface bound biomolecules and the free molecules present in the *Phyllanthus emblica* extract [21].

FT-IR studies: The FT-IR spectra shows the first band stretching at 3493.83 cm^{-1} indicating an O-H stretch of alcohols and phenolic compounds [22] (Fig. 2). *Phyllanthus emblica* fruit has a rich content of ascorbic acid, tannins, gallic acid and ellagic acid which are responsible for the reduction of gold ions to gold nanoparticles [23]. Besides O-H stretching, there is a presence of C-H bond at 2074.77 cm^{-1} and a band at 1637.99 cm^{-1} corresponds to amide I band of proteins [24]. The above observations give a clear idea of the functions of proteins, polyphenols and ascorbic acid in providing stability to the AuNPs.

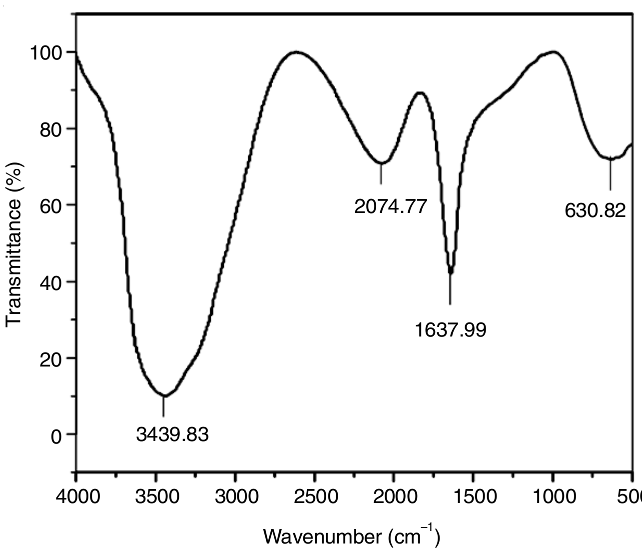

Fig. 2. FT-IR spectra of as-synthesized AuNPs

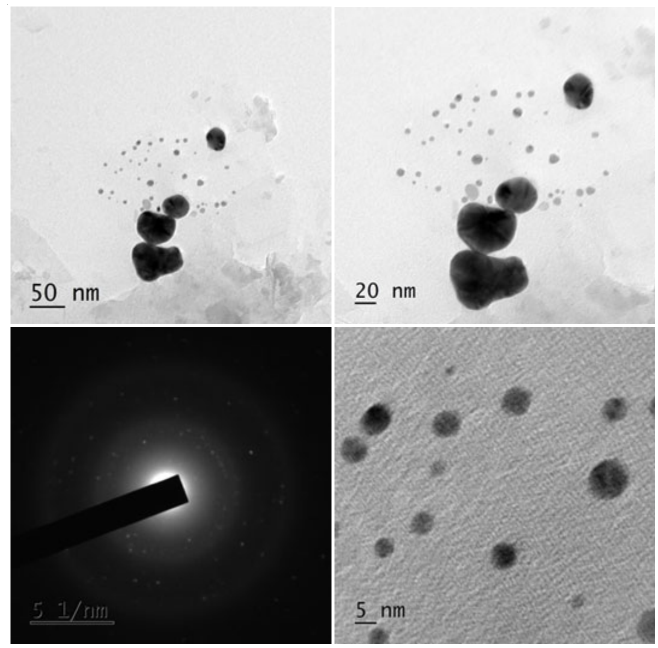

Fig. 3. HRTEM and SAED images of AuNPs synthesized with 0.3 g of fruit *Phyllanthus emblica* extract

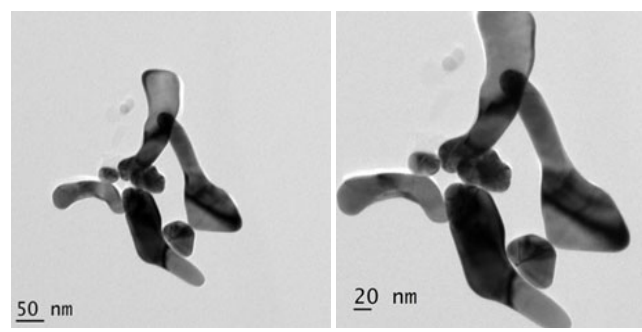

Fig. 4. TEM images of boot shaped AuNPs

The morphology of as-synthesized AuNPs were investigated using HR-TEM and selected area electron diffraction (SAED) analysis are shown in Fig. 3. The particle size is calculated to be in the range of 7.45 to 50.45 nm when the reaction is carried out with the optimum condition for UV-visible spectroscopy (0.3 g of *Phyllanthus emblica* fruit extract). The size distribution of AuNPs is uniformly spherical and well dispersed in the reaction solution. The SAED results confirmed the presence of bright rounded fringes and hence indicating high crystallinity of AuNPs.

When the quantity of *Phyllanthus emblica* extract is increased between 0.7-1.0 mL, boot shaped nanoparticles are observed with slight agglomeration and non-uniform dispersion. The uneven morphology can be attributed to an increased ascorbic acid level in the fruit causing the bioreduction of AuNPs (Fig. 4). The shape of AuNPs plays an important function in exploring its applications and hence constant and small sized spherical morphology prove to be far more beneficial for photocatalytic reactions, drug delivery and antimicrobial activities [25].

Dynamic light scattering (DLS) and zeta potential (ZP) studies: The particle size distributions of as-synthesized gold nanoparticles relative to the intensity measurements are obtained from dynamic light scattering studies as shown in Fig. 5. The polydispersity index is found to be 0.366 with particle sizes ranging from 16 to 50 nm. Some larger sized particles are observed and can be accounted to the presence of biomolecules engulfing the surface of AuNPs [26].

Fig. 6 shows the stability of as-synthesized AuNPs using *Phyllanthus emblica* fruit extract. The zeta deviation and zeta potential values were observed to be 5.25 mV and -9.92 mV, respectively. The negative value of zeta potential suggests the presence of negative charged ions in the *Phyllanthus emblica* extract that causes electrostatic stability of AuNPs [27].

Photocatalytic activity of AuNPs on the reduction of methylene blue dye: The catalytic activity of AuNPs is studied in the presence of sodium borohydride on methylene blue dye. Methylene blue has an absorption peak at 664 nm and the addition of $NaBH_4$ independently to the medium cannot facilitate the reduction in the intensity of absorption peaks [28]. The addition of AuNPs can accelerate an electron transfer from donor BH_4^- to acceptor methylene blue facilitating a decrease in the absorption intensity of methylene blue and converting

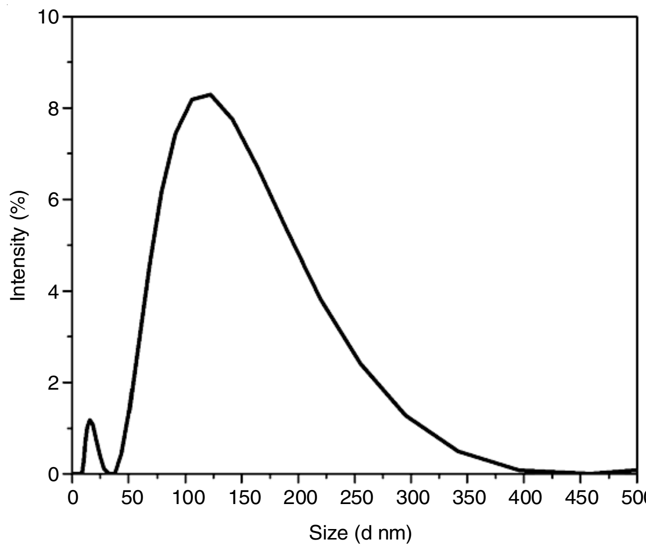

Fig. 5. Particle size distribution from DLS study

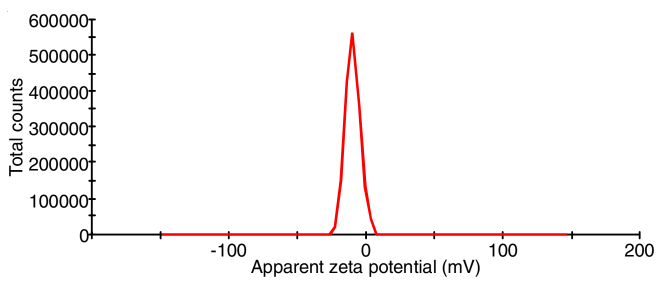

Fig. 6. Stability of AuNPs from zeta potential study

it to leuco-methylene blue (LMB). The visual observation of the colour changing from dark blue to colourless confirms the pseudo-first-order kinetics mechanism [29]. Fig. 7 shows the UV-visible absorption spectrum of methylene blue dye with 92.4 % degradation in a time duration of 10 min.

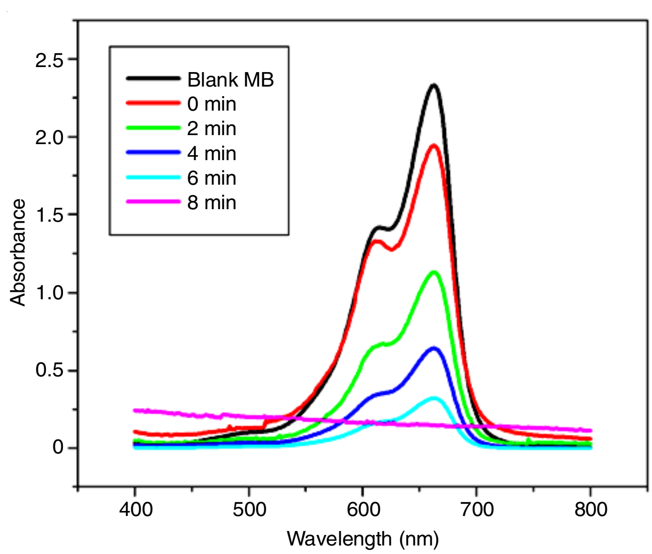

Fig. 7. Degradation of methylene blue in a time period of 8 min

Conclusion

The present study demonstrates a simple green synthesis approach for the synthesis of stable AuNPs from the aqueous fruit extract of *Phyllanthus emblica*. Optical and spectroscopic studies confirmed the stability and spherical size distribution by 0.3 mL of fruit extract composition. The SAED pattern and zeta potential studies affirmed the high crystallinity and stability of as-synthesized AuNPs. The small sized particles activate the catalytic mechanism and hence accelerate the rapid degradation of methylene blue dye. The current study can have an effective applicability for the removal of toxic chemicals from wastewater.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. M.P. Patil and G.D. Kim, *Appl. Microbiol. Biotechnol.*, **101**, 79 (2017); https://doi.org/10.1007/s00253-016-8012-8.
2. A.K. Shukla and S. Iravani, *Environ. Chem. Lett.*, **15**, 223 (2017); https://doi.org/10.1007/s10311-017-0618-2.
3. T.A. Dankovich, *Environ. Sci. Nano*, **1**, 367 (2014); https://doi.org/10.1039/C4EN00067F.
4. D. Bose and S. Chatterjee, *Indian J. Microbiol.*, **55**, 163 (2015); https://doi.org/10.1007/s12088-015-0512-1.
5. H.M. Pinheiro, E. Touraud and O. Thomas, *Dyes Pigments*, **61**, 121 (2004); https://doi.org/10.1016/j.dyepig.2003.10.009.
6. A. Paz, J. Carballo, M.J. Pérez and J.M. Domínguez, *Chemosphere*, **181**, 168 (2017); https://doi.org/10.1016/j.chemosphere.2017.04.046.
7. X. Chen, Z. Wu, D. Liu and Z. Gao, *Nanoscale Res. Lett.*, **12**, 143 (2017); https://doi.org/10.1186/s11671-017-1904-4.
8. S. Sarina, E.R. Waclawik and H. Zhu, *Green Chem.*, **15**, 1814 (2013); https://doi.org/10.1039/c3gc40450a.
9. X. Ke, X. Zhang, J. Zhao, S. Sarina, J. Barry and H. Zhu, *Green Chem.*, **15**, 236 (2013); https://doi.org/10.1039/C2GC36542A.
10. M. Vanaja, K. Paulkumar, M. Baburaja, S. Rajeshkumar, G. Gnanajobitha, C. Malarkodi, M. Sivakavinesan and G. Annadurai, *Bioinorg. Chem. Appl.*, **2014**, Article ID 742346 (2014); https://doi.org/10.1155/2014/742346.
11. J. Saha, A. Begum, A. Mukherjee and S. Kumar, *Sustain. Environ. Res.*, **27**, 245 (2017); https://doi.org/10.1016/j.serj.2017.04.003.
12. K.B. Ayaz Ahmed, S. Subramanian, A. Sivasubramanian, G. Veerappan and A. Veerappan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **130**, 54 (2014); https://doi.org/10.1016/j.saa.2014.03.070.
13. B. Paul, B. Bhuyan, D.D. Purkayastha, M. Dey and S.S. Dhar, *Mater. Lett.*, **148**, 37 (2015); https://doi.org/10.1016/j.matlet.2015.02.054.
14. M. Guo, W. Li, F. Yang and H. Liu, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **142**, 73 (2015); https://doi.org/10.1016/j.saa.2015.01.109.
15. X. Liu, C. Cui, M. Zhao, J. Wang, W. Luo, B. Yang and Y. Jiang, *Food Chem.*, **109**, 909 (2008); https://doi.org/10.1016/j.foodchem.2008.01.071.
16. Habib-ur-Rehman, K.A. Yasin, M.A. Choudhary, N. Khaliq, Atta-ur-Rahman, M.I. Choudhary and S. Malik, *Nat. Prod. Res.*, **21**, 775 (2007); https://doi.org/10.1080/14786410601124664.
17. P.S. Ramesh, T. Kokila and D. Geetha, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **142**, 339 (2015); https://doi.org/10.1016/j.saa.2015.01.062.
18. T. Maruyama, Y. Fujimoto and T. Maekawa, *J. Colloid Interface Sci.*, **447**, 254 (2015); https://doi.org/10.1016/j.jcis.2014.12.046.
19. S. Francis, S. Joseph, E.P. Koshy and B. Mathew, *Environ. Sci. Pollut. Res. Int.*, **24**, 17347 (2017); https://doi.org/10.1007/s11356-017-9329-2.
20. B. Ankamwar, C. Damle, A. Ahmad and M. Sastry, *J. Nanosci. Nanotechnol.*, **5**, 1665 (2005); https://doi.org/10.1166/jnn.2005.184.

21. P. Rajasekharreddy, P. Usha Rani and B. Sreedhar, *J. Nanopart. Res.*, **12**, 1711 (2010); https://doi.org/10.1007/s11051-010-9894-5.
22. J.Y. Song, H.K. Jang and B.S. Kim, *Process Biochem.*, **44**, 1133 (2009); https://doi.org/10.1016/j.procbio.2009.06.005.
23. B. Sharma, D.D. Purkayastha, S. Hazra, L. Gogoi, C.R. Bhattacharjee, N.N. Ghosh and J. Rout, *Mater. Lett.*, **116**, 94 (2014); https://doi.org/10.1016/j.matlet.2013.10.107.
24. R. Mata, A. Bhaskaran and S.R. Sadras, *Particuology*, **24**, 78 (2016); https://doi.org/10.1016/j.partic.2014.12.014.
25. S. Baker and S. Satish, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **150**, 691 (2015); https://doi.org/10.1016/j.saa.2015.05.080.
26. V. Ahluwalia, J. Kumar, R. Sisodia, N.A. Shakil and S. Walia, *Ind. Crops Prod.*, **55**, 202 (2014); https://doi.org/10.1016/j.indcrop.2014.01.026.
27. M. Ali, B. Kim, K. D. Belfield, D. Norman, M. Brennan and G.S. Ali, *Mater. Sci. Eng. C*, **58**, 359 (2016); https://doi.org/10.1016/j.msec.2015.08.045.
28. H. Han, D. Pan, X. Wu, Q. Zhang and H. Zhang, *J. Mater. Sci.*, **49**, 4796 (2014); https://doi.org/10.1007/s10853-014-8179-2.
29. J. Das and P. Velusamy, *J. Taiwan Inst. Chem. Eng.*, **45**, 2280 (2014); https://doi.org/10.1016/j.jtice.2014.04.005.