ORICPublications
www.oricpub.com

Online available since 2016/ August /19 at www.oricpub.com

Journal of Chemistry and Materials Research
Vol. 5 (4), 2016, 68–73

ISSN: 2381-3628
JCMR
Journal of Chemistry and Materials Research
www.oricpub.com/jcmr

Original Research

Photocatalytic Degradation of Malachite Green Using Silver Nanoparticles Synthesised from Gooseberry Extract

S. Pakya Lakshmi, S. Dhanya and D. Sheeba *

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil-629004, Tamilnadu, India.

Received 11 June 2016; received in revised form 10 August 2016; accepted 13 August 2016

Abstract

The biosynthesis of nanoparticles has been proposed as a cost effective and environmental friendly alternative to chemical and physical methods. Biosynthesis of silver nanoparticles using gooseberry extract is investigated. This extract acts as a reducing and stabilizing agent for the production of silver nanoparticles. The gooseberry extract is added to 2 mM silver nitrate solution, after exposing the silver ions to the extract, rapid reduction of silver ions is observed leading to the formation of silver nanoparticles. The formation of silver nanoparticles is primarily detected within 10 minutes by the change of colour from colourless to reddish-brown. The synthesized nanoparticles are characterized by using UV-Visible and Fourier transform infrared spectroscopy. The UV-Visible spectrum shows an absorption peak at 429 nm due to Surface Plasmon Resonance. The photocatalytic activity of the synthesised silver nanoparticle is examined by the degradation of malachite green under visible light illumination. The rate of photodegradation and degradation efficiency of malachite green with silver nanoparticles for one hour and forty minutes is 1.18 x 10^{2} sec^{-1} and 69.23 %. The absorption kinetics of the malachite green follows the pseudo-first order mechanism.

Keywords: Green synthesis; Gooseberry extract; Silver nitrate; Silver nanoparticles; Photocatalytic degradation; Degradation efficiency.

1. Introduction

Green synthesis of nanoparticles has been proposed as a cost effective and environmental friendly alternative to chemical and physical methods. Plant mediated synthesis of nanoparticles is a green chemistry approach that interconnects nanotechnology and plant biotechnology. Nanobiotechnology is one of the most promising areas in modern nanoscience and technology. This emerging area of research interlaces various disciplines of science such as physics, chemistry, biology and material science. Nanoparticles are usually ≤ 100 nm in each spatial dimension and are commonly synthesized using top-down and bottom-up strategies [1]. Owing to their high surface-to-volume ratio, surface energy, spatial confinement and reduced imperfections, metal nanoparticles have characteristic physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties as opposed to bulk materials [2]. Recent advancements in nanotechnology have led to the expansive growth in the synthesis of nanosized particles, wires, and tubes for potential applications in different fields. Due to their Surface Plasmon Resonance (SPR), Enhanced Rayleigh Scattering and Surface Enhanced Raman Scattering in metal nanoparticles, quantum size effect in semiconductors and supermagnetismin magnetic materials, nanoparticles are considered as building blocks of the next generation of optoelectronic, electronics, and various chemical and biochemical sensors [3].

At first nanoparticle synthesis are usually carried out by various physical and chemical methods like laser ablation, pyrolysis, lithography, chemical vapour deposition, sol-gel technique and electro deposition, which are very expensive and hazardous [4,5]. Hazardous substances such as sodiumborohydride, tetrakishydroxymethyl- phosphonium chloride (THPC), poly-N-vinyl pyrrolidone (PVP), and hydroxylamine have been used for the synthesis of nanoparticles in the traditional wet methods. Other dry methods such as UV irradiation,

* Corresponding author:
E-mail address: sheebajeense@gmail.com (***D. Sheeba***).

aerosol and lithography are also not considered environment-friendly. The use of such toxic chemicals is still the subject of paramount concern because toxic chemicals on the surface of nanoparticles and non-polar solvents in the synthesis limit their applications in clinical fields. Therefore, the biosynthesis of clean, bio-compatible, non-toxic and environment-friendly nanoparticles produced both extracellularly and intracellularly deserves merit [6]. Among noble metal nanoparticles, silver nanoparticles (AgNPs) have received considerable attention owing to their attractive physiochemical properties. The use of environmentally benign materials like plant extracts, bacteria and fungi for the synthesis of AgNPs offers numerous benefits of eco-friendliness and compatibility for pharmaceutical, biomedical and agricultural applications as they do not use toxic chemicals in the synthesis protocols. The role of AgNPs as an anticancer agent should open new door in the field of medicine. Silver nanoparticles should serve as one of the best ways of treating diseases that involve cell proliferation and cell death [7].Green synthesis of AgNPsby various plants and microorganisms has been reported. However, the potential of plants as biological materials for the synthesis of nanoparticles and their compatibility to biological systems is yet to be fully explored. Several researchers have achieved success in the plant mediated biological synthesis of AgNPs using extracts obtained from Anacardiumoccidentale [8], Gloriosasuperba [9], Hibiscus cannabinus [10], Malvaparviflora [11], Ocimum-tenuiflorum [12], Sesbaniagrandiflora [13], Mangiferaindica [14], Prosopisjuliflora [15] and Cocculushirsutus [16].

Water is a unique substance because it can naturally renew and cleanse itself by allowing pollutants to settle out (sedimentation) or break down or dilute the pollutants to a point where they are no more harmless. However this natural process is time consuming and is difficult when large concentrations of contaminants are released into water bodies. Dyes belong to the class of synthetic organic compounds and are widely used in the textile industry. Dyes usually have synthetic origin and complex aromatic molecular structures make them very stable and more difficult to biodegrade [17]. Hence, removal of colour from dye bearing waste water is a potential problem because of the difficulties faced in treating it by conventional methods. The removal of these non-biodegradable organic chemicals from the environment is a crucial ecological problem. Many techniques, such as activated carbon sorption, flocculation, electrocoagulation, UV-light degradation and redox treatments, are being routinely used for fading dyes [18]. However, due to the ineffectiveness of these techniques in some way or the other, the present scenario requires better and improved wastewater treatment measures. Recently, metal nanoparticles were reported as effective photocatalysts for degrading chemical complexes, under ambient temperature with visible light illumination [19]. This can be achieved by increasing the optical path of photons leading to a higher absorption rate of nanoparticles in the presence of a local electrical field [20]. Among the nanoparticles AgNPs are good, highly efficient and stable photocatalysts under ambient temperature with visible light illumination for degrading organic compounds and dyes. Moreover, scientists have also shown considerable interest in using nanoparticles for the photocatalytic degradation of dyes [21,22].

Investigations on the biosynthesis of AgNPs with plant extracts have been made so far and the present study concentrates on the biosynthesis of AgNPs using the gooseberry extract. Gooseberry is commonly known as amla and it belongs to the family Phyllanthaceae, one of the important herbal drugs used in Ayurvedic system of medical preparations against a variety conditions such as liver injury, atherosclerosis and diabetes [23,24]. Gooseberry is highly nutritious and is one of the richest sources of vitamin-C, amino acids and minerals. It contains several chemical constituents like tannins, alkaloids and phenols. Among all hydrolysable tannins, Emblicanin A and B, gallic acid, ellagic acid are reported to possess biological activity [25]. The green synthesised AgNPsfrom gooseberry extract is characterized by UV-visible spectroscopy, Fourier transform infrared spectroscopy. The photocatalytic activity of the synthesised silver nanoparticles is examined by the degradation of malachite green under visible light illumination and the observed results are discussed in the present study.

2. Experimental Section

Fresh and ripened gooseberry fruit were obtained from the local market. Silver nitrate used for the synthesis of silver nanoparticles and malachite green for the degradation studies were procured from Merck. Double-distilled deionized water was used to perform the experiments.

2.1.Preparation of gooseberry extract

Ripened gooseberry was used for the preparation of the extract. 25 g of this ripened fruit was thoroughly washed with distilled water, dried and cut into small pieces. Grind the pieces by a pestle and mortar and the resulting extract was filtered using Whatmann filter paper. The filtrate was collected and then centrifuged for about 8,000 rpm for about 10 minutes. The supernatant extract was collected and used as reducing agent for the synthesis of AgNPs.

2.2.Preparation of silver nanoparticles

Aqueous solution of 2 mM silver nitrate ($AgNO_3$) was prepared and used for the synthesis of silver nanoparticles. 10 ml of the extract was added to 90 ml of 2 mM aqueous $AgNO_3$ solution in a 250 ml Erlenmeyer flask and incubated at room temperature. The sample colour changes from colorless to reddish-brown colour within 10 minutes indicate the formation

of AgNps. Ninety-five percent of the bioreduction of Ag^+ ions occurred within 1 hour. The synthesised AgNPs were centrifuged at 15,000 rpm for 5 min and subsequently dispersed in sterile distilled water to get rid of any uncoordinated biological materials. The pellet of AgNPs collected at the bottom of the centrifuge tube was collected, dried and stored at –4 °C.

2.3.Characterization Techniques

The absorption spectral measurements of AgNPs and the photodegradation of dye were carried out using Shimadzu UV-1800 spectrophotometer. FTIR analysis of the dried AgNPs was carried out through the potassium bromide (KBr) pellet (FTIR grade) method in 1:100 ratio and spectrum was recorded using Shimadzu IR Affinity-1 Fourier transform infrared spectrophotometer with the range of 4000-400 cm^{-1} at the resolution of 4 cm^{-1}.

2.4.Photocatalytic degradation

The degradation of malachite green was studied by taking 50 ml of 8.0×10^{-6} M of the dye and 0.1 g of the synthesised AgNPs in the presence and absence of light. For photodegradation the mixture was exposed to a 200 W tungsten lamp (Philips) of 60.0 $mWcm^{-2}$ light intensity. A water filter was used to cut off thermal radiation just to ensure illumination by visible light. The pH of the solution was measured by a digital pH meter (Systronics Model) and the pH was maintained at 7.5. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals. Malachite green exhibits the maximum absorption at 620 nm, and the concentration of malachite green was monitored by the change of the absorption (A) at 620 nm in the photocatalytic reaction process. The degradation efficiency (η) was described by the equation: $\eta = (A_0 - A)/A_0 \times 100$ %; (A_0 and A was the absorption intensities at the beginning and after photocatalytic reaction for certain time).

3. Results and Discussion

An inexpensive, versatile, and very reproducible method for large scale synthesis and characterization of AgNPs by reduction process using gooseberry extract is reported in this section. This fruit extract can act both as reducing and stabilizing agents. The synthesised AgNPs also act as a good photocatalyst for the degradation of malachite green.

3.1.Absorption spectral analysis of AgNPs

The formation of AgNPs is preliminary confirmed by colour change followed by UV-Visible spectrophotometric analysis. Reduction of Ag^+ into AgNPs during exposure to the fruit extract could be followed by colour change. The formation of AgNPs is primarily detected by the change of colour from colour less to brown (Fig. 1). The colour of AgNPs depends on the intensity and the size of nanoparticles. Silver nanoparticle exhibits brown colour in aqueous solution due to the surface plasmon resonance phenomenon, which results from collective oscillations of their conduction band electrons in response to electromagnetic waves. Absorption spectra of AgNPs formed in the reaction media after 10 minutes has an absorbance peak at 429 nm, broadening of peak indicated that the particles are poly dispersed (Fig. 2). Similar results are also obtained for the green synthesis of silver nanoparticles from Euphorbia hirtaL and Cissus Quadrangularis [26,27].

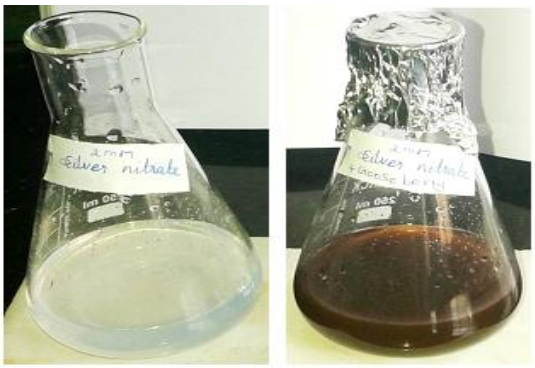


Fig. 1. Colour change of $AgNO_3$ before and after the formation of AgNPs

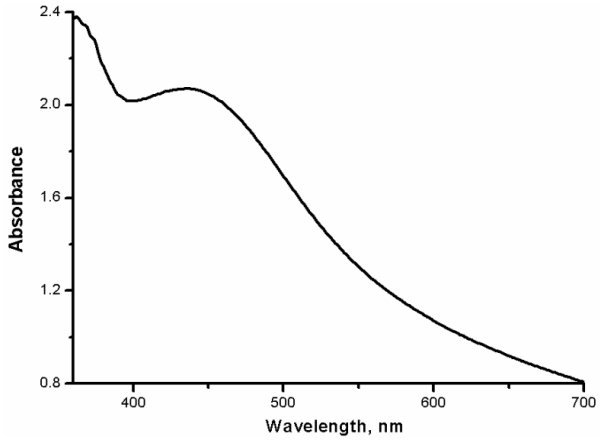


Fig. 2. Absorption spectrum of AgPNs formed after 10 minutes

3.2.FTIR analysis of AgNPs

The FTIR spectrum of the synthesised AgNPs (Fig.3) shows a prominent band at around 3261 cm^{-1} signified the O–H stretching of alcohols or phenols. Absorption band at 1745 cm^{-1} is due to C=O stretching modes of esters present in ascorbic acid. The vibration band at 1240 cm^{-1} of fruit extract which is the characteristic signal of C–O group of polyols is almost disappeared in the reaction solution. The polyols in gooseberry

extract reduces Ag^+ ions to metallic silver, and the polyols got oxidized to unsaturated carbonyl groups rendering a broad peak at 1745 cm^{-1}. The present ascorbate ions could also act as a reducing agent for the conversion of Ag^+ to Ag^0. Here, the ascorbic acids present in the plant extract take a significant role for the reduction of Ag^+ to Ag^0 at room temperature. The absorption bands at around 1060 cm^{-1} is due to the bending vibration of C–OH groups and the asymmetric stretching band of C–O–C groups of carbohydrates. The bands in the range of 500–650 cm^{-1} are assigned to the out-of-plane bending vibrations of C–H groups. These bands became less intense in the reaction solution which indicated that AgNPs are capped with the organic moieties of the gooseberry extract. Ascorbic acid present in the gooseberry extract may act as reducing as well as stabilizing agent for the formation of AgNPs.

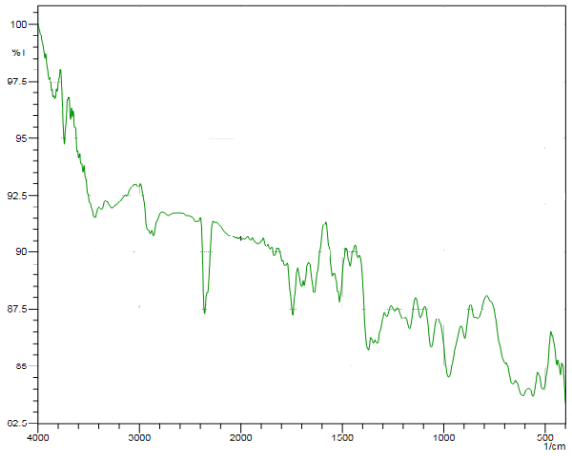
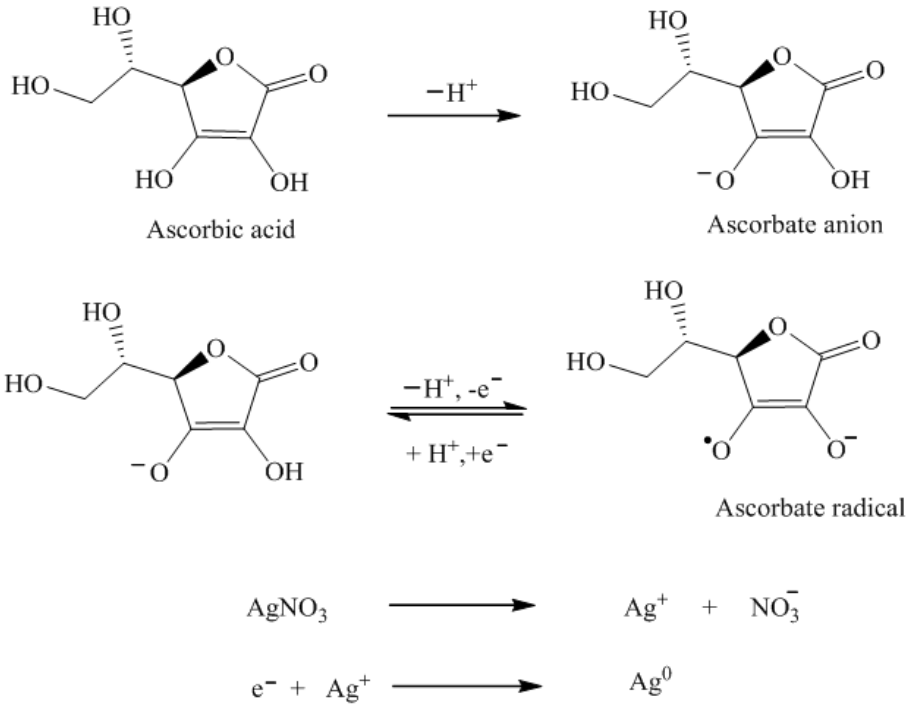


Fig. 3. FTIR spectrum of synthesised AgNPs

The mechanism for the reduction of Ag^+ ion to Ag^0 is due to the presence of water-soluble antioxidative substances like ascorbic acid which is present in the gooseberry extract. Ascorbic acid is a reducing agent and can reduce, and thereby neutralize, reactive oxygen species leading to the formation of ascorbate radical and an electron. This free electron reduces the Ag^+ ions to Ag^0 (Scheme 1).

3.3.Photocatalyticdegradation of malachite green

The experiments are conducted in dark as well as in light. An aliquot of 2 ml is taken out from the reaction mixture at regular time intervals and absorbance is measured spectrophotometrically at a wavelength of 620 nm. It is observed that the absorbance of the solution decreases with increasing time intervals showing thereby that the dye undergo degradation with increasing time of exposure. The results for the degradation of malachite green with and without AgNPs in the presence and absence of light are mentioned in the Tables 1 and 2. A plot of 1 + *log A* versus time is linear and follows pseudo-first order kinetics (Fig. 4), where *A* is the absorbance of the medium at a particular time *t*. The rate constant (*k*) is determined from the slope of the straight line by following



Scheme 1. Ascorbic acid reduction of Ag^+ to Ag^0

expression, $k = -2.303 \times$ Slope.

The rate of degradation of malachite green without catalyst in dark as well as in light is 0.21×10^2 sec^{-1} and 0.43×10^2 sec^{-1}. The rate of degradation of malachite green in the presence of 0.1 g AgNPs in dark as well as light is 0.45×10^2 sec^{-1} and 1.18×10^2 sec^{-1} respectively. The degradation efficiency (η) of malachite green in dark as well as in light without AgNPs is 19.23 % and 34.61 %. The η of malachite green with AgNPs is 34.62 % (dark) and 69.23 % (light) respectively. From these results it is clear that the AgNPs synthesised from gooseberry extract act as an efficient photocatalyst for the degradation of malachite green.

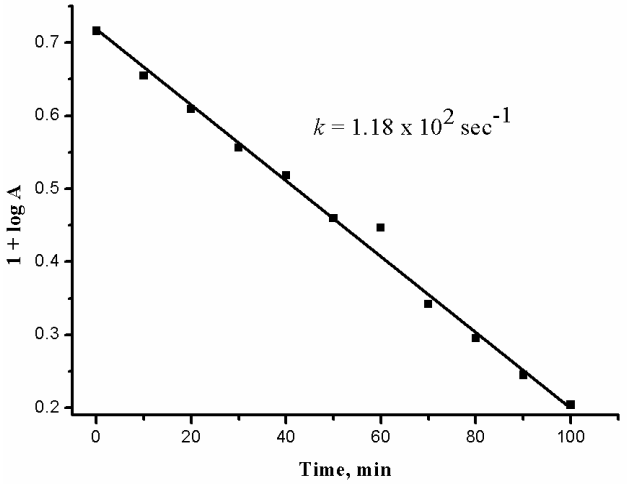


Fig. 4. Plot of 1 + log Avs time for malachite green with AgNPs in the presence of light

Table 1 Photodegradation of malachite green (8.00 × 10-6 M) in the absence and presence of light at pH 7.5

Time (min)	Absorbance (A) in dark	Absorbance (A) in light	(1 + log A) in dark	(1 + log A) in light
0.0	0.52	0.52	0.7160	0.7160
10	0.51	0.51	0.7076	0.7076
20	0.50	0.49	0.6989	0.6901
30	0.49	0.47	0.6901	0.6721
40	0.48	0.43	0.6812	0.6334
50	0.47	0.42	0.6721	0.6232
60	0.46	0.41	0.6627	0.6127
70	0.45	0.38	0.6532	0.5797
80	0.44	0.37	0.6434	0.5682
90	0.43	0.35	0.6334	0.5440
100	0.42	0.34	0.6232	0.5314

Table 2 Degradation of malachite green (8.00 × 10-6 M) with AgNPs (0.1 g) in the presence and absence of light at pH 7.5

Time (min)	Absorbance (A) in dark	Absorbance (A) in light	(1 + log A) in dark	(1 + log A) in light
0.0	0.52	0.52	0.7160	0.7160
10	0.50	0.45	0.6989	0.6532
20	0.49	0.40	0.6901	0.6020
30	0.46	0.36	0.6627	0.5563
40	0.43	0.33	0.6334	0.5185
50	0.42	0.30	0.6232	0.4771
60	0.41	0.28	0.6127	0.4471
70	0.39	0.22	0.5910	0.3424
80	0.37	0.18	0.5682	0.2552
90	0.35	0.17	0.5440	0.2304
100	0.34	0.16	0.5314	0.2041

4. Conclusion

The present investigations deals about the green synthesis of AgNPs from gooseberry extract and this synthesised nanoparticle are characterized by UV-Visible and FTIR spectral analysis. The reduced AgNPs show a characteristic absorption peak at 429 nm due to the surface plasmon resonance phenomenon. The FTIR examination of the samples confirms the involvement of ascorbic acid in the reduction and stabilization of the AgNPs. The degradation of malachite green using the AgNPs as photocatalyst has been examined in the presence and absence of light. The absorption kinetics of the dye followed the pseudo–first order mechanism.The rate of photodegradation and degradation efficiency of malachite green with 0.1 g AgNPs is 1.18 x 10^{2} sec^{-1} and 69.23 %. Kinetic studies and degradation efficiencyreveals that the green synthesised AgNPs act as an efficient photocatalyst for the degradation of malachite green. The photodegradation mechanisms of AgNPs proposed in this study may shed some light on future applications of the technology for the decolouration of dyes due to cost-effective, and eco-friendly.

References

[1] Narayanan, K.B. and Sakthivel, N. (2011). Green synthesis of biogenic metal nanoparticles by terrestrial and aquatic phototrophic and heterotrophic eukaryotes and biocompatible agents. Adv. Colloid. Interface Sci., 169(2), pp. 59– 79.

[2] Daniel, M.C. and Astruc, D. (2004). Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. Chem. Rev., 104(1), pp. 293 – 346.

[3] Ramanaviciusa, A., Kausaite, A., and Ramanaviciene, A. (2005). Biofuel cell based on direct bioelectrocatalysis. Biosens. Bioelectron., 20, pp. 1962 – 1967.

[4] Ankamwar, B., Chaudhary, M. and Mural, S. (2005). Gold nanotriangles biologically synthesized using tamarind leaf extract and potential application in vapour sensing. Synth. React. Inorg. Met. Org. Chem., 35, pp. 19 – 26.

[5] Roy, N., and Barik, A., (2010). Green synthesis of silver nanoparticles from the unexploited weed resources. Int. J. Nanotechnol. Appl., 4 (2) 95 – 101.

[6] Narayanan, K.B. and Sakthivel, N. (2010). Biological synthesis of metal nanoparticles by microbes. Colloid Interface Sci., 156(2), pp.1 – 13.

[7] Vaidyanathan, R., Kalishwaralal, K., Gopalram, S. and Gurunathan, S. (2009). Nanosilver- the burgeoning therapeutic molecule and its green synthesis. Biotechnol. Adv., 27(6)924 – 937.

[8] Sheny, D.S., Joseph, M. and Daizy, P. (2011). Phytosynthesis of Au, Ag and Au–Ag bimetallic nanoparticles using aqueous extract and dried leaf of Anacardiumoccidentale. SpectrochimActa Part A Mol Biomol Spectrosc., 79(1), pp.254 – 262.

[9] Ashokkumar, S., Ravi, S. and Velmurugan, S. (2013). Green synthesis of silver nanoparticles from Gloriosasuperba L. leaf extract and their catalytic activity.Spectrochim. Acta Part AMolBiomolSpectrosc., 115, pp. 388 – 392.

[10] Bindhu, M.R. and Umadevi, M. (2013). Synthesis of monodispersed silver nanoparticles using Hibiscus cannabinus leaf extract and its antimicrobial activity. Spectrochim. ActaPart A Mol BiomolSpectrosc., 101, pp. 184 – 190.

[11] Zayeda, M.F., Eisa, W.H. and Shabaka, A.A. (2012). Malvaparviflora extract assisted green synthesis of silver nanoparticles, Spectrochim. Acta Part A Mol Biomol Spectrosc., 98, pp.423 – 428.

[12] Patil, R.S., Kokate, M.R., and Kolekar, S.S. (2012). Bioinspired synthesis of highly stabilized silver nanoparticles using Ocimumtenuiflorum leaf extract and their antibacterial activity, Spectrochim. Acta Part AMolBiomolSpectrosc., 91, pp. 234 – 238.

[13] Das, J., Das, P.M., and Velusamy, P. (2013). Sesbaniagrandiflora leaf extract mediated green synthesis of antibacterial silver nanoparticles against selected human pathogens. Spectrochim. Acta Part A Mol Biomol Spectrosc., 104, pp. 265 – 270.

[14] Philip, D. (2011). MangiferaIndica leaf assisted biosynthesis of well-dispersed silver nanoparticles. Spectrochim. Acta Part A Mol Biomol Spectrosc., 78, pp. 327 – 331.

[15] Raja, K.,Saravanakumar, A., andVijayakumar, R. (2012). Efficient synthesis of silver nanoparticles from Prosopisjuliflora leaf extract and its antimicrobial activity using sewage.Spectrochim. Acta Part A MolBiomolSpectrosc., 97, pp. 490 – 494.

[16] Thiruppathi, C., Kumaravel, P., Duraisamy, R., Prabhakaran, A.K., Jeanie, T., Sivaperumal, R., and Karthick, P.A. (2013).Biofabrication of Silver nanoparticles using Cocculushirsutus leaf extract and their antimicrobial efficacy. Asian J. Pharm. Tech., 3, pp. 93 – 97.

[17] Daneshvar, N., Ayazloo, M., Khataee, A.R., and Pourhassan, M. (2007). Biological decolourisation of dye solution containing malachite green by microalgae Cosmarium sp. Bioresource Technology, 98(6), pp. 1176 – 1182.

[18] Kumar, A., Choudhary, P., andVerma, P. (2011). A comparative study on the treatment methods of textile dye effluents. Global J. Environ. Res., 5(1), pp. 46 – 52.

[19] Mohamed, R.M., Mkhalid, I.A., Baeissa, E.S., and Al-Rayyani, M.A. (2012). Photocatalytic degradation of methylene blue by Fe/ZnO/SiO_2 nanoparticles under visible light. J. Nanotechnol., Doi:10.1155/2012/329082.

[20] Garcia, M.A. (2012). Surface plasmons in metallic nanoparticles: fundamentals and applications. J. Phys. D Appl. Phys., 44(28), pp.1 – 20.

[21] Wang, P., Huang, B., Qin, X., Zhang, X., Dai, Y., Wei, J., and Whangbo, M.H. (2008). Efficient and stable photocatalyst under visible light. Chem. Eur. J., 14, pp. 10543–10546.

[22] Selvam, G.G., and Sivakumar, K. (2015). Phycosynthesis of silver nanoparticles and photocatalytic degradation of methyl orange dye using silver (Ag) nanoparticles synthesized from Hypneamusciformis (Wulfen) J.V. Lamouroux. Appl. Nanosci., 5, pp. 617–622.

[23] Dasaroju, S. and Gottumukkala, K. (2014). Current trends in the research of Emblicaofficinalis (amla). A pharmacological perspective. Int. J. Pharm. Sci. Rev. Res., 24(2) pp. 150 – 159.

[24] Rehman, H., Yasin, K.A., Choudhary, M.A., Khaliq, N., Rahman, A., Choudhary, M.I., and Malik, S. (2007). Studies on the chemical constituents of Phyllanthusemblica, Natural Product Research 21(9), pp. 775 – 781.

[25] Scartezzini, P., Antognoni, F., Raggi, M.A., Poli, F. and Sabbioni, C. (2006). Vitamin C content and antioxidant activity of the fruit and of the Ayurvedic preparation of Emblica of ficinalis Gaertn. J. Ethnopharmacol., 104(2), pp.113 – 118.

[26] Elumalai, E.K., Prasad, T.N.V.K.V., Kambala, V., Nagajyothi, P.C. and David, E. (2010). Green synthesis of silver nanoparticle using Euphorbia hirta L and their antifungal activities. Archives of Applied Science Research 2(6), pp. 76 – 81.

[27] Vanaja, M., Gnanajobitha, G., Paulkumar, K., Rajeshkumar, S., Malarkodi, C. and Annadurai, G. (2013). Phytosynthesis of silver nanoparticles by Cissusquadrangularisinfluence of physicochemical factors. Journal of Nanostructure in Chemistry, http://www.jnanochem.com/content/3/1/17.