https://doi.org/10.30799/jnst.230.19050203 J. Nanosci. Tech. - Volume 5 Issue 2 (2019) 658–661

Share Your Innovations through JACS Directory

Journal of Nanoscience and Technology

Visit Journal at http://www.jacsdirectory.com/jnst

ISSN: 2455-0191

Study on Optical Properties of Green Synthesized Silver Nanoparticles for Surface Plasmon Resonance

H.G. Bhangale[1], S.G. Bachhav[2], D.M. Nerkar[3], K.M. Sarode[2], D.R. Patil[2,*]

[1]*JDMVP's Arts, Commerce and Science College, Yawal – 425 301, Maharashtra, India.*
[2]*Nanomaterial Research Laboratory, R.C. Patel ACS College, Shirpur – 425 405, Maharashtra, India.*
[3]*Department of Physics, Sathaye College, Vile Parle (E), Mumbai – 400 057, Maharashtra, India.*

ARTICLE DETAILS

Article history:
Received 29 March 2019
Accepted 16 April 2019
Available online 06 May 2019

Keywords:
Green Synthesis
pH Effect
Catalytic Activity

ABSTRACT

In the present study green, rapid, extracellular synthesis of silver nanoparticles was achieved under alkaline conditions using *Penicillium* species. The synthesis of silver nanoparticles is greatly influenced by the pH value of the reaction medium and studied visually as well as using UV-visible spectrophotometer. The SPR absorption bands appeared in the range between 408 nm and 415 nm confirm the formation of the silver nanoparticles. Silver nanoparticles prepared at pH value 10 were further characterized using XRD, SEM, TEM, photoluminescence spectroscopy. X-ray diffraction analysis exhibited the crystalline nature of the prepared silver nanoparticles with face centered cubic structure. The prepared silver nanoparticles were spherical in shape as revealed from SEM and TEM images with the sizes in the range between 11 to 19 nm. The emission spectra were recorded at 530 nm when excited at 400 nm in photoluminescence spectroscope. The prepared silver nanoparticles were evaluated for their catalytic activity in the reduction of MB by $NaBH_4$ and exhibit the excellent results.

1. Introduction

The electrical, optical, chemical properties of the metallic nanoparticles are functions of size and shape of the nanoparticles [1-4]. Interaction between incident light and free electrons on the surface of metallic nanoparticles causes the electrons to oscillate. Cloud of oscillating electrons on theses nanoparticle's surface is known as plasmon. Plasmons are the deep area of research and are the key driver of engineering at the nanoscale. When the frequency of incident light matches with the frequency of free electrons oscillations, resonance is established. This phenomenon is known as surface plasmon resonance. Colours exhibited by the metallic nanoparticles are due to this SPR [5]. Surface plasmon resonance exhibited by the metallic nanoparticles is the function of their size, shape and liquid medium in which particles are suspended. Shift in LSPR wavelength tolerates the nanoparticles for sensing the chemical and biological molecules [6]. For Nobel metal nanoparticles such as silver and gold SPR absorption band lies in visible region of the spectrum. Size dependent variation in colours was displayed by silver and gold nanoparticles [7].

Silver nanoparticles are reported for their size and shape dependent optical [8, 9], catalytic [10, 11] and antimicrobial activities [12]. Due to the size dependent nature of plasmon it might be possible to develop electronic or photonic devices based on excitation and detection of plasmon [13]. The intensity of the brown colour for silver nanoparticles was depends on the pH value of the reaction solution [7].

Several reports are available for the synthesis of silver nanoparticles by usual physical and chemical methods. But in these methods of fabrications, nanoparticles were achieved through the involvement and release of toxic chemicals which affect the environment. So, the green synthesis routes in which natural reducing and stabilizing agents used are preferred for the fabrication of silver nanoparticles. Fungi comprise large quantity of enzymes extracellularly due to which extracellular synthesis of nanoparticles is possible [14]. Fungi such as *Aspergillus flavus* [15], *Aspergillus niger* [16], *Trichoderma asperelum* [17] and *Penicillium* species [17-19]. Shown their potential for the production of silver nanoparticles.

Green synthesized silver nanoparticles were reported for their catalytic performance and hence might be applicable for the maintenance of the environment. Silver nanoparticles synthesized using Kashayam Guggulutiktham exhibit size dependent catalytic performance in the reduction of MB [20]. Silver nanoparticles of different shapes synthesized by simple solvothermal method exhibited their shape dependent catalytic activity for the oxidation of styrene [21].

Present investigation reports the fast, extracellular synthesis of silver nanoparticles using *Penicillium* species. Effect of pH values of the reaction solutions was studied on the optical property SPR revealed by the silver nanoparticles.

2. Experimental Methods

Chemicals $AgNO_3$ and 0.1 N NaOH were used of analytical grade. Fungal species *Penicillum* species NCIM 1313 was obtained from National Chemical Laboratory Culture Collection Centre, Pune.

2.1 Preparation of Fungal Filtrate

The fungal organism *Penicillium* species was grown in a sterile liquid media potato dextrose broth [22]. After 7 days of incubation under static condition at 30 °C, the mycelial mat was observed on the media. The mycelia were separated using Whatman No.1 filter paper. The mycelia harvested on the paper was washed extensively using deionized water to remove the trace of the media component. Fresh ten gram of mycelia was suspended in 100 mL deionized water and incubated at 30 °C under shaking condition at 110 rpm for 72 h. After incubation period fungal mycelia was separated by filtration through Whatmann No.1 filter paper and the obtained filtrate [23] was used for the production of silver nanoparticles.

2.2 Production of Silver Nanoparticles

Five flasks each containing equal amount of fungal filtrate and $AgNO_3$ solution with final concentration of 1 mM were adjusted at different pH values 7-11 and all these flasks were incubated at 30 °C under shaking condition at 110 rpm for 72 h. The pH value of the reaction solution was adjusted by using 0.1 N NaOH solution.

*Corresponding Author:dr.drpatil@gmail.com(D.R. Patil)

https://doi.org/10.30799/jnst.230.19050203

Cite this Article as: H.G. Bhangale, S.G. Bachhav, D.M. Nerkar, K.M. Sarode, D.R. Patil, Study on optical properties of green synthesized silver nanoparticles for surface plasmon resonance, J. Nanosci. Tech. 5(2) (2019) 658–661.

2.3 Characterization

Formation of silver nanoparticles was observed visually by monitoring the change in colour. Variation in the intensity of the colour is the criterion used to study the effect of pH on the preparation of silver nanoparticles. UV-visible spectroscopy is the technique used to confirm the formation of silver nanoparticles and to study the influence of pH value of the reaction solution in the synthesis of nanoparticles. Alteration in colour intensity and absorption band in UV-visible spectra was used as the measure for the detection of effect of pH on the optical properties (SPR) of the silver nanoparticles.

The fungal filtrate was subjected to FTIR spectroscopy and scanned in the range of 500 to 4000 cm^{-1}. The presence of feasible biomolecules responsible for the reduction of silver ions and stabilization of the prepared nanoparticles were evaluated using FTIR analysis.

The powder form of samples was subjected to X-ray diffraction analysis to determine crystal structure. The diffracted intensities were recorded with 2θ in the range 20° to 80° with CuKα radiation. Thin films of colloidal solution of silver nanoparticles were prepared on glass slides and exposed to scanning electron microscopy (SEM S-4800) for size and shape details. TEM images of the prepared silver nanoparticles were obtained on Philips CM 200 Transmission electron microscope. Photoluminescence spectra of the prepared silver nanoparticles were recorded in Perkin Elmer LS 55 spectrofluorometer at room temperature. Both the excitation and emission slit widths were kept 5 nm and the entire scanning was done at the speed of 100 nm/minute. The catalytic performance of the prepared silver nanoparticles was evaluated for the reduction of MB by $NaBH_4$.

3. Results and Discussion

3.1 Visual Observation

The fungal filtrate (Fig. 1a) and $AgNO_3$ solution (not shown) maintain their original colours even after 72 h of incubation but the colour of fungal filtrate treated with $AgNO_3$ changes from light yellow to brown is the preliminary indication of the formation of the silver nanoparticles Fig. 1b. Five flasks in Fig. 2 displaying the variation in the intensity colour with increase in pH value of the reaction medium. The intensity of colour was increases with increase in pH value. It suggests that as the pH value increases rate of reduction of silver ions increases and result in faster nanoparticle production [24]. The appearance of the brown colour was due to surface plasmon resonance exhibited by formed silver nanoparticles [25].

Fig. 1 (a) *Penicillium* fungal filtrate and (b) synthesized AgNPs

Fig. 2 Variation in colour intensity with pH value

3.2 UV-Visible Spectroscopy

UV-visible absorption spectroscopy is the technique used to study surface plasmon resonance exhibited by silver nanoparticles prepared at different pH value. UV-visible spectra of fungal filtrate and those of silver nanoparticles prepared at different pH values are depicted in Fig. 3. Fungal filtrate shows the absorption at 237 nm due to amide band and 277 nm which are due to tryptophan and tyrosine residue present in the protein molecule [26]. Fungal filtrate doesn't show any absorbance peak in the visible region.

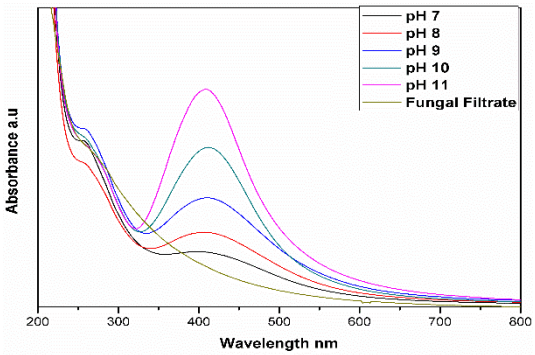

Fig. 3 UV-visible absorption spectra of fungal filtrate and filtrate treated with $AgNO_3$ at different pH values

Fungal filtrate treated with $AgNO_3$ solution showed the absorption peaks between 408 and 415 nm confirms the formation of silver nanoparticles. The SPR absorption band occurred due coherent oscillation of free electrons at the surface of metal nanoparticles [27]. Fig. 3 depicts that as the pH value increases the SPR curve becomes sharp and the peak was shifted towards blue end of the spectrum. The surface plasmon resonance shifts to higher energies which might be due to decrease in size of nanoparticles [8]. Under alkaline form of the reaction medium large numbers of functional groups are available to bind silver ions and hence large number of small sized AgNPs is produced [28].

It is clear from the absorption spectra that the maximum absorbance wavelengths (λ_{max}) blue shifted from 415 to 408 nm by increasing the pH value from 7 to 11. The maximum absorbance wavelength (λ_{max}) is associated with the conduction band energy according to quantum theory of metal nanoparticles [29].

The conduction band energy, E_{cb} (eV) can be calculated directly from the UV-visible absorption spectra by using the following Einstein's photon energy equation,

$$E_{cb} = \frac{hc}{\lambda_{max}}$$

where λ_{max} is the maximum absorbance wavelength, h is the Planck constant and c is the speed of light. Since, it can be seen that the conduction band energy is found to be 3.02 eV for silver nanoparticle prepared at pH value 11.

3.3 FTIR Analysis

FTIR spectrum of the *Penicillium* filtrate is shown in Fig. 4. The bands appeared at 657, 1070, 1249, 1357, 1643, 2077 and 3363 cm^{-1} indicates the involvement of different compounds and groups in the biosynthesis of silver nanoparticles.

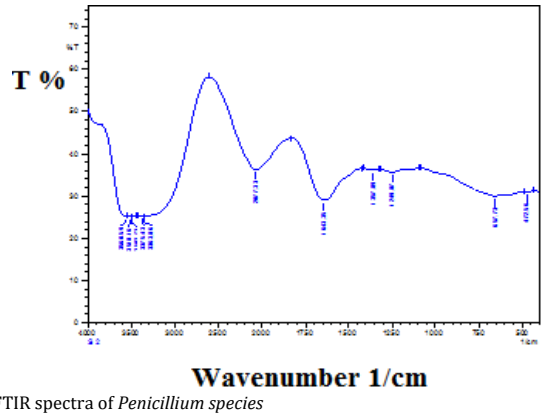

Fig. 4 FTIR spectra of *Penicillium species*

3.4 X-Ray Diffraction Analysis

XRD pattern of the prepared silver nanoparticles is shown in Fig. 5 which revealed the intensity peaks at 2θ values of 37.9°, 43.5°, 63.8° and 77.5°. The peaks are indexed to (111), (200), (220) and (311) planes respectively. XRD analysis suggests that prepared silver nanoparticles were crystalline in nature with fcc structure. It was matched with standard

https://doi.org/10.30799/jnst.230.19050203

Cite this Article as: H.G. Bhangale, S.G. Bachhav, D.M. Nerkar, K.M. Sarode, D.R. Patil, Study on optical properties of green synthesized silver nanoparticles for surface plasmon resonance, J. Nanosci. Tech. 5(2) (2019) 658–661.

JCPDS No. 43-0649. Also, the samples' crystallite size was found to 16.69 nm (Table 1), which calculated by using Scherer equation from the full width at the half maximum (FWHM) peak broadening of the high-intensity peak, (1 1 1) of the XRD graphs.

$$D(nm) = \frac{k\lambda}{\beta cos\theta} \quad (2)$$

where D is the crystalline size (nm); k is the shape factor, which is equal to 0.94 for sphere particles; β is the full width of the diffraction line at half of the maximum intensity measured in radians; λ is the X ray wavelength of Cu Kα = 0.154 nm; θ is Bragg angle.

Table 1 XRD analysis of synthesized Ag nanoparticles

2θ	θ	$cos\theta$	FWHM in radians	Size nm
37.9	19	0.946	0.0087	16.69

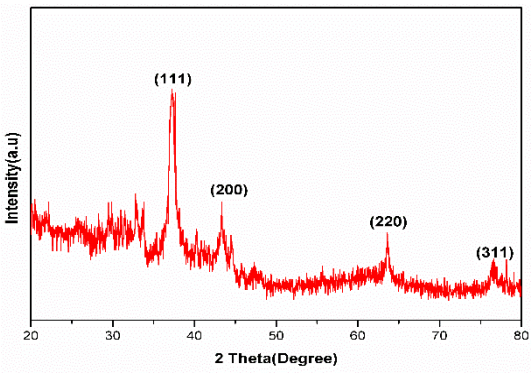

Fig. 5 XRD pattern of AgNPs

3.5 Scanning Electron Microscopy

Scanning electron micrograph of the prepared silver nanoparticles is shown in the Fig. 6. It clearly indicates that the nanoparticles were spherical in shape with uniform distribution and in the size range between 11 nm to 15 nm.

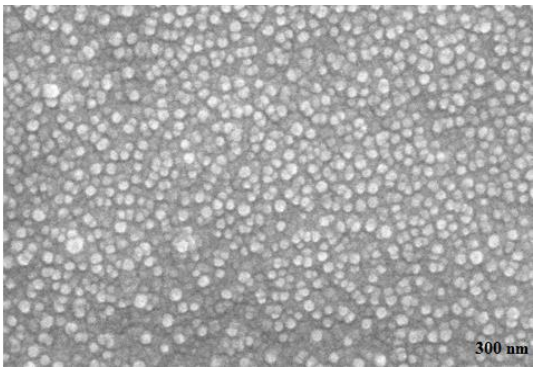

Fig. 6 Scanning electron micrograph of prepared AgNPs

3.6 Transmission Electron Microscopy

TEM images of the synthesized silver nanoparticles are depicted in Fig. 7(a) revealed that the particles were spherical in shape. The size of the nanoparticles was in the range of 9 to 19 nm. Selected area electron diffraction pattern shown in Fig. 7(b) indicates that prepared nanoparticles possess crystalline nature with face centered cubic geometry.

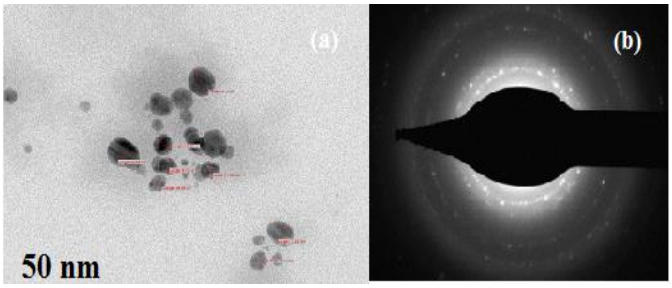

Fig. 7 (a) TEM image and (b) SAED pattern of AgNPs

3.7 Photoluminescence Spectra

The PL spectra of prepared colloidal solution of silver nanoparticles are depicted in Fig. 8. The emission peak was obtained in the visible region at 530 nm when excited at 400 nm. The luminescence of the nanoparticles is due to the excitation of free electrons from occupied 'd' band into higher excited states above the Fermi level which is then followed by relaxation to lower level. The energy losses of the electron result in luminescence. The optical properties of the silver nanoparticles depend on the interband and intraband transition between electronic states [30].

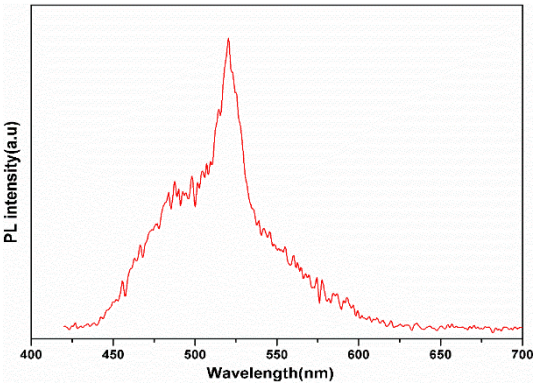

Fig. 8 PL emission spectra of AgNPs

3.8 Catalytic Activity

For the evaluation of the catalytic activity of prepared silver nanoparticles, the reduction of MB by $NaBH_4$ was studied [31, 32]. The reaction was carried in two tubes each contain 2ml of M.B. which is blue in colour. 0.5 mL $NaBH_4$ was poured in both tubes. Colloidal solution of 0.3 ml was added in solution of tube 2. The reaction was monitored visually as well as using UV-visible spectrometer. Immediately the reaction starts and, in few minutes, (2 minutes) the solution in tube 2 becomes colourless while the solution in tube 1 remained blue for several hours Fig. 9(a).

Fig. 9(b) shows that MB has a maximum absorbance at 663.5 nm but when the AgNPs solution was added in tube 2 the peak drops in few (two) minutes. This indicates the reduction of MB was catalyzed due to silver nanoparticles. One absorbance peak was observed at 400 nm which may be due to presence of silver nanoparticles.

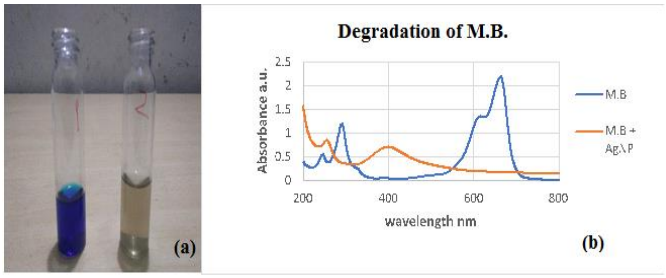

Fig. 9 Catalytic degradation of MB by $NaBH_4$

4. Conclusion

The optical properties of green synthesized silver nanoparticles were greatly influenced by the pH value of the reaction medium. The SPR curve sharpened and the peak was shifted towards blue end with increase in pH value. It is possible to produce large number of small, stable silver nanoparticles at a rapid rate under alkaline environment. Silver nanoparticles prepared using *Penicillium* species causes the reduction of MB in few minutes (120 seconds).

References

[1] Matthew R. Dirmyer, Joshua Martin, George S. Nolas, Ayusman Sen, John V. Badding, Thermal and electrical conductivity of size-tuned bismuth telluride nanoparticles, Small 5 (2009) 933-937.
[2] K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, George C. Schatz, The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment, J. Phys. Chem. B 107 (2003) 668-677.
[3] Vesna V. Vodnik, Dusan K. Bozanik, Natasa Bibic, Zoran V. Saponjic, Jovan M. Nedeljkovic, Optical properties of shaped silver nanoparticles, J. Nanosci. Nanotechnol. 8 (2008) 1-5.
[4] Vicki H. Grassian, When size really matters? Size-dependent properties and surface chemistry of metal and metal oxide nanoparticles in gas and liquid phase environments, J. Phys. Chem. C. 47 (2008) 18303-18313.

https://doi.org/10.30799/jnst.230.19050203

Cite this Article as: H.G. Bhangale, S.G. Bachhav, D.M. Nerkar, K.M. Sarode, D.R. Patil, Study on optical properties of green synthesized silver nanoparticles for surface plasmon resonance, J. Nanosci. Tech. 5(2) (2019) 658–661.

[5] Jayasmita Jana, Mainak Ganguly, Tarasankar Pal, Enlightening surface plasmon resonance of metal nanoparticles for practical spectroscopic application, Royal Soc. Chem. 6 (2016) 86174-86211.
[6] A. Katherine, Willets, P. Richard, Van Duyane, Localized surface plasmon resonance spectroscopy and sensing, Annu. Rev. Phys. Chem. 58 (2007) 267-297.
[7] M.D. Balakumaran, R. Ramchandran, P. Balashanmugam, D.J. Mukeshkumar, Mycosynthesis of silver and gold nanoparticles: Optimization, characterization and antimicrobial activity against human pathogens, Microbial Res. 182 (2016) 8-20.
[8] Klaus B. Mogensen, Katrin Kneipp, Size-dependent shifts of plasmon resonance in silver nanoparticles films using controlled dissolution: Monitoring the onset of surface screening effects, J. Phys. Chem. C 48 (2014) 28075-28083.
[9] Vincenzo Amendola, Osman M. Bakr, Francesco Stellacci, A study of the surface plasmon resonance of silver nanoparticles by the discrete dipole approximation method: Effect of shape, size, structure, and assembly, Plasmonic. 5 (2010) 85-97.
[10] S. Bhakya, S. Muthukrishnan, M. Sukumaran, M. Muthukumar, T. Senthil Kumar, M.V. Rao, Catalytic degradation of organic dyes using synthesized silver nanoparticles: A green approach, Jour. Bioremed. Biodegrad. 6(5) (2015) 1000312-1-9.
[11] Luis M. Molina, Sungsik Lee, Kristian Sell, Giovanni Barcaro, Alessandro Fortunelli, et al., Size- dependent selectivity and activity of silver nanoclusters in the partial oxidation of propylene to propylene oxide and acrolein: A Joint experimental and theoretical study, Catal. Today 160 (2011) 116-130.
[12] M.A. Raza, Z. Kanwal, A. Rauf, A.N. Sabri, S. Riaz, S. Naseem, Size-and shape - dependent antibacterial studies of silver nanoparticles synthesized by wet chemical routes, Nanomater. (Basel) 4 (2016) 1-26.
[13] http://news.stanford.edu/news/2012/march/plasmons-atomic-scale-032612.html (Accessed on: 26.03.2018)
[14] A.K. Gade, P. Bonde, A.P. Ingle, P.D. Marcato, N. Duran, M.K. Rai, Exploitation of *Aspergillus niger* for synthesis of silver nanoparticles, Jour. Biobased Mater. Bioenergy 2 (2008) 1-5.
[15] Navin Jain, Arpit Bhargava, Sonali Majumdar, J.C. Tarafdar, Jitendra Panwar, Extracellular biosynthesis and characterization of silver nanoparticles using *Aspergillus flavus* NJP08: A mechanism perspective, Nanoscale 3 (2011) 3635-3641.
[16] Gaikwad Sagar, Bhosale Ashok, Green synthesis of silver nanoparticles using *Aspergillus niger* and its efficacy against human pathogens, Eur. J. Exper. Biol. 5 (2012) 1654-1658.
[17] P. Mukharjee, M. Roy, B.P. Mandal, G.K. Dey, P.K. Mukherjee, J. Ghatak, A.K. Tyagi, S.P. Kale, Green synthesis of highly stabilized nanocrystalline silver particles by a non-pathogenic and agriculturally important fungus *T. asperellum,* Nanotechnol. 19 (2008) 075103-1-7.
[18] Dattu Singh, Vandana Rathod, Shivaraj Ninganagouda, Jyoti Hiremath, Ashishkumar Singh, Jasmine Mathew, Optimization and characterization of silver nanoparticle by endophytic fungi *Penicillium* Sp. isolated from *Curcuma longa* (Turmeric) and application studies against MDR *E. Coli* and *S. aureus*, Bioinorg. Chem. Application 2014 (2014) 408021-1-8.
[19] K.S. Hemath Naveen, Gaurav Kumar, L. Karthik, K.V. Bhaskara Rao, Extracellular synthesis of silver nanoparticles using the filamentous fungus *Penicillium sp.*, Arch. Appl. Sci. Res. 6 (2010) 161-167.
[20] V.S. Suvith, D. Philip, Catalytic degradation of methylene blue using biosynthesized gold and silver nanoparticles, Spectrochim. Acta A: Mol. Biomol. Spect. 118 (2014) 526-532.
[21] Run Xu, Dingsheng Wang, Jiatao Zhang, Yadong Li, Shape-dependent catalytic activity of silver nanoparticles for the oxidation of styrene, Chem. Asian. J. 1 (2006) 888-893.
[22] M. Govindappa, H. Farheen, C.P. Chandrappa, Channabasava, V. Rai Ravishankar, B. Raghavendra Vinay, Mycosynthesis of silver nanoparticles using extract of endophytic fungi, *Penicillium* species of *Glycosmis mauritiana*, and its antioxidant, antimicrobial, anti-inflammatory and tyrokinase inhibitory activity, Adv. Nat. Sci. Nanosci. Nanotech. 7 (2016) 035014-1-9.
[23] Shahnaz Majeed, Anima Nanda, Biosynthesis and assessment of silver nanoparticles with sparfloxacin and ofloxacin synthesized from *Penicillium* sp. on some bacterial pathogens, Int. J. Appl. Biol. Pharm. Technol. 5 (2014) 108-114.
[24] T.L. Riddin, M. Gericke, C.G. Whitely, Analysis of the inter and extracellular formation of platinum nanoparticles by *Fusarium Oxysporum* F. sp. Lycopersici using response surface methodology, Nanotechnology 17 (2006) 3482-3489.
[25] S.S. Shankar, A. Rai, A. Ahmad, M. Sastry, Rapid synthesis of Au, Ag, and bimetallic Au core-Ag shell nanoparticles using Neem (*Azadirachta indica*) leaf broth, J. Colloid Interf. Sci. 275 (2004) 496-502.
[26] S.F. Bhainsa, S.F. DSouza, Extracellular biosynthesis of silver nanoparticles using the fungus *Aspergillus fumigatus*, Colloids Surf. B. Biointerf. 47 (2006) 160-164.
[27] U. Kreibig, M. Vollmer, Optical properties of metal clusters, Springer, Berlin, 1995.
[28] M. Sathishkumar, K. Sneha, Y.S. Yun, Immobilization of silver nanoparticles synthesized using *Curcuma longa* tube powder and extract on cotton cloth for bacterial activity, Jour. Biores. Technol. 101 (2010) 7958-7965.
[29] E. Gharibshahi, E. Saion, Influence of dose on particle size and optical properties of colloidal platinum nanoparticles, Int. J. Mol. Sci. 13 (2012) 14723–14741.
[30] Vasireddy Ramakrishna, Paul Rima, Mitra Apurba Krishna, Green synthesis of silver nanoparticles and the study of the optical properties, Nanomater. Nanotechnol. 2(8) (2012) 1-6.
[31] K. Francis Princy, S. Manomi, R. Philip, A. Gopinath, Antibacterial and catalytic efficacy of biosynthesized silver nanoparticles using marine seaweed *Padina tetrasromatica*, Nano Bimed. Eng.1 (2016) 16-23.
[32] Liangwei Du, Qiuhong Xu, Meiying Huang, Liang Xian, jia-Xum Feng, Synthesis of small silver nanoparticles under light radiation by fungus *Penicillium oxalicum* and its application for the catalytic reduction of methylene blue, Mater. Chem. Phys. 160 (2015) 40-47.

https://doi.org/10.30799/jnst.230.19050203

Cite this Article as: H.G. Bhangale, S.G. Bachhav, D.M. Nerkar, K.M. Sarode, D.R. Patil, Study on optical properties of green synthesized silver nanoparticles for surface plasmon resonance, J. Nanosci. Tech. 5(2) (2019) 658–661.