



Photocatalytic and Antibacterial Potential of Green Synthesized Silver Nanoparticles by Using Leaf Extract of *Syzygium cumini*

M. Arshad¹, A. Qayyum^{2*}, A. Asrhad¹, S. Ahmad² and A. Sultan²

¹Department of Chemistry, Govt. Post Graduate Islamia College, Gujranwala, Pakistan

²Department of Chemistry, University of Agriculture, Faisalabad, Pakistan

Dr.arshadgcu@gmail.com; abdul_qayyum2000@yahoo.com; aishbutt18@gmail.com; Sohaira.ahmad@gmail.com, amarasultan85@yahoo.com

ARTICLE INFO

Article history :

Received : 29 October, 2016

Revised : 16 December, 2016

Accepted : 23 December, 2016

Keywords:

Green synthesis

Characterization

Antibacterial activity

Photocatalytic activity

ABSTRACT

Silver nanoparticles were successfully synthesized by leaf extract of *Syzygium cumini*. The phytochemicals present in *S. cumini* leaf extract were used for stabilization and reducing agent for the synthesis of silver nanoparticles. The stabilization of silver nanoparticles with phytochemicals was justified using Fourier-transform infrared spectroscopy. Scanning electron microscopy was performed for the morphology of morphology of nanoparticles which showed the cabbage flower like structure. X-ray diffraction analysis showed that the size of synthesized nanoparticles was found as 12.13nm. Effect of temperature was observed by using thermo gravimetric analysis which revealed the thermal stability till 300°C. Antibacterial potential by a disc diffusion assay showed significant results. Photocatalytic activity of silver nanoparticles showed that gradual increases of degradation (%) of methyl orange dye occur with respect to time for 2 hrs in the interval of 10 minutes.

1. Introduction

Waste water is the major cause of environmental pollution. It contains organic as well as inorganic materials. The important source of such causes is the presence of organic dye which is toxic and non-biodegradable. The removal degradation of the organic dyes is necessary to reduce the environmental pollution. It is very difficult challenge to remove or reduce these organic dyes [1]. Significant researches have been performed to study the photocatalysts for the conversion of organic dye into harmless substances [2], Different techniques had been develop for the removal of the colored pollutant from waste water [3].

Most effective and innovative technique is the advanced oxidation processes which have potential to degrade the dyes. It involves the semiconductors as photocatalysts by light assistance decomposes the dyes [4]. Advanced oxidation process is very effective, inexpensive, nontoxic and highly reactive process [5].

Nanostructures are getting more interest for its application in various fields. A range of techniques such as various hydrothermal procedures [6, 7], chemical vapor deposition [8, 9] and conventional sputter-deposition [10, 11], technique are usually involve in the synthesis of silver nanoparticles in different morphologies and size. But these techniques are complicated control processes, expensive equipment, high vacuums and temperatures [12]. So it is the need of time to find such a synthesis

techniques which is easy and more economical. Green chemistry has plays a key role in development of the eco friendly synthesis of nanoparticles [13]. Silver nanoparticles are getting more considerable due to unique photochemical, high catalytic, UV filtering properties, antifungal and antibacterial activity [14].

The green synthesis of nanoparticles can be by carried out by using the extracts of different plants species to synthesize nanoparticles, it is one of the most important biomimetic routes. Unlike biomimetic options which usually rely on microorganisms, plant-based option is generally simpler and quicker [15]. Starting with the pioneering work of silver nanoparticles, which have been synthesized by using a myriad of natural sources. Various factors such as shape and particle size etc. effects the efficiency of photocatalytic process. So structural characteristic of metal oxide nanoparticles is critical to antimicrobial and photocatalytic potential [16]. Monodispersed and smaller size (5-15nm) silver nanoparticles have maximum antimicrobial and photocatalytic activity [17].

2. Experimental

2.1 Preparation of Leaves Extract

About 20-25g of fresh leaves of *S. cumini* were collected from Govt. Post Graduate Islamia College, Gujranwala, Pakistan followed by washing with distilled water and cutting into small pieces. Later on heated at 700°C in 250 ml glass beaker with 100ml of double

* Corresponding author

distilled water for 15 minutes. After boiling, the color of the aqueous solution changed and cooled at room temperature. The aqueous extract of plant was separated by filtration with Whatman filter paper.

2.2 Synthesis of Silver Nanoparticles

The metal ions solutions were mixed with 8ml of plant leaves extract. After few minutes, depending on the concentration of metal ions and volume of the extract, the greenish color of solution changed to dark brownish color which indicates the formation of silver nanoparticles. The solid product formed was filtered and washed with ethanol and then dried at room temperature.

2.3 Assessment of Antibacterial Potential

Antibacterial potential was studied against two bacterial strains: *Staphylococcus aureus* and *Escherichia coli*. For this, 13 g of nutrient broth was dissolved in 1L distilled water for the medium growth, media culture and homogenized the solution followed by autoclaved for 15 mins at 121°C. The bacterial structure was intermixed with media culture and placed for shaking at 37°C for 24 hrs. The inoculums used in this experiment have 1×10^8 spores / mL and was store at 4°C. The petri plates were sterilized before the transferring of media to inoculation (100 μ L/100 mL) and then poured. Then smaller filter discs were flatly laid down on growth media which contained 100 μ L of these synthesized nanoparticles and Rimphin which was used as standard. Now this media was allowed to cooled for 24 hrs. The zone was formed which showed the growth inhibition of bacteria. The zone was measured by using zone reader [18].

2.4 Assessment of Photocatalytic Activity

The photocatalytic potential of synthesized silver nanoparticles by using plant sources was performed through degrading methyl orange dye under sun light. 10mg of methyl orange was dissolved in 1000 ml deionized water to prepare the methyl orange solution. 20 mg of Ag nanoparticles was mixed in 40 ml dye solution. A control experiment was also run parallel with same condition without addition of silver nanoparticles for the comparison of changes in color. The solution was stirred for half hr and then exposed to sun light to maintain equilibrium with mixture of silver nanoparticles. The temperature during experiment was measured as 30°C. 4 mL of the mixture was taken at an interval of 10 mins and take absorbance at 460nm [19].

3. Result and Discussion

3.1. Fourier-Transform Infrared Characterization

Fourier-Transform Infrared (FTIR) spectrum was examined the possible biomolecule which act as stabilizing and capping agent of silver nanoparticles. The peaks observed for silver nanoparticles which are formed through reduction by (alkane) C (*S. cumini*) at 1221 cm^{-1}

(C-O-C) 540 cm^{-1} , 1370 cm^{-1} (O-H bonding), 1013 cm^{-1} (C-O-C linking) 1480 cm^{-1} (=NH) 1630 cm^{-1} (amide) shows the presence of terpenoids (fig. 1). It also indicates the presence of proteins and other organic molecules in the materials that may be produced by leaves extract of *S. cumini*.

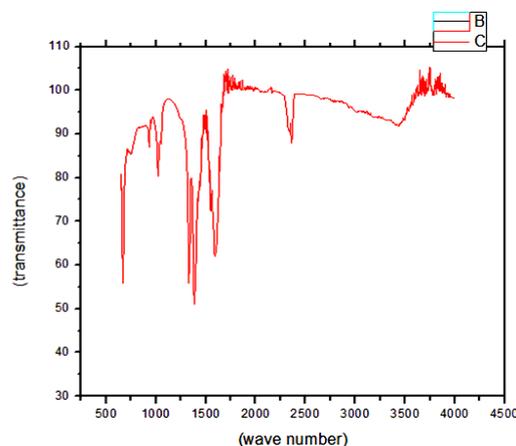


Fig.1: FT-IR spectrum of synthesized silver nanoparticles by using leaves extract of *S. cumini*

3.2 X-ray Diffraction Analysis

The crystal structure of silver nanoparticles was identified by XRD analysis at 2θ ranged from 20° to 70° . The characteristic peaks at 2θ values of 37.99, 43.93, 61.34, 64.31 and 77.55 degrees are assigned to diffraction planes (111), (200), (220) and (311), respectively. This diffraction data is well indexed with (PDF=04-0783). Some extra peaks are also observed in fig (2) which may be because of bioinorganic compounds which are present in plant extract. The average size of synthesized nanoparticles was calculated by using Scherrer equation:

$$D = k\lambda / (\beta \cos\theta) \quad (1)$$

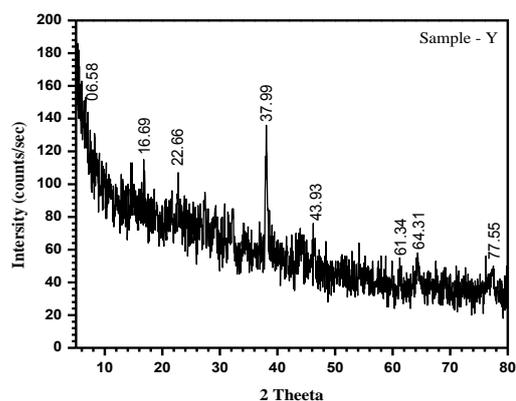


Fig. 2: XRD analysis of synthesized silver nanoparticles by using leaves extract of *S. cumini*

Where D is the particles sizes, k is the Scherrer constant, λ is the wavelength of X-ray source, β is the broadening of peaks and θ is the Bragg angle. The size of synthesized nanoparticles was found to be 12.13nm.

3.3 Scanning Electron Microscope Analysis

SEM analysis of synthesized silver nanoparticles was performed for morphology of synthesized nanoparticles. It was found that the particles are mono-dispersed just like cabbage flower as shown by fig (3).

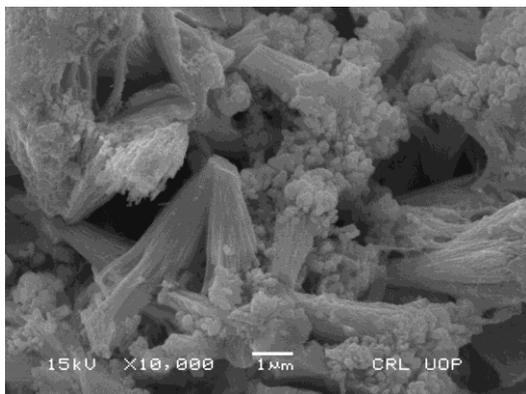


Fig.3: SEM analysis of synthesized silver nanoparticles by using leaves extract of *S. cumini*

3.4 Thermal Gravimetric Analysis

TGA analysis was carried out to study the thermal stability of silver nanoparticles which showed that nanoparticles synthesized by plant extract were started to degrade at 300°C. Fig (4) showed that first weight loss occur from 50 to 210°C which is attributed to the loss of water and organic residue present in it. The total weight loss was found upto 800°C for synthesized silver nanoparticles about 81.50%. Plant leave extract stabilized the silver nanoparticles are expected to be made up of molecules which are responsible for the reduction of silver ions.

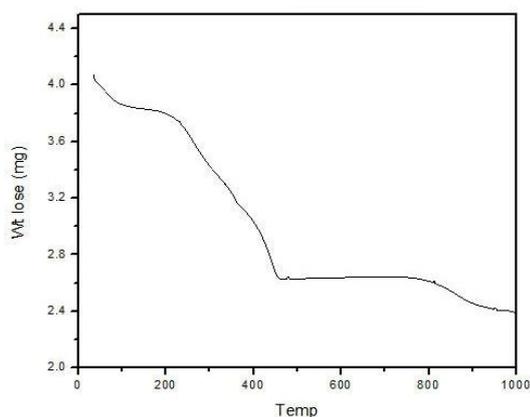


Fig. 4: TGA analysis of synthesized silver nanoparticles by using leaves extract of *S. cumini*

3.5 Antibacterial Potential

Antibacterial potential of synthesized nanoparticles was performed by disk diffusion assay against the *S. Aureus* and *E. coli* bacterial strains. The green synthesized

silver nanoparticles showed zone inhibition 19mm and 13mm by the *S. Aureus* and *E. coli*, respectively. Rifmpacin was also performed parallel, which showed 26mm and 32mm, respectively. The synthesized nanoparticles showed significant inhibition potential against both tested bacterial strains. It might be because of silver nanoparticles providing small surface size, uniform dispersion and active biomolecules [20]. Similar pattern of antibacterial potential was observed in the literature [21, 22]. Antibacterial potential of silver nanoparticles is dependent on surface area of nanoparticles due to production of Au^{+3} ions and play the function of reservoirs of Au^{+3} . The present results also confirmed the spherical shape and dispersal of silver nanoparticles [23], which lead to enhance the surface area and antibacterial potential.

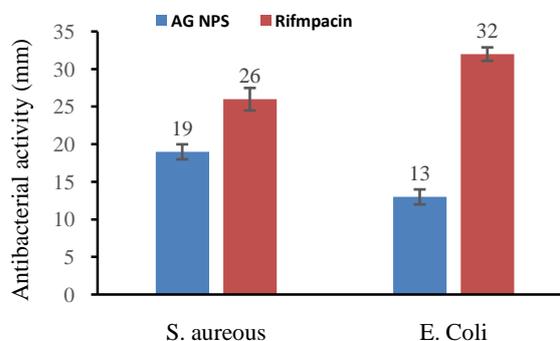


Fig. 5: Antibacterial activity of synthesized silver nanoparticles

3.6 Photocatalytic Activity

Photocatalytic activity of synthesized silver nanoparticles was performed by degrading the methyl orange (MO) dye under sun light radiation. The characteristic peaks for the absorption of MO dye were obtained at 460nm. The degradation of MO dye by using synthesized nanoparticles was indicated by the steady decrease in its absorption intensity within 2 hours. The percentage degradation was calculated by using formula

$$\% \text{age degradation} = \{(C_0 - C_t) / C_0\} * 100 \quad (2)$$

Where C_0 is the initial concentration, C_t is the concentration of MO dye at time. The control shows no change in colour of MO dye. The absorbance was found in directly relationship with the concentration. The degrading of MO dye was presented in fig (7). The previous studies by other solar irradiation and irradiation methods in the presence of non sized metal catalyst showed similar pattern [24]. MO dye contain anionic group that possess mutagenic characteristic. It is harmful for living organisms, so it must be degraded before the exposure in the environment [25].

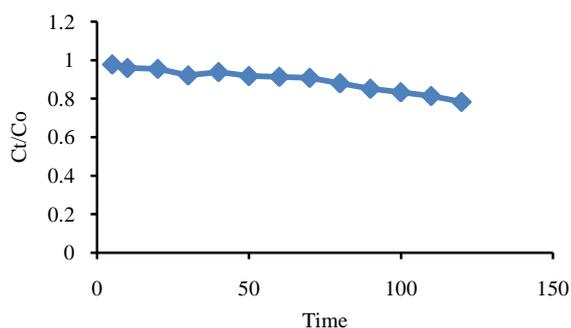


Fig. 6: Graph of C_t/C_0 vs time of photocatalytic activity

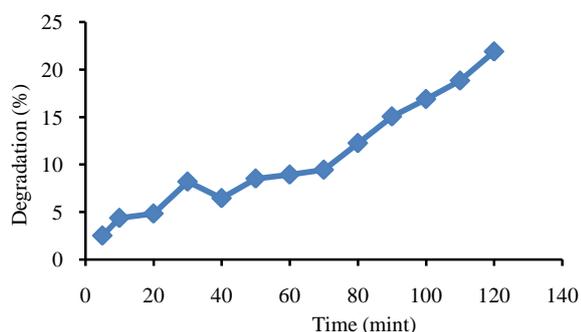


Fig. 7: % degradation of MO dye of synthesized silver nanoparticles

4. Conclusion

Silver nanoparticles were successfully synthesized by leaves extract of *S. cumini*. During experiment, the changing of solution colour is indication of formation of nanoparticles. Several techniques i.e. (FTIR, XRD, TGA, and SEM) were used for characterization of silver nanoparticles. The size of synthesized nanoparticles was found 12.13 nm with cabbage structure. Antibacterial potential of nanoparticles revealed significant results against both *S. aureus* and *E. coli* bacterial strains. The photocatalytic activity showed that a good increasing trend of degradation of dye with respect to time. Green synthesized silver nanoparticles are found to have enhanced biological applications. Due to enhanced antibacterial potential of silver nanoparticles, it is effectively used in the field of medicine as well as in food and cosmetic industries.

References

- [1] T. Robinson, G. McMullan, R. Marchant, P. Nigam, "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative", *Bioresource Technology*, vol. 77, no. 3, pp. 247-55, May 2001.
- [2] S.K. Kansal, S. Sood, A. Umar, "Mehta SK. Photocatalytic degradation of Eriochrome Black T dye using well-crystalline anatase TiO₂ nanoparticles", *Journal of Alloys and Compounds*, vol. 581 no. 01, pp.392-397, December 2013.
- [3] J. M. Peralta-Hernández, C. A. Martínez-Huitile, J. L. Guzmán-Mar, A. Hernández-Ramírez, "Recent advances in the application of electro-Fenton and photoelectro-Fenton process for removal of synthetic dyes in wastewater treatment" *Journal of Environmental Engineering and Management*, vol. 19, no. 5, pp. 257-265 September 2009.
- [4] H. R. Mardani, M. Forouzani, M. Ziari, P. Biparva, "Visible light photo-degradation of methylene blue over Fe or Cu promoted ZnO nanoparticles" *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 141, pp. 27-33, April 2015.
- [5] M. A. Fox, M. T. Dulay, "Acceleration of secondary dark reactions of intermediates derived from adsorbed dyes on irradiated TiO₂ powders", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 98, no. 1, pp. 91-101, August 1996.
- [6] L.N. Dem'yanets, L.E. Li and T.G. Uvarova, "Hydrothermal synthesis and cathodoluminescence of ZnO crystalline powders and coatings", *Journal of Crystal Growth*, vol. 87, no. 1, pp. 23-27, January 2006.
- [7] M. Guo, P. Diao and S. Cai, "Hydrothermal growth of well-aligned ZnO nanorod arrays: Dependence of morphology and alignment ordering upon preparing conditions" *Journal of Solid State Chemistry*, vol. 178, no. 6, pp. 1864-1873, June 2005.
- [8] J.Y. Park, D.J. Lee, Y.S. Yun, J.H. Moon, B.T. Lee and S.S. Kim, "Temperature-induced morphological changes of ZnO grown by metal organic chemical vapor deposition", *Journal of Crystal Growth*, vol. 276, no. 1, pp.158-64, March 2005.
- [9] H.W. Sun, G. Y. Kim, Y. S. Jung, W. K. Choi, D. J. Byun, "Growth and properties of ZnO nanoblade and nanoflower prepared by ultrasonic pyrolysis. *Journal of applied physics*", vol. 97, no. 4, pp. 1-4, February 2005.
- [10] W.T. Chiou, W.Y. Wu and J.M. Ting, "Growth of single crystal ZnO nanowires using sputter deposition", *Diamond and Related Materials*, vol. 12, no.10, pp.1841-1844, November 2003.
- [11] S.S. Lin, J. L. Huang and D. F. Li, "Effect of substrate temperature on the properties of Ti-doped ZnO films by simultaneous rf and dc magnetron sputtering" *Materials chemistry and physics*, vol. 90, no.1, pp. 22-30, March 2005.
- [12] R. Saleh and N. F. Djaja, "UV light photocatalytic degradation of organic dyes with Fe-doped ZnO nanoparticles" *Superlattices and Microstructures*, vol. 74, pp. 217-233, October 2014.
- [13] G. Sangeetha, S. Rajeshwari and R. Venkatesh, "Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: Structure and optical properties", *Materials Research Bulletin*, vol. 46, no. 12, pp. 2560-2566, December 2011.
- [14] C. Jayaseelan, R. Ramkumar, A.A Rahuman and P. Perumal, "Green synthesis of gold nanoparticles using seed aqueous extract of *Abelmoschus esculentus* and its antifungal activity, *Industrial Crops and Products*, vol.45, pp. 423-429, February 2013.
- [15] M. Stan, A. Popa, D. Toloman, A. Dehelean, I. Lung and G. Katona, "Enhanced photocatalytic degradation properties of zinc oxide nanoparticles synthesized by using plant extracts", *Materials Science in Semiconductor Processing*, vol. 39, pp. 23-29, November 2015.
- [16] A. Zielińska, E. Kowalska, J. W. Sobczka, I. Łacka, M. Gazda, B. Ohtani, J. Hupk and A. Zaleska, "Silver-doped TiO₂ prepared by microemulsion method: surface properties, bio- and photoactivity", *Separation and Purification Technology*, vol. 72, no. 3, pp. 309-18, May 2010.
- [17] A. Zielińska-Jurek, Z. Wei, I. Wysocka, P. Szweida and E. Kowalska, "The effect of nanoparticles size on photocatalytic and antimicrobial properties of Ag-Pt/TiO₂ photocatalysts", *Applied Surface Science*, vol. 353, pp. 317-25, October 2015.
- [18] M. Arshad, M. A. Farrukh, R. A. Sarfraz, A. Qayyum and S. Ali, "Structural characterization of Fe/TiO₂ nanoparticles: antioxidant and antibacterial studies", *Biointerface Research in Applied Chemistry*, vol. 6, no. 5, pp. 1497-1501, October 2016.
- [19] M. Vanaja, K. Paulkumar, M. Baburaja, S. Rajeshkumar, G. Gnanajobitha, C. Malarkodi, M. Sivakavinesan and G. Annadurai, "Degradation of methylene blue using biologically

- synthesized silver nanoparticles”, *Bioinorganic chemistry and applications*, March 2014.
- [20] A. U. Khan, Q. Yuan, Y. Wei, S. U. Khan, K. Tahir, Z. U. Khan, A. Ahma, F. Ali, S. Ali, S. Nazir, “Longan fruit juice mediated synthesis of uniformly dispersed spherical AuNPs: Cytotoxicity against human breast cancer cell line MCF-7, Antioxidant and Fluorescent Properties”, *RSC Advances*, vol. 6, no. 28, pp. 23775-23782, 2016
- [21] N. Abdel-Raouf, N.M. Al-Enazi, I.B. Ibraheem, “Green biosynthesis of gold nanoparticles using *Galaxaura elongata* and characterization of their antibacterial activity”, *Arabian Journal of Chemistry*, December 2013.
- [22] R. Nirmala, F. A. Sheikh, M. A. Kanjwal, J. H. Lee, S. J. Park, R. Navamathavan and H. Y. Kim, “Synthesis and characterization of bovine femur bone hydroxyapatite containing silver nanoparticles for the biomedical applications. *Journal of Nanoparticle Research*, vol. 13, no. 5, pp. 1917-1927, May 2011.
- [23] J.K. Patra, K. H. Baek, “Novel green synthesis of gold nanoparticles using *Citrullus lanatus* rind and investigation of proteasome inhibitory activity, antibacterial and antioxidant potential”, *International Journal of Nanomedicine*, vol. 10, pp. 7253, 2015.
- [24] P. Kumar, M. Govindaraju, S. Senthamilselvi and K. Premkumar, “Photocatalytic degradation of methyl orange dye using silver (Ag) nanoparticles synthesized from *Ulvalactuca*”, *Colloids and Surfaces B: Biointerfaces*, vol.103, pp. 658-661, March 2013.
- [25] L. Yu, J. Xi, H. T. Chan, T. Su, D. L. Phillips, W. K. Chan, “The degradation mechanism of methyl orange under photo-catalysis of TiO_2 ”, *Physical Chemistry Chemical Physics*, vol. 14, no. 10, pp. 3589-3595, 2012.