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BIOSYNTHESIS OF COPPER OXIDE NANOPARTICLES USING *PYRUS PYRIFOLIA* LEAF EXTRACT AND EVOLVE THE CATALYTIC ACTIVITY

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Abstract - ***The present study, deals with investigating the effect of bio synthesis method. In this method, the interaction time on morphology and size of Copper oxide nanoparticles synthesized using aqueous leaf extract. The plant extracts plays a vital role in the field of nanotechnology as it is environmentally friendly and does not involve any harmful chemicals. The synthesized nanoparticles were characterized by using UV-vis spectroscopy, X – ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR) analysis, FE – SEM with EDX and AFM were carried out to determine the nature of the capping agents in each of these Pyrus Pyrifolia leaf extracts, respectively. The Photocatalytic activity of biosynthesized CuO nanoparticles was studied using methylene blue under solar irradiation and these nanoparticles showed efficacy to degrading the dye within a few hours of exposure.***

KeyWords: Copper oxide nanoparticles, *Pyrus Pyrifolia*, XRD, FT-IR, UV-Vis, FESEM, EDX, AFM, Photocatalytic activity**.**

1. INTRODUCTION

In recent years, Bio synthesis of nanoparticles is an important approach in nanotechnology [1]. Nanotechnology has appealed many researchers from several fields like biotechnology, physics, chemistry, material science, engineering and medicine. Nanoparticles are synthesized by physical and chemical Methods; these are suffering from drawbacks like expensive reagent, hazardous reaction condition, longer time, tedious process to isolate nanoparticles [2, 3]. Metal oxide nanoparticles (NPs) are important due to their applications in optoelectronics, nanodevices, nanoelectronics, nanosensors, information storage, and catalysis. Among various metal oxide NPs, CuO has attracted particular attention because it is the simplest member in the family of copper compounds and shows a range of useful physical properties such as high temperature superconductivity, electron correlation effects, and spin dynamics [4]. Copper oxide nanoparticles have been recently found to be potentially useful in gas sensors, batteries, dye sensitized solar cells, field emission emitters and fuel cells. Human beings have been using copper (Cu) and Cu complexes for various purposes for centuries, such as water purifiers, algaecides, fungicides, and as antibacterial and antifouling agents [5, 6].

Copper oxide nanoparticles green synthesis plays a role in photocatalytic dye degradation. The enormous volume of environmental pollutants, nondegradable and carcinogenic natured colored dye effluents is discharged by the textile and paper industries. Moreover, to unique in their products most of the industry uses colour dyes, without any treatment of colouring materials are liquidated in water leads to contamination of resources. Nowadays, a photocatalytic method got the wide attention due to its effective decolorization of dyes [7].

Biosynthesis of CuO NPs have been reported by various plants such as *Acalypha indica* [1],*Phyllanthus Amarus* Leaf [8], *T. arjuna* bark extract [9], *Calotropis gigantean* leaf extract [10], *Malva sylvestris* Leaf Extract [11], aqueous extract of flowers of *Cassia alata [12], Ocimum Sanctum* Leaf Extract [13], *Gloriosa superba L.*[14], *Carica papaya* [15], *Tabernaemontana divaricate* leaf extract [16], *Aloe barbadensis* [17], *Tinospora cordifolia* [18].

In this present work, we studied the photocatalytic degradation of methylene blue dye in presence of biogenic CuO nanoparticles synthesized using *Pyrus Pyrifolia* leaf extract, which consider being the low cost, simple procedure and eco–friendly to the environment.

2. MATERIALS AND METHODS

2.1 Materials and preparation of leaf extract

Pyrus Pyrifolia plant leaves were collected from Ooty, Nilgiris district, Tamil Nadu, India. The leaves were identified and authenticated by Department of Agriculture, Annamalai University at Tamilnadu in India. The leaves were washed several times with distilled water to remove the dust particles. After that the leaves are dried in 15 days at room temperature (32 °C) and then the leaves grained

into a fine powder using mortar. The Pyrus leaf powder of 1g was taken for synthesis purpose. The weighed of 1g leaf powder were boiled with 150 ml of distilled water for 20 min at 80 °C until the colour of the aqueous solution changes from watery to brown. The extract was cooled at room temperature and filtered by Whatman No1 filter paper, stored at room temperature in order to use for further studies.

2.2 Preparation of Copper Oxide NPs

The synthesis of CuO NPs, 30 mL of *Pyrus Pyrifolia* leaves extract was taken and boiled at 80 °C by using a magnetic stirrer. When the temperature of the solution was reached at 80 °C, 1 g of copper nitrate hexahydrate (Cu $(NO_3)_2$ $6H_2O$) was added. The mixture was boiled until it changed to a green colour paste. Then the paste was collected in a ceramic crucible and heated using muffle furnace at 400 °C for 3 hrs. Finally, we got black colour powder; it was stored in properly labeled containers and used for further Characterization.

2.3 Characterization

UV–Vis spectrophotometer (Shimadzu -1800) was used to obtain the absorption spectrum of the CuO Nps wave length is 200–800 nm. The purity and crystalline size were characterized by X-ray diffractometer (XPERT-PRO) using Cu-K radiation of wavelength λ =1.541 Å of synthesized Copper oxide nanoparticles. The FTIR spectra of plant leaf extract and synthesized Copper oxide nanoparticles were recorded by KBr pellet method using FTIR spectrometer (range 4000–400 cm^{-1}) (Shimadzu). The morphology of the synthesized CuO NPs were observed by Field emission scanning electron microscopy (FE – SEM, supra- 55, India) and the elemental composition by recording (EDX, BRUKER, India). The surface morphology studies were carried out using Atomic force Microscope.

2.4 Photocatalytic activity of CuO nanoparticles

The Photocatalytic activity of these synthesized CuO Nps was studied by degradation of methylene blue under sunlight irradiation. Initially, the preparation of dye solution by dissolving 1 mg powder of methylene blue in 100 ml of distilled water (10 mg/l concentration). 10 mg of CuO nanoparticles was added with 50 ml dye solution of methylene blue and the mixture was stirred magnetically for 30 min in darkness before exposing to sunlight. A control was prepared and kept under the similar condition for comparing any change in color of the dye solution. The colloidal suspension was then put under sunlight irradiation with constant stirring. The average temperature of the ambience during the experiment was found to be around 30 °C with 3.30 hrs mean sun shine duration. At frequent time intervals (every 30 min), 5ml of suspension was taken from the colloidal mixture and centrifuged at 5,000 rpm for 15 min to obtain clean supernatant soup of the tested dye. The soup was then scanned at different wavelength from 200 to 800 nm using the Shimadzu -1800 UV–Vis spectroscope to study the dye degradation in presence of CuO nanoparticles.

3. Result and Discussion

3.1 X-ray diffraction analysis

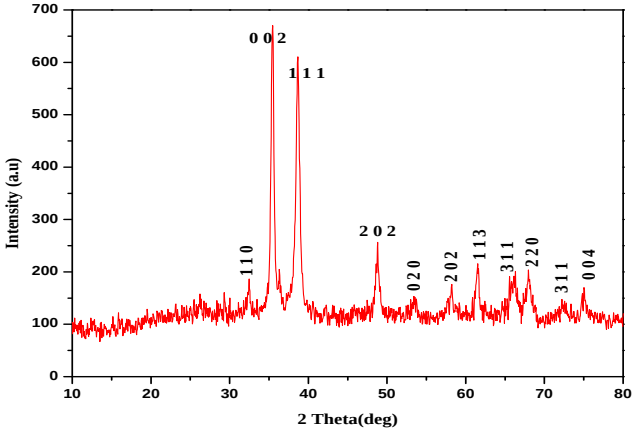


Fig. 1. XRD patterns of CuO nanoparticles.

Table1: The structure and geometric parameters of CuO NPs

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
32.4933	65.01	0.2952	2.75558	11.81
35.4796	**550.29**	**0.2952**	**2.53019**	**100.00**
38.7000	469.00	0.3444	2.32674	85.23
48.7555	114.43	0.3936	1.86780	20.80
53.5962	25.50	0.6888	1.70997	4.63
58.2338	63.74	0.2952	1.58436	11.58
61.5734	85.93	0.3444	1.50620	15.61
66.0191	69.75	0.7872	1.41514	12.67
68.0193	82.94	0.3936	1.37832	15.07
72.4536	24.90	1.1808	1.30450	4.53
74.9254	30.52	0.5904	1.26748	5.55

The XRD pattern of synthesized CuO nanoparticles from leaf extract of *P. Pyrifolia* is shown in Fig. 1. The diffraction peaks appearing at 2θ of 32.49, 35.47, 38.70, 48.75, 53.59, 58.23, 61.57, 66.01, 68.01, 72.45 and 74.92 (deg) were assigned to planes of (110), (111), (111), (202),

(020), (202), (113), (311), (220), (311) and (004) respectively. The sharp and narrow diffraction peaks indicating highly crystalline structure nature and also phase purity of nano particles. The bio-synthesized CuO nanoparticles has monoclinic phase when compare data from JCPDS card No. 45 – 0937. From the XRD pattern average size calculated by using Scherer's equation (1).

$$D = \frac{K\lambda}{\beta Cos\theta}\ \text{Å} \qquad \text{-- (1)}$$

Where D is the average crystallite size in Å, K is the shape factor , λ is the wavelength of X-ray (1.5406 Å) CuKα radiation, θ is the Bragg's angle, and β is the corrected line broadening of the NPs. The average grain size was found to be 22 nm.

3.2 UV–Vis absorption spectroscopy analysis

Fig.2. Depicts the UV–vis spectrum of bio synthesized copper oxide nano particles using *P. Pyrifolia* leaf extract. The CuO NPs was dispersed in liquid ammonia with a concentration of 0.1 wt%, sonicated for uniform dispersion of CuO Nps and so subjected for UV – visible spectrophotometric measurements. The CuO Nps exhibiting the optical absorption peak at wavelength of 395 nm.

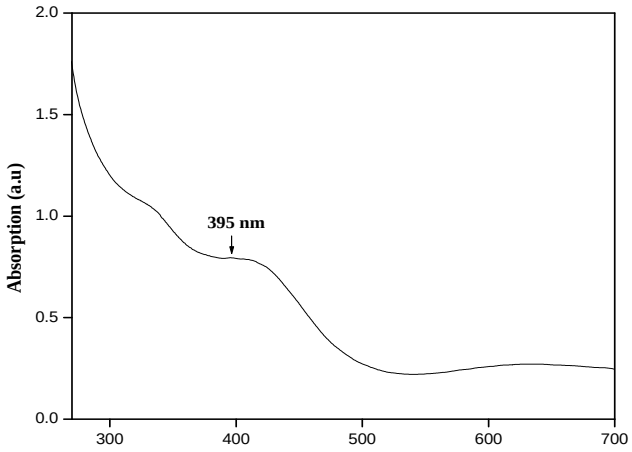


Fig.2. shows UV–Visible spectra of CuO nanoparticles.

3.3 FTIR Analysis of CuO Nps

FTIR spectroscopy analysis was carried out to find the functional groups of biomolecules that were bound specifically along the copper oxide nanoparticles surface. The FTIR spectra of bio-synthesized CuO nanoparticles and leaf powder of *P. Pyrifolia* were shown in Fig. 3. The spectrum depicted bands at 528 cm^{-1}, 669 cm^{-1} are assigned to M–O stretching of CuO (M–O). The broad and strong absorption bands were 3435 cm^{-1}, 2362 cm^{-1} corresponds to O–H stretching H–bonded alcohols, phenols, C–H stretching aldehydes [20]. 2924 cm^{-1} C–H stretching alkanes, 1637 C=O stretching and N–H bend 1° amines, 1423 cm^{-1},1024 cm^{-1} C–O stretching [6].

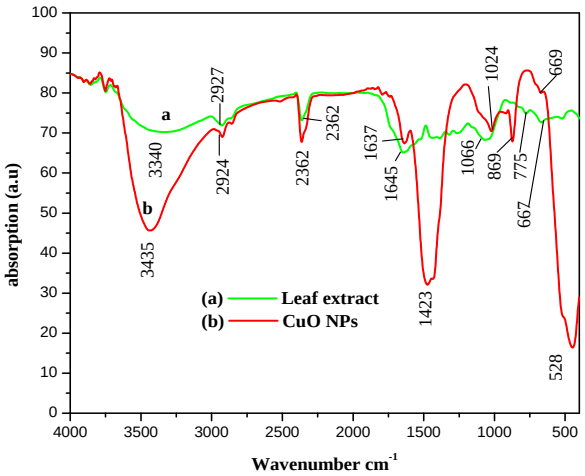
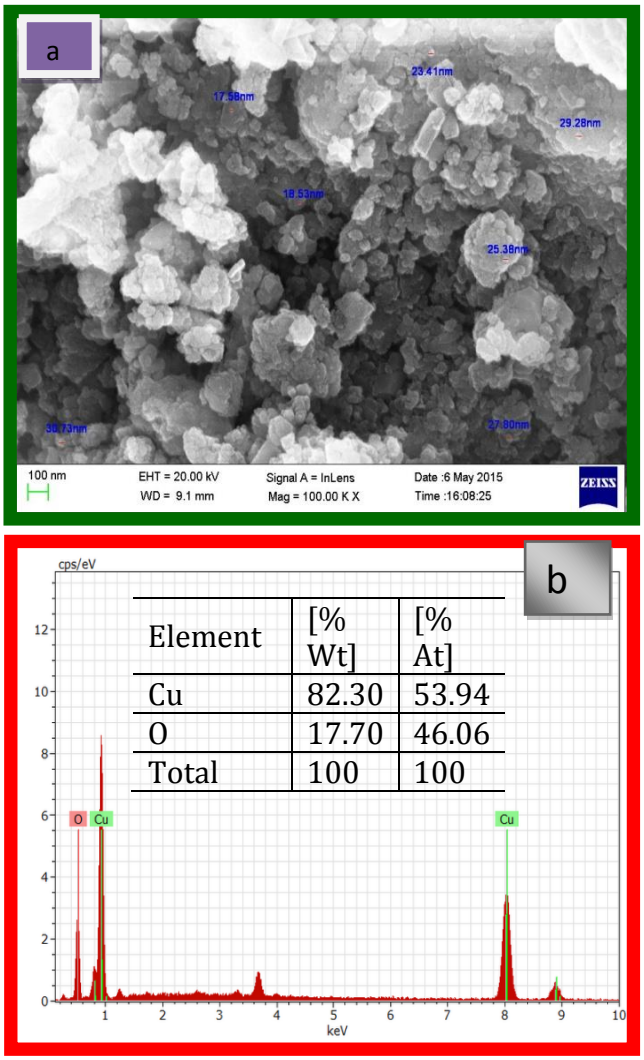


Fig.3. FT-IR spectra of (a) leaf powder of *Pyrus Pyrifolia* (b) bio synthesized CuO nanoparticles

3.4 FE-SEM Micrographic image of CuO Nps with EDX spectrum

The surface morphology and micro structure of CuO Nps is investigated by using FE-SEM analysis as shown in Fig. 4(a). It clearly shows that the particles are small and uniform size, almost spherical in nature which is free from agglomeration [9, 19]. The particle size was starting from 17 to 30 nm having some deviation. The average particle size of CuO nano particles was detected as 24 nm. The result of XRD pattern and FE- SEM was concordat. The chemical composition of bio synthesized CuO Nps was revealed by EDX spectrum. From the spectrum strong peaks observed from and small peak observed from O elements. The atomic and weight percentage of Cu and O are 53.94, 46.06, 82.30, and 17.70 respectively.



Element	[% Wt]	[% At]
Cu	82.30	53.94
O	17.70	46.06
Total	100	100

Fig.4. (a) FE-SEM image of synthesized CnO NPs. (b) EDX image of CuO Nps

3.5 AFM analysis of CuO NPs

The surface topology of bio-synthesized CuO Nps was analyzed by AFM analysis. The AFM image depicts that fractal, porous, homogeneous and densely packed small grains are observed over the entire surface of scanned area. The average grain size was found to be 22.5 nm from 3D profile image. However, maximum of particles observed within 12.5 nm.

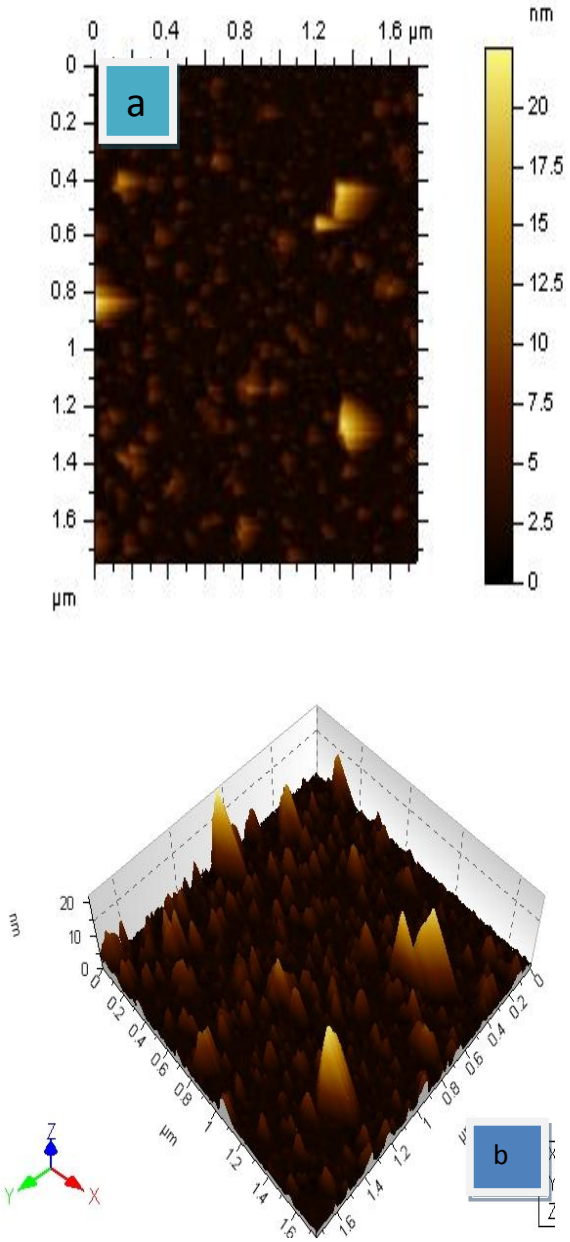


Fig.5. (a) and (b) depicts 2D and 3D structure of green synthesized CuO Nps micrograph image.

3.6 Analysis of Photocatalytic activity

The Photocatalytic activity of the biosynthesized CuO nanoparticles was evaluated by degradation of methylene blue under solar irradiation. Dye degradation was visually detected by gradual change in the color of the dye solution from deep blue to colorless (Fig. 6). The characteristic absorption peak for methylene blue was noticed at 657 nm. The control exhibited no change in coloration during exposure in sunlight. The degradation of the dye in presence of biogenic CuO nanoparticles was verified by the decrease of the peak intensity (at 657 nm) during 3.30 hrs of exposure in sunlight (Fig. 7).

Fig.6. Gradual change in dye color from blue to colorless denotes dye degradation

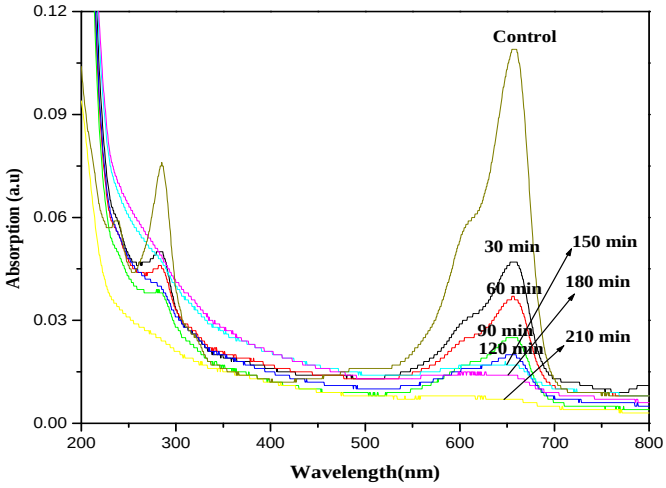


Fig.7. UV spectra of photocatalytic degradation of methylene blue with reaction time

The dye degradation (%) was calculated using the following equation 2 and its variance with the time of solar exposure is shown in Fig.8.

Dye degradation (%) =

$[(C_0 - C_t / C_0)] \times 100$ -------- (2)

Where C_0 is the initial concentration of the methylene blue solution and C_t is the concentration of the dye solution after t hours of exposure in solar irradiation. All dye concentrations were measured by taking the value of absorbance at 657 nm in the UV–Vis spectra as the concentration is directly proportional to the absorbance value. The solar light was found to be more effective than other irradiation techniques for degrading dyes as reported by the previous studies (20, 21).

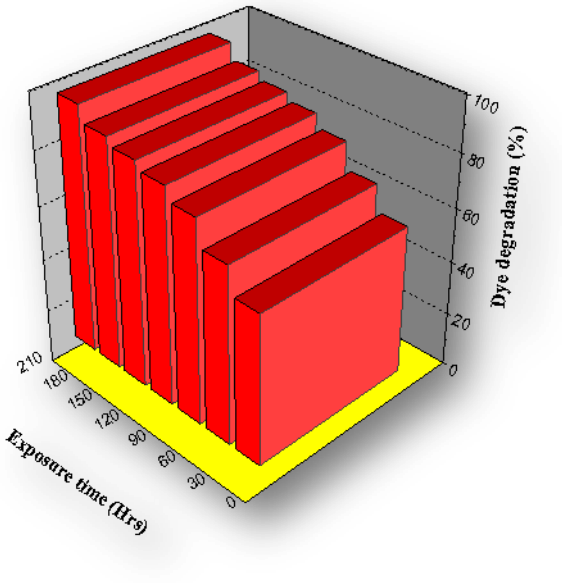


Fig.8. 3D bar graph shows the variation of dye degradation at different exposure time

4. CONCLUSION

In this present study, eco-friendly inexpensive, simple and novel approach of the biosynthesized CuO Nps using *P. Pyrifolia* leaf extract have been reported. Powder XRD, FE – SEM, EDX, AFM, FTIR and UV–visible. The techniques were utilized to affirm the CuO nanoparticles. The photocatalytic result concludes that these biogenic CuO nanoparticles have efficiency to degrade methylene blue under solar irradiation. Hence, they can find applications in textile industry and water treatment plants.

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Reference

1. Rajeshwari Sivaraj., Pattanathu K.S.M. Rahman., P. Rajiv., S. Narendhran., R. Venckatesh., 2014. Biosynthesis and characterization of Acalypha indica mediated copper oxide nanoparticles and evaluation of its antimicrobial and anticancer activity. Molecular and Biomolecular Spectroscopy 129: 255–258.
2. Lanje A. S., Sharma S. J., Pode R. B., Ningthoujam R. S, 2010. Synthesis and optical characterization of copper oxide nanoparticles. Advances in Applied Science Research 1(2): 36-40.
3. Yang G., Chai S., Xiong X., S. Zhang., YU L., Zhang P, (2012). Preparation and tribological properties of surface modified Cu nanoparticles Trans. Nonferrous Met. Soc. China 22(2): 366−372.
4. Maqusood Ahamed., Hisham A. Alhadlaq., M. A. Majeed Khan., Ponmurugan Karuppiah., and Naif A. Al-Dhabi., 2014. Synthesis, Characterization, and Antimicrobial Activity of CopperOxideNanoparticles. Journal of Nanomaterials. Article ID 637858.
5. Dongdong Li., Jun Hu., Ruqian Wu., and Jia G Lu., 2010. Conductometric chemical sensor based on individual CuO nanowires. Nanotechnology. 21: 485502.
6. Vinod Vellora., Thekkae Padil., Miroslav Černík., 2013. Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. International Journal of Nanomedicine. 8: 889–898.
7. Renu Sankar., Perumal Manikandan., Viswanathan Malarvizhi., Tajudeennasrin Fathima., Kanchi Subramanian Shivashangari., Vilwanathan Ravikumar., 2014. Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121: 746–750.
8. N. P. S. Acharyulu., R. S. Dubey., V. Swaminadham., R. L. Kalyani Pratap Kollu., S. V. N. Pammi, 2014. Green Synthesis of CuO Nanoparticles using Phyllanthus Amarus Leaf Extract and their Antibacterial Activity against Multidrug Resistance Bacteria. International Journal of Engineering Research & Technology (IJERT) Vol. 3 Issue 4.
9. S. Yallappa., J. Manjanna., M.A. Sindhe., N.D. Satyanarayan., S.N. Pramod., K. Nagaraja, 2013. Microwave assisted rapid synthesis and biological evaluation of stable copper nanoparticles using T.arjuna bark extract Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 110: 108–115.
10. Jitendra Kumar Sharma., M. Shaheer Akhtar., S. Ameen., Pratibha Srivastava., Gurdip Singh, 2015. Green synthesis of CuO nanoparticles with leaf extract of Calotropis gigantea and its dye sensitized solar cells applications. Journal of Alloys and Compounds 632: 321–325.
11. Awwad, A.M., Albiss, B.A, Salem N.M. 2015. Antibacterial Activity of synthesized Copper Oxide Nanoparticles using *Malva sylvestris* Leaf Extract. SMU Medical Journal, Volume – 2, No. 1.
12. Jayalakshmi A., Yogamoorthi, 2014.Green synthesis of copper oxide nanoparticles using aqueous extract of flowers of *Cassia alata* and particles characterization. International Journal of Nanomaterials and Biostructures 4(4): 66-71.
13. Vasudev D. Kulkarni., Pramod S. Kulkarni, 2013. Green Synthesis of Copper Nanoparticles Using Ocimum Sanctum Leaf Extract. International Journal of Chemical Studies. Vol. 1 No. 3.
14. H. Raja Naika., K. Lingaraju., K. Manjunath., Danith Kumar., G. Nagaraju., D. Suresh., H.Nagabhushana, 2015. Green synthesis of CuO nanoparticles using *Gloriosa superba* L. extract and their antibacterial activity. Journal of Taibah University for Science 9: 7–12.
15. Renu Sankar., Perumal Manikandan., Viswanathan Malarvizhi., Tajudeennasrin Fathima., Kanchi Subramanian Shivashangari., Vilwanathan Ravikumar, 2014. Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121: 746–750.
16. Rajeshwari Sivaraj, Pattanathu K.S.M. Rahman., P. Rajiv., Hasna Abdul Salam, R. Venckatesh 2014. Biogenic copper oxide nanoparticles synthesis using Tabernaemontana divaricate leaf extract and its antibacterial activity against urinary tract pathogen. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 133: 178–181.

17. Sangeetha Gunalan., Rajeshwari Sivaraj., Rajendran Venckatesh 2012. Aloe barbadensis Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: Optical properties Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 97: 1140–1144.
18. Udayabhanu., P.C. Nethravathi., M.A. Pavan Kumar., D. Suresh., K. Lingaraju, H. Rajanaika., H. Nagabhushana., S.C Sharma 2015. Tinospora cordifolia mediated facile green synthesis of cupric oxide nanoparticles and their photocatalytic, antioxidant and antibacterial properties Materials Science in Semiconductor Processing 33: 81 –88
19. Jitendra Kumar Sharma., M. Shaheer Akhtar ., S. Ameen., Pratibha Srivastava., Gurdip Singh, 2015.Green synthesis of CuO nanoparticles with leaf extract of Calotropisgigantea and its dye-sensitized solar cells applications, Journal of Alloys and Compounds 632: 321–325.
20. Kansal SK., Singh M., Sudo D, 2008. Studies on TiO2/ZnO photocatalysed degradation of lignin. J Hazard Mater 153:412–417.
21. Kumar P., Govindaraju M., Senthamilselvi S., Premkumar K., 2013. Photocatalytic degradation of methyl orange dye using silver nanoparticles synthesized from Ulva lactuca. Colloids Surf B:Biointerfaces 103:658–661.

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