GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES (CuONPs), CHARACTERISATION AND ITS PHOTOCATALYTIC ACTIVITY BY USING *ADHATODA VASIKA* LEAF EXTRACT.

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Abstract

A green synthesis method was used to synthesis CuONPs using *Adhatoda Vasika* leaves. UV, XRD, FTIR, SEM and EDS techniques confirmed the synthesised CuONPs. XRD analysis revealed that particles are monoclinic and crystalline with an average size of 14nm. The particles have some agglomeration and also spherical shape which were detected using SEM images. EDS analysis confirmed the presence of copper and oxygen elements in CuONPs. According to the FTIR results, the phytochemicals in the leaf extract generate the growth of CuONPs. Additionally, green synthesised CuONPs successfully performed photocatalytic degradation of Rhodamine B dye under visible light irradiation.

Keywords: *Adhatoda Vasika* leaf extract, CuONPs, Green synthesis, Photocatalytic degradation.

1. INTRODUCTION:

The green synthesis of nanomaterials of different sizes and shapes is attractive because of its advantage over other methods such as cost-effectiveness, non-toxicity and lower reaction temparatures[1, 2]. Nanoparticles (NPs) can range in size from 1 to 100 nm and can be metallic or non-metallic. NPs are obtaining a lot of interest from several scientific disciplines due to their optical, electrical, and thermal stability[3]. So, CuONPs have the greatest priority. NPs can be synthesised using top-down or bottom-up methods. The physical synthesis of NPs includes top-down approach[4] and bottom-up approach[5] via electrochemical synthesis[6], chemical synthesis[7, 8] and polyol reduction[9].

The degradation and removal of dye from wastewater is performed by membrane filtration, oxidation, photochemical degradation, electrolysis, and sludge process[10,11]. Due to their strong adsorption, improved photocatalytic, and redox characteristics[12], nanomaterials have successfully carried out the mentioned methods. CuONPs plays the unique role of catalytic properties[13], effective removal of inorganic ions[14] and organic pollutants[15] from the contaminated water[16]. Because of these peculiar physicochemical properties in wastewater treatment[17], it replaced silver, gold, platinum NPs and also eco-friendly with low-cost easy synthesis[18,19].

The identification of Adhatoda vasica Nees/Justicia adhatoda is made with the available literature. It is a well-known plant drug used in Ayurveda. It is very commonly known as Malabar nut tree. The local names of the plant are Ya-Zui-Hua in China, Nongmangkha-agouba (Manipuri), Adasaramu (Telugu), Alduso (Gujarati), Adadodai (Tamil), Vasaka (Sanskrit), Atalotakam (Malayalam) and Adusoge (Kannada) in India. It is a small evergreen shrub having broad leathery leaves. The leaves have a light green colour on top and deep green beneath. The leaf becomes brownish-green colour when it is dried and it tastes bitter[20]. The aqueous extract of A. vasica leaves contain phytochemicals such as alkaloids, tannins, saponins and phenols[21-26]. They also contain sugars, proteins and amino acids such as glycine.

The current study describes the photocatalytic degradation of Rhodamine B dye by CuONPs, which were synthesised from an aqueous leaf extract of the *Adhatoda Vasika* plant.

2. MATERIALS AND METHODS

2.1. Collection of plants:

Adhatoda Vasika plant leaves were plucked from the place near Theni. The Department of Botany at Cardamom Planters' Association College in Bodinayakanur, Theni, Tamil Nadu, India, verified the authenticity of the plant materials that had been collected. To eliminate dust particles, the leaves were washed three times with tap water and then twice with double-distilled water. They were dried at room temperature for an hour to remove the moisture in the leaves.

2.2. Preparation of plant extract:

The extract was prepared by mixing 20 gm of fresh leaves of *Adhatoda Vasika* and were washed several times with distilled water to remove the dust. The leaves were cut into small pieces once they had dried fully. 5g of chopped *Adhatoda Vasika* leaves were boiled in 25ml of deionized water for 30 minutes at 80°C. The resulting brown solution is passed through a Whatman No.1 filter paper to remove dust particles and then the filtrate is stored at 4°C for the synthesis of CuONPs.

2.3. Synthesis of copper oxide nanoparticles:

The CuONPs were synthesised by adding 20 ml of 1 mM copper nitrate to 1 ml, 2 ml, and 3ml of *Adhathda Vasika* extract into three cuvettes. The solution was mixed at room temperature with continuous stirring at 80°C for four hours, respectively. When compared to other plant parts (seeds and fruit), *Adhatoda Vasika* leaves had the best ability to reduce copper nitrate, as proved by the apparent color change[27]. The deep blue solution gradually changed over a few hours into a precipitate of brownish blue CuONPs that landed at the bottom of the container. CuONPs were collected and repeatedly cleaned with ethanol. The precipitate was put into a ceramic crucible and heated in a furnace for 5 hours at 350°C. The black CuONPs powder was stored in properly labeled containers and used for further characterization.

2.4. Characterisation of synthesised CuONPs:

ELICO SL-159 UV-Visible spectrophotometer is the basic instrument used to analyse absorption spectra of synthesised CuONPs. X-ray diffraction pattern of CuONPs was obtained using a powder diffractometer (X-ray diffractometer Ultima IV, Rigaku, Japan). Scanning Electron Microscopy was performed using JEOL SM-7600F, Japan model to record morphological characters of synthesised NPs. Oxford-EDS system analysed the elemental constituent of the prepared NPs.

2.5. PHOTOCATALYTIC DEGRADATION OF RHODAMINE B:

Under visible light irradiation, the photocatalytic activity of the CuONPs for the degradation of RhB was studied. The experiment was conducted using the 300 W tungsten halogen lamp equipped with Heber Visible Annular Type Photo Reactor. A borosilicate immersion jacketed tube with an outlet and inlet for water circulation to cancel IR radiation in the immersion well. The light was placed inside the chamber. A highly polished anodized metal reflector is installed inside the chamber surface. The test tube had 8 cm depth, internal diameter was 1.6 cm and 10 cm distance between the test tubes and the bulb. To provide enough oxygen for the photochemical process, the photo reactor was maintained open to the air. In the current work, 1×10^{-5} M dye concentration was utilized. In each experiment 50 mL of dye solution was mixed with 5 mg of the photocatalyst (CuO-NPs), which was then sonicated in a sonicator for approximately 15 minutes. At regular intervals of time, the solution is put into the photo reactor. 5 ml of sample were then removed from the reactor and centrifuged to record the degradation of RhB dye using a UV-Vis spectrophotometer. The reaction time was between 0 and 50 minutes.

The degradation (η) of RhB was calculated by the formula:

$$\eta = (A_0 - A_t)/A_0 \times 100$$

where, A_0 is the initial absorbance at time t = 0, A_t is the absorbance at time t.

3. RESULTS AND DISCUSSION:

3.1. UV–visible absorption spectra of CuONPs:

Fig.1 showed UV – visible spectra of CuONPs using *Adathoda vasika* leaf extract with different concentrations. The surface Plasmon resonance changes the color of the reaction mixture which indicates the formation of CONPs[28]. The spectrum wavelength of 258, 259 and 260nm are absorption peaks of the three prepared CuONPs. The decrease in the band gap values of 4.81eV, 4.79eV and 4.77eV in CuONPs is attributed to the quantum confinement effect[29,30,31].

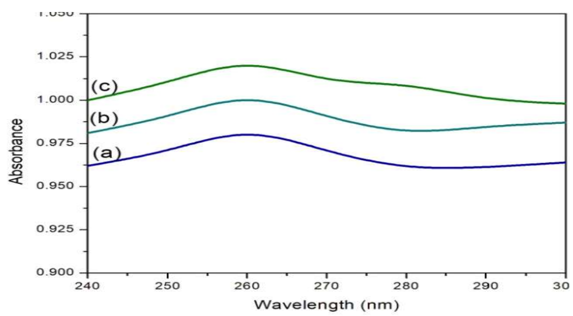

Fig.1.UV-visible spectra of CuONPs at different concentrations of *Adathoda vasika* leaves extract of (a)1mL (b) 2mL (c) 3mL

3.2. XRD analysis:

XRD patterns of CuONPs were depicted in Fig.2, which also revealed that it has crystalline nature and monoclinic structure. The XRD results showed no peaks of impurity. The XRD spectrum of CuONPs revealed several tiny, distinct diffraction peaks at (100), (-111), (111), (-202), (020), (202), (-113), and (220), respectively[32]. A JCPDS Card No. 05-0667 was used to compare the XRD pattern of NPs. Debye-Scherrer formula $D = k\lambda/\beta\cos\theta$[33,34] which found the crystalline size of CuONPs was 14nm.

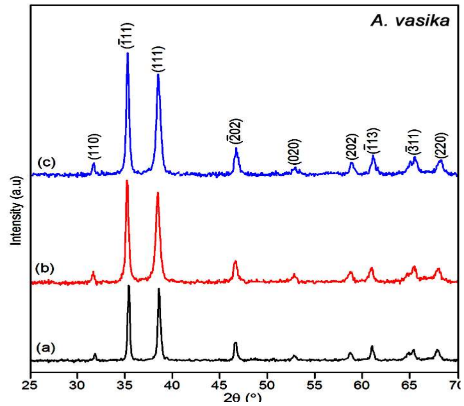

Fig.2.XRD patterns of CuONPs prepared at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

3.3. FTIR ANALYSIS:

Based on the peak value in the region of infrared radiation, FTIR spectroscopy located the functional groups of the active components. Fig.3 displayed the FTIR spectra of synthesised CuONPs. The O-H groups of alcohols and phenols are responsible for the broad and intense peak at about 3440 cm^{-1}. In the synthesised CuONPs, this peak shifted to the lower field at 3393 cm^{-1}. Stretching of the C-H band is attributed to the band at 2850 cm^{-1}. Alcohols, phenolic groups, and C-N stretching vibrations of amines have been identified as the sources of the observed peaks in the range of 680-1454 cm^{-1}. The 510 cm^{-1} main peak, which should be a stretching of Cu-O, was found. The bands at 1630 cm^{-1} of the leaf extract shifted to a lower field at 1600 cm^{-1} in the product of CuONPs using different leaves [extracts35,36].

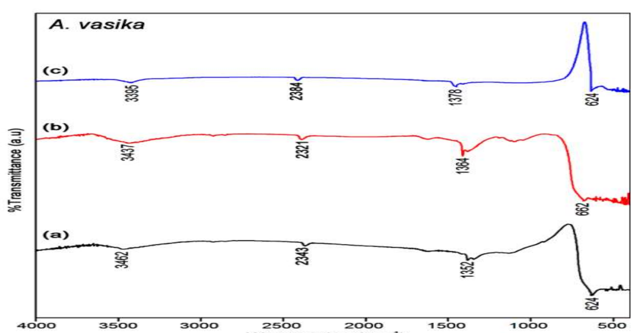

Fig.3.FTIR patterns of CuONPs at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

3.4. SEM analysis:

SEM analysis was used to describe the morphology of synthesised CuONPs. Fig.4 showed the SEM images of these NPs. It can be viewed that the formation of these NPs are well dispersed and evenly distributed in all direction. SEM showed that the NPs are somewhat agglomerated as either a result of the plant extract's stickiness.

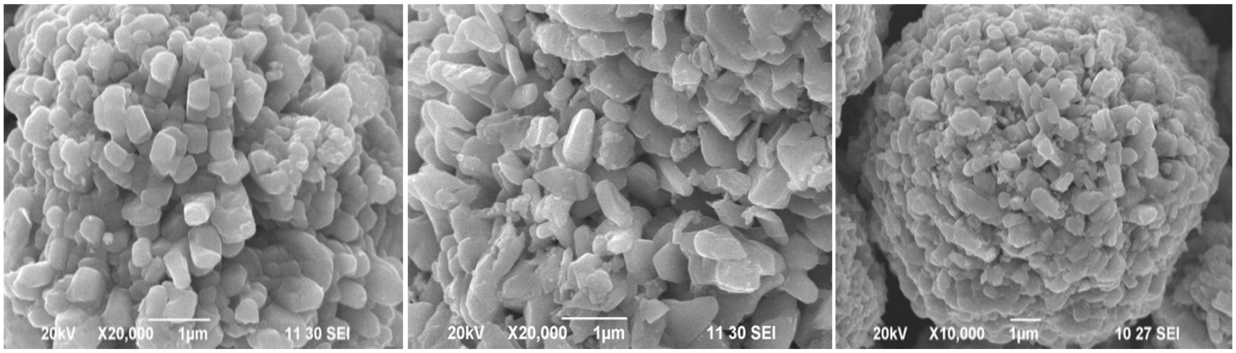

Fig.4.SEM images of CuONPs prepared at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

3.5. EDS Analysis:

The purity of the prepared CuONPs was verified by the EDS analysis. CuO is identified by oxygen and copper in the EDS spectra. Copper (Cu) and oxygen (O) had weight compositions of 49.21 and 50.79 percent, respectively. The extrinsic organic moieties are attributed to the adsorption of the metallic nanoparticles during contact with extract during bioproduction.

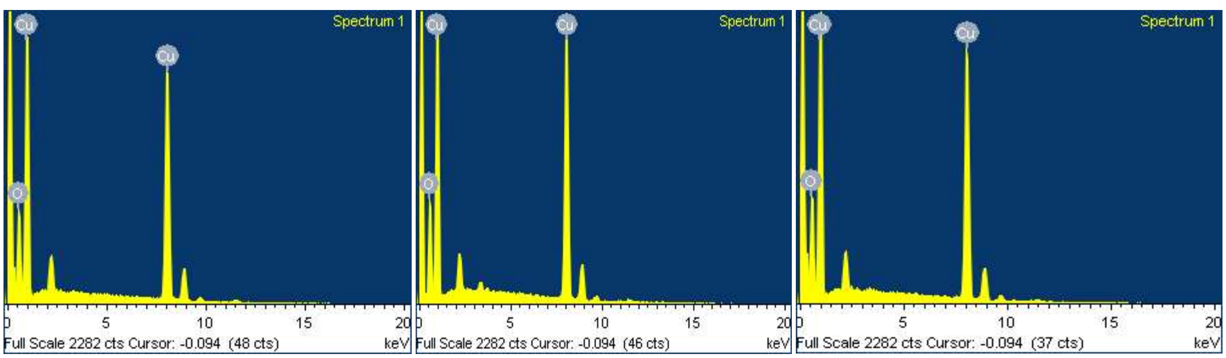

Fig.5.EDS images of CuONPs prepared at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

4. PHOTOCATALYTIC ACTIVITY:

Photocatalytic activity of Rhodamine B(Rh B) was done by synthesised CuONPs and the absorption spectrum for the Rh B of the visible light is shown in Fig.6. A general decrease in the absorbance (concentration) of dye is observed with time. Specifically 84%, 92 %, and 97% are dye degradation of 1mL, 2mL and 3mL concentration of CuONPs in RhB dyes, respectively.

The Rhodamine B dye showed the utmost percentage degradation rates per CuO specimen by the close of the 50 minutes exposure time[37]. However, CuONPs exhibited excellent degradation.

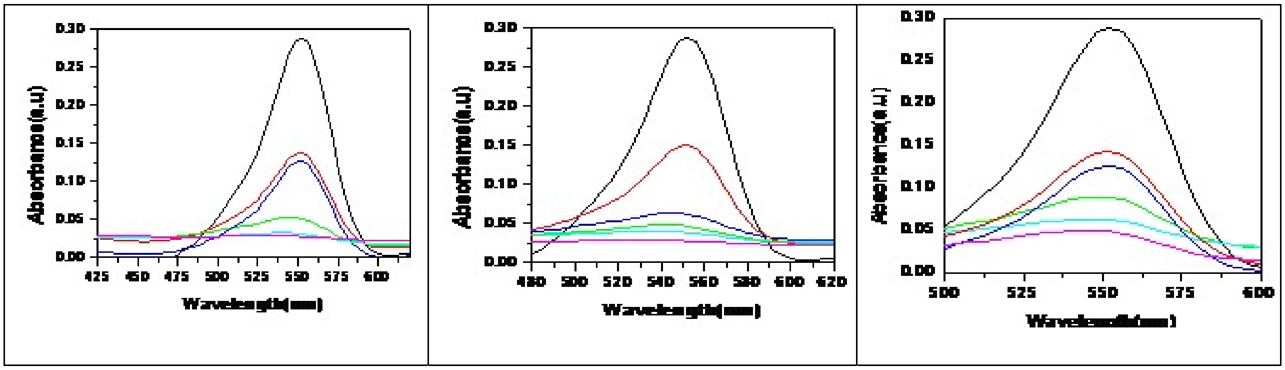

Fig.6. Photocatalytic activity of CuONPs at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

7.1. Percentage of Dye degradation:

The time required for the degradation of Rhodamine B was studied from 0 to 50 minutes. As the time increases, the absorbance of solution decreases with the increase in % degradation, which indicates that dye is photo catalytically degraded on irradiation. The removal percentage of decolorisation was calculated and drawn graphically. The maximum time was 50 minutes with 97% color removal respectively. This confirms the rapid reaction of CuONPs Photodegradation of Rhodamine B dye solutions with CuONPs.

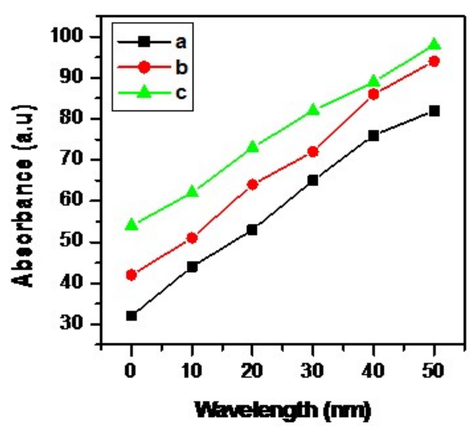

Fig.7.Dye degradation of CuONPs at different concentration of *Adathoda vasika* leaves extract (a) 1mL (b) 2mL (c) 3mL

8. Conclusion

In summary, the green syntheses of CuONPs had been efficiently synthesised through *Adathoda Vasika* leaf extract with none toxic reagent. The green synthesised CuONPs were characterised by various techniques UV–Vis spectroscopy, XRD, FTIR and SEM analysis confirmed that the CuONPs show only a monoclinic phase and an average grain size of 14nm. Degradation of Rhodamine B was performed to investigate the photocatalytic activity of the CuONPs, which was observed to be very efficient. Photocatalytic degradation of RhB becomes exhibited by way of CuONPs with photodegradation efficiency of 97%. Since the green synthesised CuONPs showed efficient photocatalytic degradation of Rhodamine B which can be used as a catalyst in the reduction of dyes, other toxic material and industrial effluents.

9. References

1. Niji Abraham, Dr. V S John, Dr. P. Suja Prema Rajini, Green Synthesis And Characterization Of Copper Oxide Nanoparticles Using A Red Seaweed Gracilaria Edulis, International Journal of Engineering Science Invention (IJESI), Volume 7 Issue 10 Ver III , Oct 2018, PP: 09-13.
2. Sulaiman, Ghassan M, Tawfeeq A T & Jaaffer M D, Biogenic synthesis of copper oxide nanoparticles using *olea Europaea* leaf extract and evaluation of their toxicity activities: An *in vivo* and *in vitro* study, Biotechnology Progress 34 (1), 218-230, 2018. 70, 2018.
3. P. Gong, H. Li, X. He, K. Wang, J. Hu, W. Tan, X. Yang, Preparation and antibacterial activity of Fe3O4@ Ag nanoparticles, Nanotechnology 18 (2007) 285604.
4. J. An, D. Wang, Q. Luo, X. Yuan, Antimicrobial active silver nanoparticles and silver/polystyrene core-shell nanoparticles prepared in room-temperature ionic liquid, Mater. Sci. Eng. C 29 (2009) 1984–1989.
5. G. Madhumitha, G. Elango, S.M. Roopan, Biotechnological aspects of ZnO nanoparticles: overview on the synthesis and its applications, Appl. Microbiol. Biotechnol. 100 (2016) 571–581.
6. F. Yang, K. Cheng, T. Wu, Y. Zhang, J. Yin, G. Wang, D. Cao, Au–Pd nanoparticles supported on carbon fiber cloth as the electrocatalyst for H2O2 electro reduction in acid medium, J. Power Sources 233 (2013) 252–258.
7. A.Nemamcha, J.L. Rehspringer, D. Khatmi, Synthesis of Palladium nanoparticles by sonochemical reduction of palladium (II) nitrate in aqueous solution, J. Phys. Chem. B 110 (2006) 383–387.
8. Mizukoshi, K. Sato, T.J. Konno, N. Masahashi, Dependence of photocatalytic activities upon the structures of Au/Pd bimetallic nanoparticles immobilized on TiO2 surface, Appl. Catal. B Environ. 94 (2010) 248–253.
9. Y. Xiong, J. Chen, B. Wiley, Y. Xia, S. Aloni, Y. Yin, Understanding the role of oxidative etching in the polyol synthesis of Pd nanoparticles with uniform shape and size, J. Am. Chem. Soc. 127 (2005) 7332–7333.

10. Rajendran, M. M. Khan, F. Gracia, J. Qin, V. K. Gupta, and S.Arumainathan (2016). Ce3+-ion-induced visible-light photocatalytic degradation and electrochemical activity of ZnO/CeO2 nanocomposite, Scientific Report, 2016, 6, 31641.
11. S. N. Jain and P. R. Gogate, Treatment of dye containing real industrial effluents using NaOH-activated Ficus racemosa and Prunus dulcis based novel adsorbents (2019). International Journal of Environmental Research 13 (2), 337-347 .
12. M. Y. Rather, and S. Sundarapandian, (2020), Magnetic iron oxide nanorod synthesis by Wedelia urticifolia (Blume) DC. leaf extract for methylene blue dye degradation. Applied Nanoscience, 2020, 10, 2219–2227.
13. N. Nagar and V. Devra (2018).Green synthesis and characterization of copper nanoparticles using Azadirachta indica leaves, Material Chemistry and Physics,2018, volume(213), 44–51.
14. S. Raina, A. Roy, and N. Bharadvaja (2020). Degradation of dyes using biologically synthesised silver and copper nanoparticles, Environmental Nanotechnology Monitoring & Management 13(1):100278.
15. E. A. Deliyanni, N. K. Lazaridis, E. N. Peleka, and K. A. Matis (2004). Metals removal from aqueous solution by iron-based bonding agents. Environmental Science and Pollution Research. 11(1), 18–21.
16. J. Yan, L. Han, W. Gao, S. Xue, and M. Chen, Biochar supported nanoscale zerovalent iron composite used as per sulfate activator for removing trichloroethylene, Bioresource Technology, 175(2015), 269–274.
17. M. Ghaedi, H.Z. Khafri, A. Asfaram, A. Goudarzi, Response surface methodology approach for optimization of adsorption of Janus Green B from aqueous solution onto ZnO/Zn (OH) 2-NP-AC: kinetic and isotherm study, Spectrochim. Acta Mol. Biomol. Spectrosc. 152 (2016) 233–240.
18. J. A. Eastman, S. U. S. Choi, S. Li, W. Yu, and L. J. Thompson (2001), Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, Applied Physics. Letter. 78 (6), 718–720.
19. N. Nazar, I. Bibi, S. Kamal, M. Iqbal, S. Nouren, K. Jilani, M. Umair, and S. Ata (2018), Zn-doped SiO_2 nanoparticles preparation and characterization under the effect of various solvents: Antibacterial, antifungal and photocatalytic performance evaluation, International journal of biological macromolecules 106, 1203-1210.
20. T.P. Singh, O.M. Singh, H.B. Singh, Adhatoda vasica Nees: phytochemical and pharmacological profile, Nat. Prod. J. 1 (2011) 29–39.
21. S. Maurya, D. Singh, Quantitative analysis of total phenolic content in Adhatoda vasica Nees extract, Int. J. Pharm. Technol. 2 (4) (2010) 2403–2406.
22. A.Karthikeyan, V. Shanthi, A. Nagasathaya, Preliminary phytochemical and antibacterial screening of crude extract of the leaf of Addhatoda vasica. L, Int. J. Green Pharm. (2009) 78–80.
23. N. Chattopadhyay, G. Nosalova, S. Saha, S.S. Bandyopadhyay, D. Fleskova, B. Ray, Structural features and antitussive activity of water extracted polysaccharide from Adhatoda vasica, Carbohydr. Polym. 83 (2011) 1970–1974.
24. D.K. Jha, L. Panda, P. Lavanya, S. Ramaiah, A. Anbarasu, Detection and Confirmation of alkaloids in leaves of adhatoda and bioinformatics approach to elicit its anti-tuberculosis activity, Appl. Biochem. Biotechnol. 168 (2012).
25. P.R. Kanthale, V.H. Panchal, Pharmacognostic study of adhatoda vasica Nees, Biosci. Discov. 6 (1) (2014) 49–53.

26. A.H. Amin, D.R. Mehta, A bronchodilator alkaloid (vasicinone) from Adhatoda vasica Nees, Nature 1317 (1959) 184
27. Mahmoodi S, Elmi A & Hallaj-nezhadi S, Copper Nanoparticles as Antibacterial Agents, Journal of Molecular Pharmaceutics & Organic Process Research, 2018, Vol 6(1): 140.
28. P. Mukherjee, A. Ahmad, D. Mandal, S. Senapati, S.R. Sankar, M.I. Khan, M. Sastry, Bioreduction of $AuCl_4^-$ ions by the fungus, Verticillium sp. and surface trapping of the gold nanoparticles formed, Angew. Chem. Int. Ed. 40 (2001) 3585–3588.
29. J. Xia, H. Li, Z. Luo, K. Wang, S. Yin, Y. Yan, Ionic liquid-assisted hydrothermal synthesis of three-dimensional hierarchical CuO peach stone-like architectures, Applied Surface Science 256 (2010) 1871–1877.
30. Z. Yang, J. Xu, W. Zhang, A. Liu, S. Tang, Controlled synthesis of CuO nanostructures by a simple solution route, Journal of Solid State Chemistry 180 (2007) 1390–1396.
31. 30.A.Ahmad, S. Senapati, M.I. Khan, R. Kumar, M. Sastry, Extracellular biosynthesis of monodisperse gold nanoparticles by a novel extremophilic actinomycete, Thermomonospora sp, Langmuir 19 (2003) 3550–3553.
32. 31.M. Kowshik, S. Ashtaputre, S. Kharrazi, W. Vogel, J. Urban, S.K. Kulkarni, K.M. Paknikar, Extracellular synthesis of silver nanoparticles by a silver-tolerant yeast strain MKY3, Nanotechnology 14 (2002) 95.
33. 32.Krithiga N, Jayachitra A, Rajalakshmi A (2013) Synthesis, characterization and analysis of the effect of copper oxide nanoparticles in biological systems. Indian Journal of Nanoscience. 1:6–15.
34. Sankar, R., Manikandan, P., Malarizhi, V., Fathima, T., Shivashangari, K.S., Ravikumar,V.(2014) Green synthesis of colloidal copper oxide nanoparticles using Carcia papaya and its application in photocatalytic dye degradation. Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy. 121, 746-750.
35. Rahman, A., Ismail, A., Jumbianti, D., Magdalena, S., Sudrajat, H. (2009) Synthesis of copper oxide nanoparticles by using Phormidium cyanobacterium. Indo. J. Chem. 9, 355-360.
36. Honary, S., Barabadi, H., Fathabad, E.G.,Naghibi, F. (2012) Green synthesis of copper oxide nanoparticles using Penicilium aurantiogriseum, Penicilium citrinum and Penicilium waksmanii. Digest J. Nanomater. Biostruct. 7, 999-1005.
37. Rafique, M., I. Sadaf, M.B. Tahir, M.S. Rafique, G. Nabi, T. Iqbal, and K. Sughra, Novel and facile synthesis of silver nanoparticles using Albizia procera leaf extract for dye degradation and antibacterial applications. Materials Science and Engineering: C, 2019.