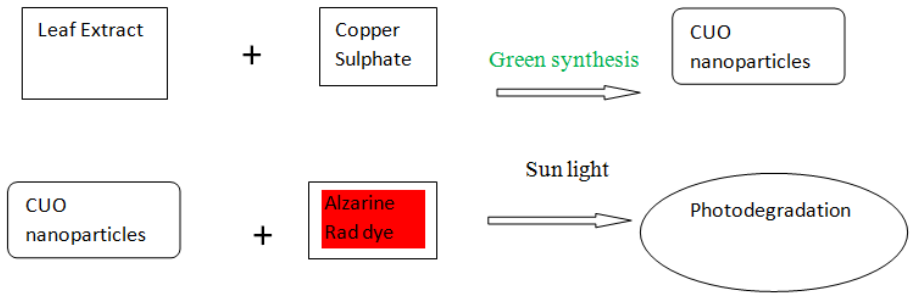
RESEARCH ARTICLE OPEN ACCESS

A Noval Synthesis of Copper Oxide Nanoparticles By *Arevalanata* Leaf Extract And Their Photocatalytic Degradation

Seeram. Hari Prasad[1*], G.Susheela Bai[1], B.Kishore Babu[1]
Department of Engineering Chemistry, Andhra University, Visakhapatnam, India
Corresponding Author E-mail: hari1986chem@gmail.com.

GRAPHICAL ABSTRACT:



ABSTRACT:
Copper oxide nano particles are prepared by green method by using *Arevalanata*leaf extract. Green method is best suitable method for preparation of nano particles because no harmful and non toxic chemical are used. The characterization of synthesized copper oxide nano particles were done by technique like UV-VISIBLE, FT-IR, SEM, TEM, XRD, EDX. These copper oxide nano particles was used to photo degradation on Alzarine red dye. The percent of degradation is73.23after 180 minutes.

Key Words: Copper oxide nanoparticles, Alzarine red dye *Arevalanata*, green method.

Date of Submission: 08-11-2017 Date of acceptance: 25-11-2017

I. INTRODUCTION

Nanotechnology plays an important role in modern research. Copper oxide nano particles attracted researchers due to their unique properties and wide range of applications like high temperature super conductors [1], catalyst [2], electrical [3], Magentresistent material [4], gas sensors [5]. Copper oxide belongs to P-Type semiconductors and its band gap energy is 1.7ev [6]. Copper oxide compounds show potent biocidal properties [7]. There are many routes to prepare copper oxide nano particles like Sonochemical [8], microwave irradiations[9], alkoxidebased route [10], sol–gel method [11],electrochemical methods[12]. Synthesis of copper oxide nano particles in chemical methods are little toxic due to harmful chemical used.

Green method is best suitable method for preparation of copper oxide nano particles due to any harmful chemical are not used in this method and it is cost effective, eco-friendly. There are many reports to the synthesis of copper oxide nano particles by plants extracts such as *Gloriosasuperba*L.extract [13], *Phyllanthusamarus* [14], *centellaasiatica* (L.) [15], *Aspergillus niger fungi* [16], *gum karaya*[17].

In this present work we report green synthesis of copper oxide nano particles by leaves extract of Arevalanata, and their characterization were done by various techniques. These copperb oxide nano particles were applied to photo degradation study on Alzarine red dye.

II. MATERIAL AND METHODS

2.1 MATERIALS:

Copper sulphatepenta hydrated ($CUSO_45H_2O$), sodium hydroxide(NaOH) areanalytical grade purchased from local market,Visakhapatnam. Deionised water was used inthroughout the experiment.*Arevalanata*plants were collected from rural areas and agricultural lands of Visakhapatnam, Andhra Pradesh.whole plant was washed several time with tap water andwashed several time with distill water, and separated The leaves. which are dried in a dark place at room temperature.

2.2 Preparation of leaf extract

The dried leaves were cut into small pieces and take 10gm of small pieces in to 250mlErlenmeyerconical flask and add 100ml of double deionized water after boiled for 20 min at 60^0C. After cooling, the extract was filtered using what man No.1filter paper and stored at 4^0C for further usuage. The colour of the extract was light brown.

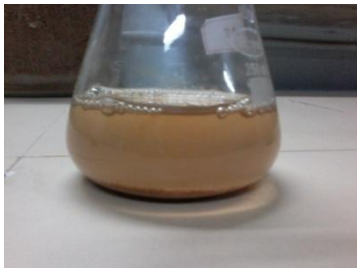


Figure1: Arevalanata leaves extract.

2.3 Preparation of copper sulphate solution

Accurate amount of 1mmol copper sulphate solution is prepared by dissolving 0.0622gm of $CuSO_4$ in 250 ml of double distilled water and stored in clean, dried reagent bottle.

Figure 2: copper sulphate solution

2.4 Preparation of copper oxide nanoparticles

10 ml of leaf extract is added to a 90ml of 1 mmol copper sulphatesolution and stirred magnetically at room temperature. The colour of the solution changes from blue to light green colour. Then the mixture is heated at 80^0C for 20 minutes followed by addition of 5ml of 1M sodium hydroxide drop by drop. A light blue colourprecipitate is formed immediately.The green precipitate is then taken out and washed repeatedly for 3 times with deionized water followed by ethanol to remove the impurities. In the next step the precipitate is collected in to a clean crucible and calcinated at 200^0C for three hours. Finally, we get copper oxide nanoparticles.

Leaf extract + Copper salt solution ⟶ capped-copper nanoparticles

Capped-copper nanoparticles $\xrightarrow{\Delta + NaOH}$ capped copper hydroxide

Capped copper hydroxide $\xrightarrow{\text{calcinated}}$ capped-copper oxide nanoparticles

Figure 3: Formation of CuO nanoparticles.

III. CHARACTERIZATION TECHNIQUES

The formed CuO nanoparticles are characterized by using UV-Vis Spectrophotometer (systronics-2201), FTIR (IR-prestige-21 Shimadzu), XRD (X-pro petro,) SEM (Philips-XL-30), TEM (JEM-1230 JEOL).

IV. PHOTODEGRADATION

The photocatalytic activity of green synthesized CuO nanoparticles is tested against aqueous solution of Alzarine red dye. 40 ppm stock solution is prepared by dissolving 40 mg of Alzarine red dye in one litre double distilled water. 25 ml of 40 ppm solution is taken into 50ml clean glass beaker and 0.06 mg of green synthesized CuOnano catalystis added. This solution mixture is exposed to sun radiation under continuous stirring for 3 hours.

In every 30 minutes of time intervals, 5 ml of reaction mixture is taken out into centrifuging tubes and centrifuged. The filtrate is examined using UV-Visible spectrophotometer to monitor the absorption maximum values.The readings are noted in Table (6.1). Before exposure to the sun radiation, the aqueous Alzarine red dye solution gives UV-visible absorption maximum value at 424nm, which in subsequent experiments under sunlight reduces in absorption. The pink colour of the solution is found to slowly decolourise within an exposure time of 3 hours.

V. RESULTS AND DISCUSSIONS

5.1. UV-Visible spectrum studies

The green synthesized CuO nanoparticles are dispersed in demineralised water and subjected to UV-Visible absorption study. The wave length range which used in UV-Visible spectrophotometer is 350-500nm.The UV-Visible spectrum is shown in figure (6.3). The solution gives absorption

maximum peak at 425 nm.The maximum absorption peak is due to surface plasmon absorption of metal oxide CuO nanoparticles.

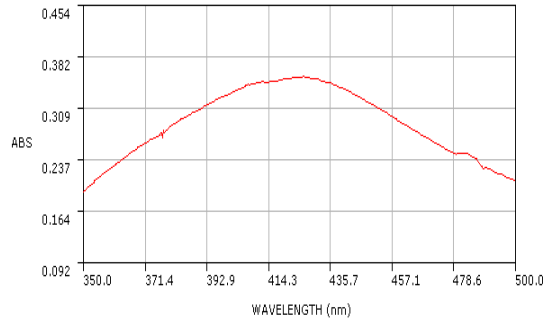


Figure 4: UV-Visiblespectra of CuO nanoparticles.

5.2.FTIR spectrum studies

The FTIR spectrum obtained for CuO nanoparticles by leaf extract of *Arevalanata* is shown in Figure (6.4). The band at 3390cm^{-1}correspods to strong O-H stretching of H-bonded alcohols and phenols. the peak at 1624cm^{-1}corresponds to carbonyl stretching frequency in amide functional group. The bands appeared at 1460cm^{-1} and1385cm^{-1} due to C=C stretching frequency of aromatic functional groups. The band at 1111cm^{-1} corresponds to C-O stretching frequency of alcohols and amides. The peak at 779 cm^{-1} corresponds to C-H stretching. The peaks corresponding to 601cm^{-1} and 628cm^{-1} are assigned to M-O stretching of copper oxide.

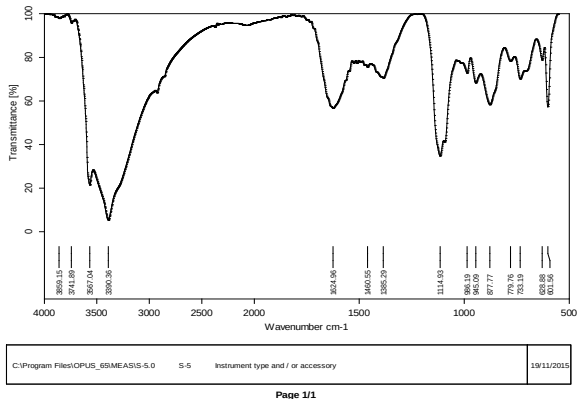


Figure 5: FTIR spectrum of CuO nanoparticles.

5.3. XRD studies

The XRD spectrum of synthesiszied CuO nanoparticles from *Arevalanata*is shown in Figure (5.5).The peaks appearing at 2θ values of 32.58^{o}, 35.07^{o}, 48.95^{o}, 53.40^{o}, 58.14^{o}, 61.63^{o}, 66.67^{o}, 72.21^{o}, 74.78^{o} correponds to theBragg's reflections of(110) (111) (202) (020) (202) (113) (311) (311) (004) planes respectevely.The above diffraction peaks indicate crystalline monoclinic structure of CuOnanoparticles. The data is in good agreement with JCPDS card no-45-0937.The average size of CuO nanoparticles iscalculated by using Debye-Scherer equation.

$$D = K\lambda / \beta \cos \theta$$

The maximum peak appears at 2theta value of 32.58^{o} which corresponds to an average size of 49 nm for the copper oxide nanoparticle.

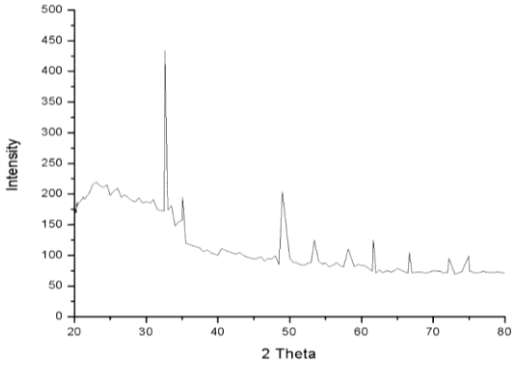


Figure 6.5: XRD spectrum of CuO nanoparticles

5.4.SEM analysis

The SEM images obtained for the green synthesized CuOnanoparticles is shown in Figure (6.6). The images of copper oxide nanoparticles indicate spherical morphology with a size in the range of 47-70 nm.

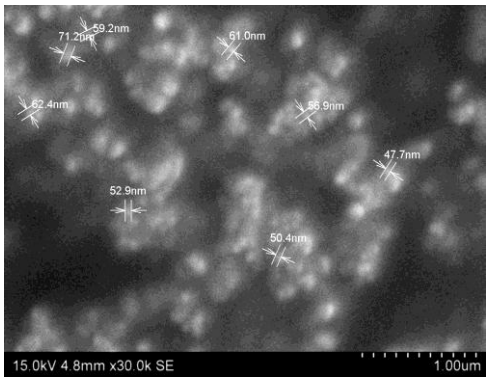


Figure 6: SEM images of synthesized CuO nanoparticles

5.5. EDX studies

The EDX spectrum of green synthesized CuO nanoparticles formed from *Arevalanata* leaf extract is shown in Figure (6.7 and 6.8). From EDX spectrum the composition of copper and oxygen is 59.59% and 40.41%.

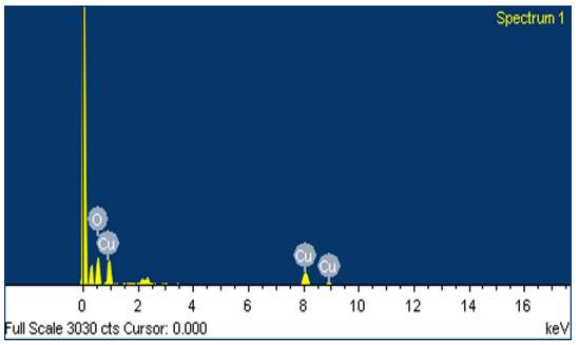


Figure 7:EDX of CuO nanoparticles

Element	Weight%	Atomic%
O K	40.41	72.93
Cu K	59.59	27.07
Totals	100.00	

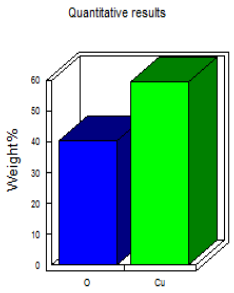


Figure 8:Quantitative results of CuO nanoparticle

5.6. TEM studies

The TEM image of synthesized CuO nanoparticles from leaf extract of *Arevalanata*is shown in Figure (6.9). It is obvious from the image that the copper oxide nanoparticles are spherical with 100 nm size.

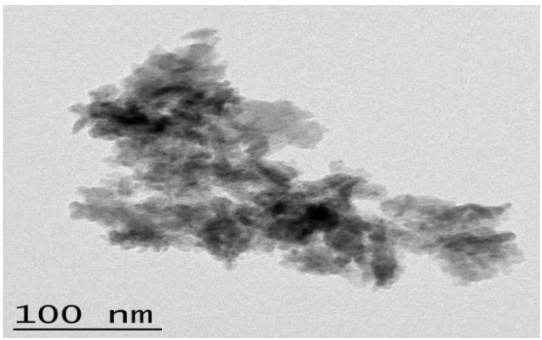


Figure 9: TEM image of CuO nanoparticles.

5.7.Photodegradation

The green synthesized copper oxide nanoparticles are used as a photo catalyst in in the degradation of organic dye Alzarine red dye. The dark pink colour of Alzarine red dye is slowly decolourised on the addition of copper oxide nanoparticles. The time duration for the degradation reaction is 3 hours. The degradation experiment is pictorially shown in Figure (6.10).

Figure 10:Colour change observed in Alzarine red dye

5.7. (a) Time vs absorption graph

The degradation study is evaluated by using time vs light absorption graph by collecting absorption data using UV-Visible spectrum at various time intervals. The results are given in Table-1 and shown graphically in Figure (6.11). 40 ppm solution gives absorption maximum value of 0.695. this value decreases slowly on the addition of CuOnanoparticles along with time.

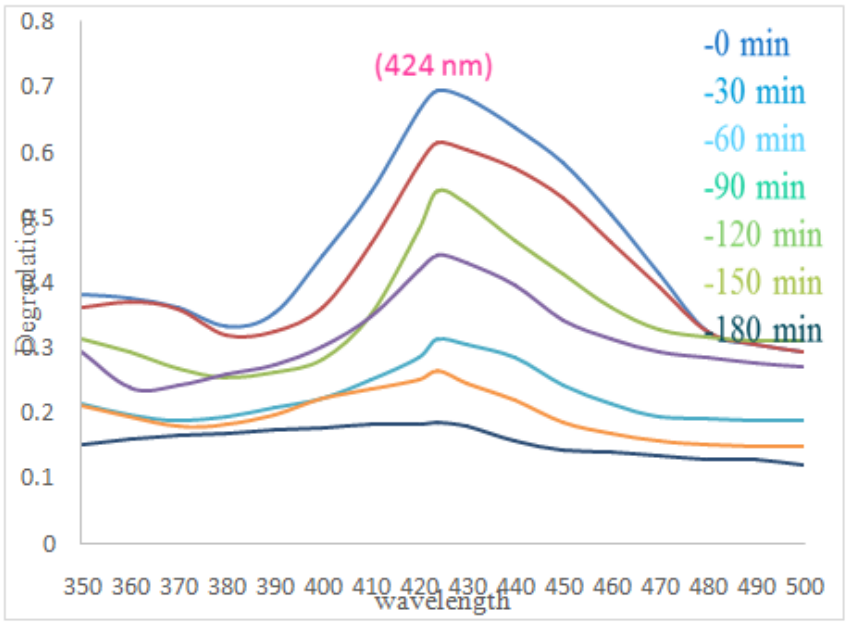


Figure 11: Degradation graph of Alzarine red

5.7. (b) Time vs % of degradation

The photo catalytic efficiency of CuO nanoparticles is evaluated by calculating the percent degradation (calculated using the equation shown below) at various intervals of time. The corresponding graph is shown in Figure (6.12). After 3 hours of the reaction time the degradation is 73.23%. thus the graph indicates that % degradation increases with time.

$$\% \text{ of degradation} = [(A_0\text{-}A)/A] \times 100$$

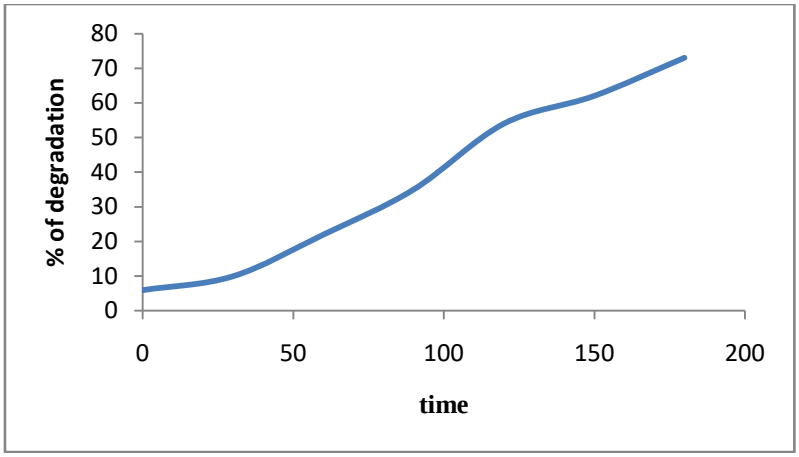


Figure 12: Time vs % degradation graph

5.7.(c) Time vs 2+log(A) graph

The kinetic study of the photodegradation reaction is evaluated by plotting a graph between time and 2+log(A) values given in Table (6.3) is shown in Figure (6.13). It gives a straight line with a negative slope. The slope is found to be 0.0129.the plot indicates that photo degradation of Alzarine red aqueous solution carried out by green synthesized CuO nanoparticles follows pseudo first order reaction.

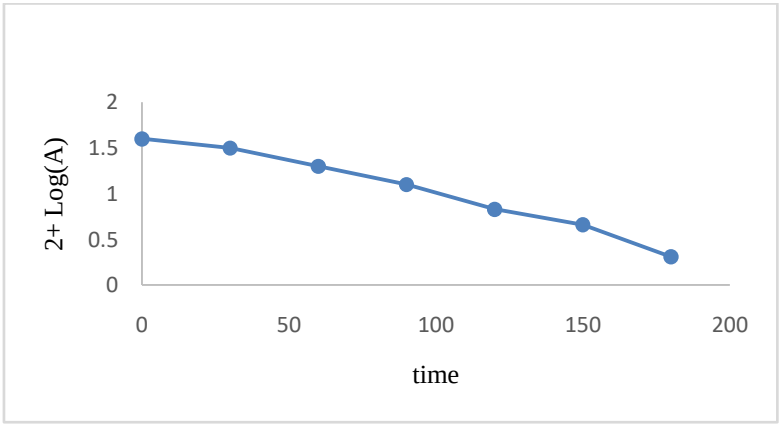


Figure 6.13: Time vs 2+log(A) graph of CuO nanoparticles

5.7. (d) Time vs log(A_0/A)

The kinetics of photodegradation can also be studied by plotting the time vs Log(A_0/A) values. A plot gives a straight line with a positive slope. The slope is 0.0081

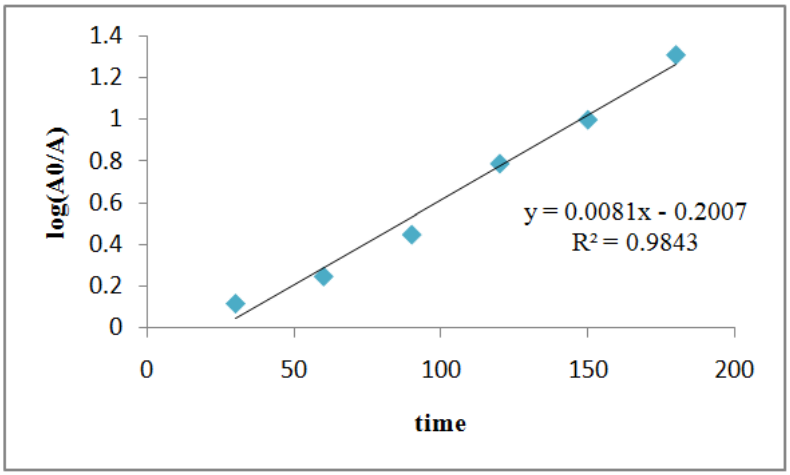


Figure 13: Time vs log(A_0/A) graph of CuO nanoparticles

The rate constant of the degradation reaction of Alzarine red using green synthesized CuO nanoparticles is calculated by following equation.

$K = (2.303 \times M) /60$

$K= (2.303\times0.008)/ 60$

$K= 3.0706 \times10^{-4}$ Sec^{-1}

The rate constant obtained from above equation is 3.0706×10^{-4} sec^{-1}.

VI. CONCLUSIONS

CuO nanoparticles are synthesized from leaf extract of *Arevalanata.* The particles are characterized by UV-VISIBLE(425nm), FT-IR, XRD(49nm), SEM-EDX and TEM. The SEM and TEM images reveal spherical morphology for the nanoparticles.

The nanoparticles are applied to the photo degradation study of dilute solutions of Alzarine red dye. The degradation study reveals that the 40 ppm dye solution could be degraded by 6 mg of CuO nanoparticles with in a time period of 3 hours producing degradation of 73.23%.

ACKNOWLEDGEMENT

Authors are very thankful to prof. G Susheelabai and B. kishorebabu for giving their valuble suggestions, department of engineering chemistry, college of engineering, Andhra university, Visakhapatnam for providing facilities and also thankful to Teqip for providing funding.

REFERENCES

[1] J.Z. Xu, J.J. Zhu, H.Y. Chen, J. Cryst. Growth 244 **(2002)** 88–94.

[2] S.K. Yip, J.A. Sauls, Phys. Rev. Lett. 69 **(1992)** 2264–2267.

[3] S. Yang, C. Wang, L. Chen, S. Chen, Mater. Chem. Phys. 120**(2010**) 296–301.

[4] P. Podhajecky, B. Klapste, P. Novak, J. Mrha, R. Moshtev, V.Manev, A. Nassalevska, J. Power Sour. 14 **(1985)** 269–275.

[5] X.G. Zheng, C.N. Xu, Y. Tomokiyo, E. Tanaka, H. Yamada, Y.Soejima, Phys. Rev. Lett. 85 **(2000)** 5170–5173.

[6] T. Ishihara, K. Kometani, M. Hashida, Y. Takita, J. Electrochem.Soc. 138 **(1991)** 173–176

[7] L. Debbichi, M.C. Marco de Lucas, J.F. Pierson, P. Krüger, J.Phys. Chem. C 116 **(2012)** 10232–10237.

[8] G. Borkow, J. Gabbay, Curr. Chem. Biol. 3 **(2009)** 272–278.

[9] R.V. Kumar, R.E. Elgamiel, Y. Diamant, A. Gedanken, Langmuir 17 **(2001)** 1406–1410.

[10] H. WangC.L. Carnes, J. Stipp, K.J. Klabunde, Langmuir 18 **(2002)** 1352–1359.

[11] Q. Zhang, Y. Li, D. Xu, Z. Gu, J. Mater. Sci. Lett. 20 **(2001)** 925–927.

[12] A.J. Yia, J. Li, W. Jian, J. Bennett, J.H. Xu, Appl. Phys. Lett. 79 **(2001)**1039–1041.

[13] H. Raja Naikaa,∗, K. Lingarajua, K. Manjunathb, DanithKumarc, G. Nagarajuc,D.Sureshd,e, H. Nagabhushana,ScienceDirectGreen synthesis of CuO nanoparticles using *Gloriosasuperba*L.extract and their antibacterial activity. Journal of Taibah University for Science 9 **(2015)** 7–12.

[14] N. P. S. Acharyulu, R. S. Dubey, V. Swaminadham, R. L. Kalyani, PratapKollu, S. V. N. Pammi*,Green Synthesis of CuO Nanoparticles usingPhyllanthusAmarus Leaf Extract and theirAntibacterial Activity Against Multidrug Resistance Bacteria. Vol. 3 Issue 4, April – (**2014)** 639-641.

[15] Henam Sylvia Devi1 and Thiyam David Singh2, Synthesis of Copper Oxide Nanoparticles by a Novel Method and its Application in the Degradation of Methyl Orange. Advance in Electronic and Electric Engineering. Volume 4, Number 1 **(2014),** pp. 83-88.

[16] R. Etefagh∗, E. Azhir, N. Shahtahmasebi, Synthesis of CuO nanoparticles and fabrication of nanostructural layer biosensors for detecting Aspergillus niger fungi. ScientiaIranica F **(2013)** 20 (3), 1055–1058.

[17] Vinod VelloraThekkaePadil Miroslav Cerník,Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. International Journal of Nanomedicine..**(2013)**8 889-898.

International Journal of Engineering Research and Applications (IJERA) is **UGC approved** Journal with Sl. No. 4525, Journal no. 47088. Indexed in Cross Ref, Index Copernicus (ICV 80.82), NASA, Ads, Researcher Id Thomson Reuters, DOAJ.

Seeram. Hari Prasad A Noval Synthesis of Copper Oxide Nanoparticles By Arevalanata Leaf Extract And Their Photocatalytic Degradation." International Journal of Engineering Research and Applications (IJERA) , vol. 7, no. 11, 2017, pp. 14-20.