



GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES USING OCIMUM SANCTUM AND VITEX NEGUNDO LEAF EXTRACT: THE STUDY OF ITS PHOTOCATALYTIC DYE DEGRADATION ACTIVITY.

S.Karthikarani¹ and Dr. G. Suresh²

¹Ph.D., Research Scholar, Department of Physics, Annamalai University

²Assistant Professor, Physics Wing, Directorate of Distance Education, Annamalai University

Abstract:- A simple, eco-friendly green synthesis of copper oxide nanoparticles (CuO-NPs) using *Ocimum sanctum* and *vitex negundo* leaf extract was reported. The prepared CuO-NPs was characterized by UV-vis spectroscopy which exhibited the surface plasmon resonance (SPR) band at 280–320 nm. SEM, TEM and EDX analysis confirmed that CuO-NPs and identified elements Cu and O. X-ray diffraction (XRD) spectrum showed the crystalline nature of the prepared CuO NPs and its particle size is 30nm. FTIR spectrum confirmed the presence of Cu–O functional groups. CuO-NPs showed significant photocatalytic activity against Rhodamine B dye. The results of this study revealed that *O. sanctum* and *V. negundo* leaf extract were found to be an effective bio-reducing agent for CuO-NPs synthesis and also the photocatalytic activity of CuO-NPs may be useful for its applications in medical and textile industries.

Keywords: Green synthesis, *Ocimum sanctum* leaf, *Vitex Negundo* leaf, Copper Oxide nanoparticles, Rhodamine B dye, Photocatalytic activity.

1.Introduction

In recent years, metal nanoparticles have gained tremendous global attention owing to its extensive applications in areas such as catalysis, electronics, mechanical, medical and optoelectronics etc^{1&2}. Fabrication of nanosized metal particles with higher surface area has attracted significant interest due to its unusual size-dependent, optical and electronic properties as well as novel applications compared to their bulk form^{3,4}. Though extensive studies have been done so far in noble metals, such as silver and gold, their exploitations are limited due to its high cost. Hence, significant interest has been risen from the scientific researchers to replace the noble metals with other metals for nanomaterials fabrication.

¹ K. Cheirmadurai, S. Biswas, R. Murali, P. Thanikaivelan, “Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources”, RSC Advances. Volumen No.37(4), (2014), Page No.19507.

² G.. Sharmila, M. Thirumarimurugan, V.M. Sivakumar, “Optical, Catalytic and Anti-bacterial Properties of Phytosynthesized CuO Nanoparticles using *Tecoma Castanifolia* Leaf Extract”, Optik-International Journal for Light and Electron Optics Volume No. 127, (2016), Page No.7822.

³ M. Shah, D. Fawcett, S. Sharma, S.K. Tripathy, G.E.J. Poinern, “Green Synthesis of Metallic Nanoparticles via Biological Entities” Materials Volume No. 8(11), (2015), Page No.7278-7308.

⁴ P. Sutradhar, M. Saha, D. Maiti, “Microwave synthesis of copper oxide nanoparticles using tea leaf and coffee powder extracts and its antibacterial activity”, Journal of Nanostructure in Chemistry, Volume No.4, (2014), Page No. 86

Copper oxide nanoparticles exhibits high potential in replacing the noble metal nanoparticles due to its low cost, optical, catalytic and high conductivity properties^{5,6,7&8}. Although, various Physio-chemical methods such as microwave-assisted synthesis, sonochemical method, spray pyrolysis⁹ etc., were employed to synthesize CuO nanoparticles, green route of synthesizing CuO nanoparticles using plant extract as a bio reducing agent, seems to be eco- friendly, cost-effective, easily available, non-toxic method to fabricate metal nanoparticles¹⁰. Plant parts like leaf, stem, root, fruit, and seed have been used for CuO-NPs synthesis because of the exclusive phytochemicals that they produce. Using natural extracts of plant parts is a very eco-friendly, cheap process and it does not involve the usage of any intermediate base groups. It takes very less time, does not involve the usage of costly equipment and precursor and gives a highly pure and quantity enriched product free of impurities¹¹. Plants are most preferred source of NPs synthesis because they lead to large-scale production and production of stable, varied in shape and size NPs. Bio-reduction involves reducing metal ions or metal oxides to 0 valence metal NPs with the help of phytochemicals like polysaccharides, polyphenolic compounds, vitamins, amino acids, alkaloids, sugar, phenolic acids, terpenoids secreted from the plant¹². Earlier reports on green synthesis of CuO nanoparticles have been investigated so far using plant extract such as *Gloriosa superba* L¹³, *Euphorbia esula* L¹⁴, *Albizia lebbeck*¹⁵, *Bifurcaria bifurcata*¹⁶, *Carica*

⁵ S. Wang, X. Huang, Y. He, H. Huang, Y. Wu, L. Hou, X. Liu, J. Zou, B. Huang, "Synthesis, growth mechanism and thermal stability of copper nanoparticles encapsulated by multi-layer graphene", Carbon, Volume No. 50 (6), (2012), Page No. 2119-2125.

⁶ S. Chandra, A. Kumar, P.K. Tomar, "Synthesis and characterization of copper nanoparticles by reducing agent", Journal of Saudi Chemical Society" Volume No.18(2), (2014), Page No.149-153.

⁷ A.B.S. Sastry, R.B.K. Aamanchi, C.S.R.L. Prasad, B.S. Murty, "Large-Scale Green Synthesis of Cu Nanoparticles", Environmental Chemistry Letters. Volumen No. 11(2), (2013), Page No. 183-187.

⁸ N.R. Dhineshababu, V. Rajendran, N. Nithyavathy, R. Vetumperumal, "Study of structural and optical properties of cupric oxide nanoparticles", Applied Nanoscience, Volume No..6(6), (2016), 933-939.

⁹ C.Y. Chiang, K. Aroh, S.H. Ehrman, "Copper Oxide Nanoparticle Made by Flame Spray Pyrolysis for Photoelectrochemical Water Splitting – Part I CuO Nanoparticle Preparation", International Journal of Hydrogen Energy, Volume No. 37, (2012), 4871-4879.

¹⁰ I. Hussain, N.B. Singh, A. Singh, H. Singh, S.C. Singh, "Green synthesis of nanoparticles and its potential application", Biotechnology Letters, Volumen No.38(4), (2016), Page No.545-550.

¹¹ M. Heinlaan, A. Ivask, I. Blinova, H.C. Dubourguier, A. Kahru, "Toxicity of nanosized and bulk ZnO, CuO and TiO₂ to bacteria *Vibrio fischeri* and crustaceans *Daphnia magna* and *Thamnocephalus platyurus*", Chemosphere, Volume No.71, (2008), Page No. 1308–1316.

¹² J. Qu, X. Yuan, X. Wang, P. Shao, "Zinc accumulation and synthesis of ZnO nanoparticles using *Physalis alkekengi* L", Environmental Pollution, Volume No.159(7), (2011), Page No. 1783–1788.

¹³ H.R. Naika, K. Lingaraju, K. Manjunath, D. Kumar, G. Nagaraju, D. Suresh, H. Nagabhushana, "Green synthesis of CuO nanoparticles using *Gloriosa superba* L. extract and their antibacterial activity", Journal of Taibah University of Science, Volume No.9, (2015), Page No.7-12.

¹⁴ M. Nasrollahzadeh, S.M. Sajadi, M. Khalaj, "Green synthesis of copper nanoparticles using aqueous extract of the leaves of *Euphorbia esula* L and their catalytic activity for ligand-free Ullmann-coupling reaction and reduction of 4-nitrophenol" RSC Advances, Volume No. 4, (2014), Page No. 47313-47318.

¹⁵ G. Jayakumarai, C. Gokulpriya, R. Sudhapriya, G. Sharmila, C. Muthukumaran, "Phytofabrication and characterization of monodisperse copper oxide nanoparticles using *Albizia lebbeck* leaf extract", Applied Nanoscience, Volume No. 5(8), (2015), Page No. 1017-1021.

papaya¹⁷ and Gum karaya¹⁸. *Ocimum sanctum* (Tulsi) an Indian origin is considered as Holy basil in India. *Ocimum sanctum* belongs to the family Lamiaceae, which is well known for its medical use. In Ayurveda, the Indian system of medicine since ancient times, *Ocimum sanctum* attributes several medicinal properties¹⁹. The plant has been widely acknowledged for the treatment of coryza, hay asthma, bowel complaints, worm infestations and kidney stones in traditional medicine²⁰. Hence it is also termed as the Queen of Herbs. The major phytochemical constituents in this genus are alkaloids, flavonoids, polysaccharides, tannins and anthracene derivatives. *Ocimum sanctum* remains as an active area of scientific research for both human nutritional needs and therapeutic applications²¹. *Ocimum sanctum* leaf broth mediated synthesis of silver^{22,23}, copper²⁴ and platinum²⁵ nanoparticles has been reported.

Vitex negundo Linn belongs to the family of verbanaceae, which is commonly known as chase tree and also called as Karu Nochi in Tamil, Nirgundi in Hindi. It is a large shrub grown in waste lands throughout India. It is one of the common plants used in traditional medicine and reported to have variety of biological and pharmacological applications²⁶. Although,

¹⁶ Y. Abboud, T. Saffaj, A. Chagraoui, A. El Bouari, K. Brouzi, O. Tanane, B. Ihssane, "Biosynthesis, characterization and antimicrobial activity of copper oxide nanoparticles (CONPs) produced using brown alga extract (*Bifurcaria bifurcata*)", Applied Nanoscience, Volume No. 4(5), (2014), 571-576.

¹⁷ R. Sankar, P. Manikandan, V. Malarvizhi, T. Fathima, K.S. Shivashangari, V. Ravikumar, "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, Volume No. 121, (2014), Page No. 746-750.

¹⁸ V.V.T. Padil, M. Cernik, "Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application", International Journal of Nanomedicine, Volume No. 8(1), (2013), 889-898.

¹⁹ Kirtikar K R and Basu B D, "Indian Medicinal Plants. 2nd Edition, Vol.3", Periodicals Experts Book Agency, Delhi, 1991, Page No. 982-983.

²⁰ Bauer R W, Kirby M D K, Sherris J C and Turck M, "Antibiotic susceptibility testing by standard single disc diffusion method", American Journal of Clinical Pathology, Volume No. 45(32), 1966, Page No. 493-496.

²¹ . Sood S, Narang D, Dinda A K and Maulik S K, "Chronic oral administration of *Ocimum sanctum* Linn. augments cardiac endogenous antioxidants and prevents isoproterenol induced myocardial necrosis in rats", Journal of Pharmacy & Pharmacology 57(1), 2005, Page No. 127- 133.

²² Garima S, Riju B, Kunal K, Ashish R S and Rajendra P S, "Biosynthesis of silver nanoparticles using *Ocimum sanctum* (Tulsi) leaf extract and screening its antimicrobial activity", Journal of Nanoparticle Research, Volume No. 13, (2011), Page No. 2981-2988.

²³ Mallikarjunaa K, Narasimha G, Dillipa G R, Praveen B, Shreedhar B and Sree Lakshmi C, "Green synthesis of Silver nanoparticles using *Ocimum* leaf extract and their characterization, Digest Journal of Nanomaterials and Biostructures", Volume No. 6(1), (2011), Page No. 181- 186.

²⁴ Vasudev D Kulkarni and Pramod S Kulkarni, "Green synthesis of copper nanoparticles using *Ocimum sanctum* leaf extract", International Journal of Chemical Studies, Volume No. 1(3), 2013, Page No. 1-4.

²⁵ Soundarrajan C, Sankari A, Dhandapani P, Maruthamuthu S, Ravichandran S, Sozhan G and Palaniswamy N, "Rapid biological synthesis of platinum nanoparticles using *Ocimum sanctum* for water electrolysis applications", Bioprocess and Biosystems Engineering, Volume No. 35 (5), (2012), Page No. 827-833.

²⁶ S.R. Baral and P.P. Kurmi PP, "A Compendium of Medicinal Plants in Nepal". Pub: Mrs. Rachana Sharma, 281 Maiju Bahal, Chabhil, Kathmandu, Nepal, (2006), Page No. 450-451.

all parts of *V. negundo* are in medicine, its leaves have the most potential for medicinal value especially in for treatment of eye-disease, tooth ache inflammation, leucoderma, enlargement of the spleen, skin-ulcers, in catarrhal fever, rheumatoid arthritis, gonorrhoea and bronchitis, anti-bacterial, anti-pyretic, anti-inflammatory, antioxidant and anti-histaminic agents²⁷.

In modern years, semiconductor photocatalysis has received considerable attention as technology viable for green energy production and water purification. The nanostructured metal oxide-based photocatalysts have attracted widespread attention due to their ability to remove organic dyes from aqueous systems efficiently. The applications of dye compounds in various industries like textile, paint, leather, paper, plastic discharges, toxic, colored effluents and contaminants, surface and ground water are wideranging. The presence of dyes in water has a serious impact on different aquatic organisms^{28,29,30}.

Their removal from waste water before human consumption is important. Among these pollutants, Rh B dye belongs to the toxic dye category and widely has been applied in the textile, leather, and paper industries. With their widespread use, it becomes necessary to remove these dyes from industrial effluents to maintain a safe and clean aqueous environment. Various semiconductor NPs act as photocatalysts for protection against environmental pollution. From the literature studies we concluded that photodegradation efficiency of CuO-NPs towards a dye depends on various parameters such as nature of the dye, synthesis route, shape and size of NPs, attachment of charge carrier separating agent to NP, adsorption capability, surface area, etc.

The present study investigated an eco-friendly, green synthesis of CuO-NPs using *O.sanctum* and *V.negundo* leaves extract and its characterization. In this work, Rh B is the target organic pollutant CuO-NPs synthesis by using *Ocimum sanctum* and *Vitex vegundo* leaves extracts at room temperature can be use for the degradation of Rhodamine B in the absent of reducing agents.

2.MATERIAL AND METHODS:

2.1.Materials:

Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99 wt %), Rhodamine B(>95.0%, Purity, Sigma-Aldrich) and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) were purchased from Merck, India. All the reagents were of analytical grade. Sample preparation and dilution was made of ultra pure water. All glasswares were washed with dilute nitric acid (HNO_3) and distilled water, then dried in hot air oven. The chemicals obtained were in the highest purity and used directly without further purification.

2.2.Sample collection :

Fresh leaves of two different plants, that is, *Ocimum sanctum* and *Vitex negundo*, free from diseases were collected from Chidambaram. Whipped with tissue paper. The leaves were identified and authenticated by Department of Agriculture, Annamalai university at Tamilnadu in India.

2.3.Preparation of leaf Extract:

²⁷ O.P.Tiwari and Y.B.Tripathi, "Antioxidant properties of different fractions of *Vitex negundo* Linn", Food Chemistry. Volume No.100: Page No. 1170-1176.

²⁸ A.A. Atia, A.M. Donia, W.A. Al-Amrani, "Adsorption/desorption Behavior of Acid Orange 10 on Magnetic Silica Modified with Amine Groups", Chemical Engineering Journal, Volume No. 150(1), 2009, Page no.55-62.

The Fresh and healthy leaves of *O.Sanctum* and *V. negundo* were collected and rinsed thoroughly first with tap water followed by distilled water to remove all the dust and unwanted visible particles. When the leaves got completely dried, they were chopped into fine pieces. Each 10gm in chopped leaves of *O.sanctum* and *V.negundo* were boiled with 50 ml distilled water at 60°C with constant stirring up to 1 hour. The extract obtained was filtered through Whatman No.1 filter paper and finally brown extract was collected for further experiment.

2.4.Synthesis of CuO-NPs:

Extraction of leaves was carried out using different amounts of the *O.sanctum* and *V.negundo* leaves extraction (2, 4 and 6ml) added to 1M $\text{Cu}(\text{NO}_3)_2$ solution in a 250ml Erlenmeyer flask for bioreduction process. The flask was then kept overnight at room temperature. The bio-reduction of copper nitrate into copper oxide nanoparticles can be confirmed by visual observation. It is clear that *O.sanctum* and *V.negundo* leaf extract initially greenish brown in color, changed to a dark brown color upon reduction of copper nitrate solution strongly indicates the synthesis of copper oxide nanoparticles. The color change was compared with control aqueous leaf extract solution. Precipitates are washed with methanol and water to get rid of any unreacted Materials and dried in air. Finally, this paste was then collected in a ceramic crucible and annealed at 300 °C for 3 hours in the Muffle furnace. A black coloured powder was obtained and this powder was carefully collected. The material was powdered using a mortar and pestle so, that got a fine powder, which is easy for further characterizations.

2.5.Characterization:

The green synthesized nanoparticles were characterized by using different spectroscopic and microscopic tools. Initial confirmation of nanoparticles was done by UV–vis spectroscopy (Spectro UV 2080, Analytical Technologies, India) to know which of the metal nanoparticles were actually reduced and which of the phytochemicals were actually involved in reduction of nanoparticles by surface plasmon resonance method. To comprehend which of the phytochemicals were actually involved in capping and stabilization of nanoparticles, the FTIR spectroscopy (ALPHA interferometer, ECO-ATR, Bruker, Ettlingen, Karlsruhe, Germany) was utilized. XRD (Shimadzu, XRD-6000) was used to analyze crystalline nature and calculate the average size of particles. Microscopic analysis with SEM (HF-3300, 300 kV SEM, Hitachi) instrument reveals the size, shape, dispersed nature and agglomerated pattern of nanoparticles. TEM micrographs were captured by analyzing the prepared grids on a Hitachi H-7650 TEM instrument at an operating voltage of 200 kV.

2.6.Photocatalytic degradation of Rhodamine B:

The photocatalytic activity of the CuO-NPs was investigated for the degradation of RhB under visible light irradiation. The photo reactor “Heber Visible Annular Type Photo reactor” equipped with 300W tungsten halogen lamp (8500 lumen) was used for the investigation. The photo reactor was comprised of a borosilicate immersion jacketed tube to hold the lamp with inlet an outlet for water circulation to cancel the IR radiation. The immersion well is held at the centre of a reaction chamber. The inner surface of reaction chamber is fitted with highly polished anodized aluminum reflector. The depth of the solution was 8 cm and the internal diameter of test tube was 1.6 cm. The distance from test tubes to lamp was 10 cm. The photoreactor was kept open to air to get sufficient oxygen for photochemical reaction. The dye with concentration of 1.0×10^{-5} M were used in the present study. In each experiment, 10mg of the prepared photocatalyst (CuO-NPs) was mixed with 50ml of above dye solution and then sonificated for about 15 minutes in a sonicator. The above reaction mixture was loaded in the photoreactor and again stirred well for about 30 minutes in dark to attain adsorption-desorption equilibrium condition, then exposed to light. To see the catalytic activity of as prepared CuO-NPs, Rh B degradation was carried out for both photocatalyst. At regular time intervals, 5 ml of sample have been collected from the reactor and then centrifuged to remove photocatalyst. After centrifugation UV-Vis absorption spectra have been taken to monitor the degradation of Rh B dye by monitoring the characteristic absorption peak intensity at ~ 554 nm. The centrifuged solution was used to monitor and the concentration of Rh B and obtained by UV-Vis. spectrophotometer. (UV-3600, Shimadzu). The reaction time ranged from 0 to 40 min. The degradation of Rh B was calculated by formula:

$$\text{Degradation}(\eta) = \frac{A_0 - A}{A_0} \times 100$$

Where, A_0 and A were the absorbance of the primal and remaining Rh B, respectively. The absorbance was measured with UV/vis spectrophotometer (UV-2100, China).

3. RESULTS AND DISCUSSION:

3.1. UV- visible:

Absorption spectra of CuO-NPs from three different concentration of leaf extract in Fig:1²⁹. In all the cases the peaks were in 311nm, 310 nm and 308nm which is the characteristic peak of CuO-NPs³⁰. In the spectrum, the peaks at 310 nm are due to metal oxide nanoparticles is due to the collective oscillation of the free conduction band electrons which is excited by the incident electromagnetic radiation. This type of resonance is seen when the wavelength of the incident light far exceeds the

²⁹ Filipic G, Cvelbar U, “Copper oxide nanowires: a review of growth”, Nanotechnology, Volume No.23(19): 2012; Page No.190201-194015..

³⁰ Gunalan sangeeta, Sivaraj Rajeswari, Venkatesh R, “Aloe barbadensis Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: Optical properties”, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume No.97: (2010), Page No.1140-1144.

particle diameter. Surface plasmon absorption band with a maximum at 310 nm indicates the formation of CuO nanoparticles³¹. The energy band gap of CuO NPs was found using the following equation (1),

$$E_g \text{ (eV)} = \frac{1240}{\lambda} \text{ -----(1)}$$

The calculated Band gap of CuO NPs was found to be 4 eV and it was comparatively higher than bulk value 1.2 eV of CuO NPs. This higher value of energy band gap for CuO nanoparticles was due to the quantum confinement effect³². Water soluble fractions like phenolic compounds, saponins and flavonoids in the aqueous leaf extract might help in the bioreduction of copper ions³³.

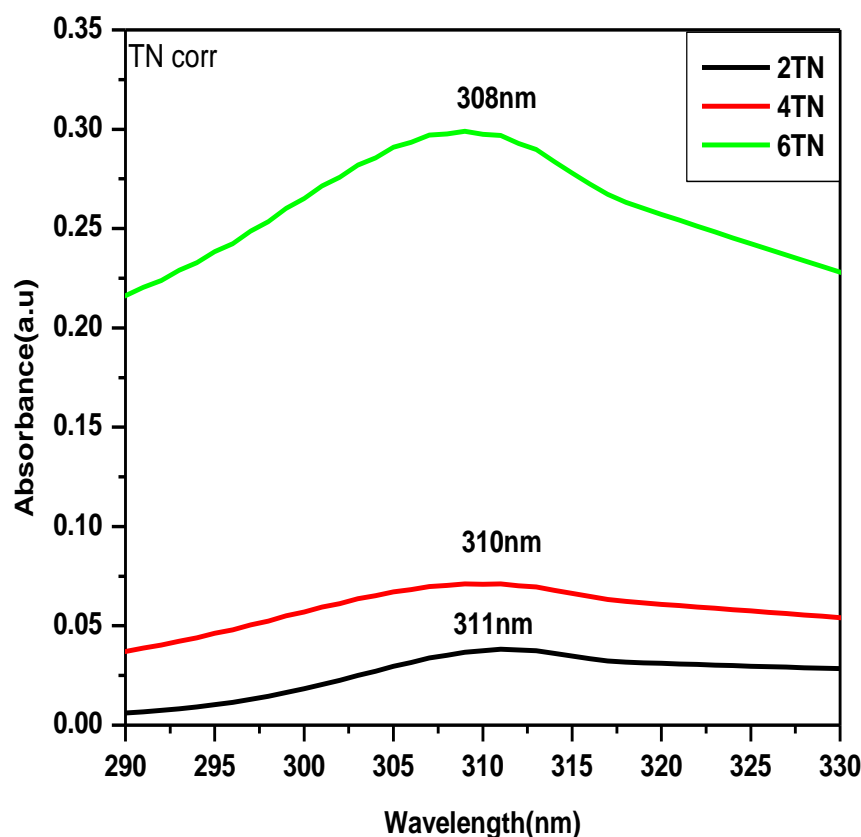


Fig.1.UV-Visible Pattern Of CuO NPs

³¹ D. Dhaneswar, B.C. Nathb, P. Phukonc, S.K. Doluia* "Synthesis and evaluation of antioxidant and antibacterial behavior of CuO nanoparticles.", J. Colloids Surf. B: Biointerfaces, Volume No. 101 (2013), Page No. 430-433.

³² M.A.Rafea and N. Roushdy, "Determination of the optical band gap for amorphous and nanocrystalline copper oxide thin films prepared by SILAR technique", J. Journal of Physics D: App Physics, Volume No. 42(1), (2008), Page No. 1-6.

³³ .K. Kesarwani and R. Gupta "Bioavailability enhances of herbal origin:an overview", .Asian Pacific Journal of Tropical Biomedicine, Volume No.3(4): (2013), Page No. 253-266.

3.2.XRD Structural analysis:

The phase identification and crystalline structure of the nanoparticles were characterized by X-ray diffraction. The CuO NPs biosynthesized from *O.sanctum* and *V.Negundo* leaf extract were confirmed by the characteristic peaks observed in the XRD patterns, as shown in Fig. 2. XRD analysis shows intense peaks at 32.4°, 35.5°, 38.7°, 48.7°, 53.4°, 58.3°, 61.5°, 66.3°, 68.0°, 72.4° and 75.2° corresponding to ($\bar{1}$ 10), (002), (111), ($\bar{2}$ 02), (020), (202), ($\bar{1}$ 13), ($\bar{3}$ 11), ($\bar{2}$ 20), (311) and ($\bar{2}$ 22) respectively. Moreover, the well-defined and sharp CuO NPs reflections in the observed XRD patterns verify the well-crystalline nature of CuO-NPs. Fig. 2. shows typical XRD patterns of the formed CuO NPs which are identical to the single phase monoclinic (JCPDS:45-0937) structure with a lattice constant $a = 4.6965 \text{ \AA}$, $b = 3.4324 \text{ \AA}$ and $c = 5.1329 \text{ \AA}$, $\beta = 99.5287^\circ$. No impurity peaks other than CuO-NPs were observed in the XRD pattern indicating the high phase purity. The broadening of the diffraction peaks indicates that the crystal size is small. The average crystallite size of the CuO NPs calculated by Debye-Scherrer's formula³⁴ as

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

where D is the particle size (nm), k is a constant equal to 0.94, λ is the wave length of X-ray radiation (1.5406 \AA), β is the full-width at half maximum (FWHM) of the peak (in radians) and 2θ is the Bragg angle (degree). It is found that the average crystallite size of the prepared sample 2TN is 33 nm, 4TN is 31 nm and 6TN is 28 nm. It is observed that increasing the concentration of leaf extract leads to decrease in crystallite size. We used the Williamson-Hall equation to calculate the strain and particle size of the sample. The W-H equation is expressed as follows:

$$\beta \cos\theta = \frac{K\lambda}{D} + 4\epsilon \sin\theta$$

In this equation, $\beta \cos\theta$ is plotted against $4\sin\theta$. Using a linear extrapolation to the plot, the intercept gives the particle size $K\lambda/D$ and the slope represents the strain (ϵ) for CuO-NPs as shown in fig.(2). The strain values were obtained to be 0.00061, -0.00030 and -0.00039 for 2TN, 4TN and 6TN respectively. The crystalline sizes of CuO-NPs calculated using the Williamson and Hall method were obtained to be 42.657 nm, 26.406 nm and 24.494 nm for the samples 2TN, 4TN and 6TN respectively. Meanwhile, the dislocation density (δ) in the sample was determined using the expression³⁵:

$$\delta = 1/D^2$$

Where, the dislocation density (δ) was estimated to be 9.00903×10^{14} , 1.21073×10^{15} and $1.29821 \times 10^{15} \text{ line/m}^2$ for 2TN, 4TN and 6TN leaf extract. The result show that the average crystallite sizes obtained from Scherrer's formula and the W-H plot show a variation. This is because of the difference in averaging the particle size distribution. The collective effect of crystallite size

³⁴ Scherrer, P. "Bestimmung der Grosse und der Inneren Struktur von Kolloidteilchen Mittels Rontgenstrahlen, Nachrichten von der Gesellschaft der Wissenschaften, Gottingen". Mathematisch-Physikalische Klasse, 2, (1918), Page No.98-100.

³⁵ S.Iliean., Y. Caglar., M. Caglar., "Preparation and characterization of ZnO thin films deposited by Sol-Gel spin coating method", Journal of Optoelectronics and Advanced Materials. Volume No.10: (2008), Page No. 2578-2583.

and lattice strain due to dislocation was cause for the peak broadening of the sample³⁶. The difference between crystallite size according to W-H and crystallite size according to Debye-Scherrer occurs, because W-H method takes into account the lattice strain of crystallite arising from defects like dislocation, imperfection and distortion.

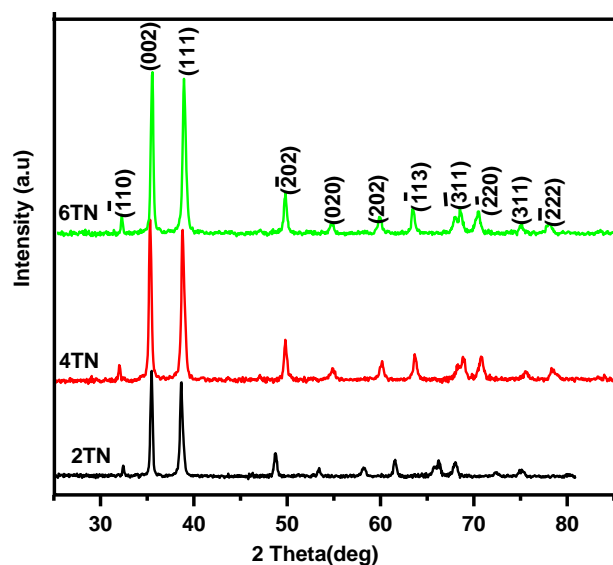


Fig. 2. XRD Pattern Of CuO-NPs

³⁶ N. Choudhury, B.K. Sarma, "Structural Analysis of Chemically Deposited Nanocrystalline PbS Films", Thin Solid Films Volume No. 519(7), (2011), Page No. 2132-2134

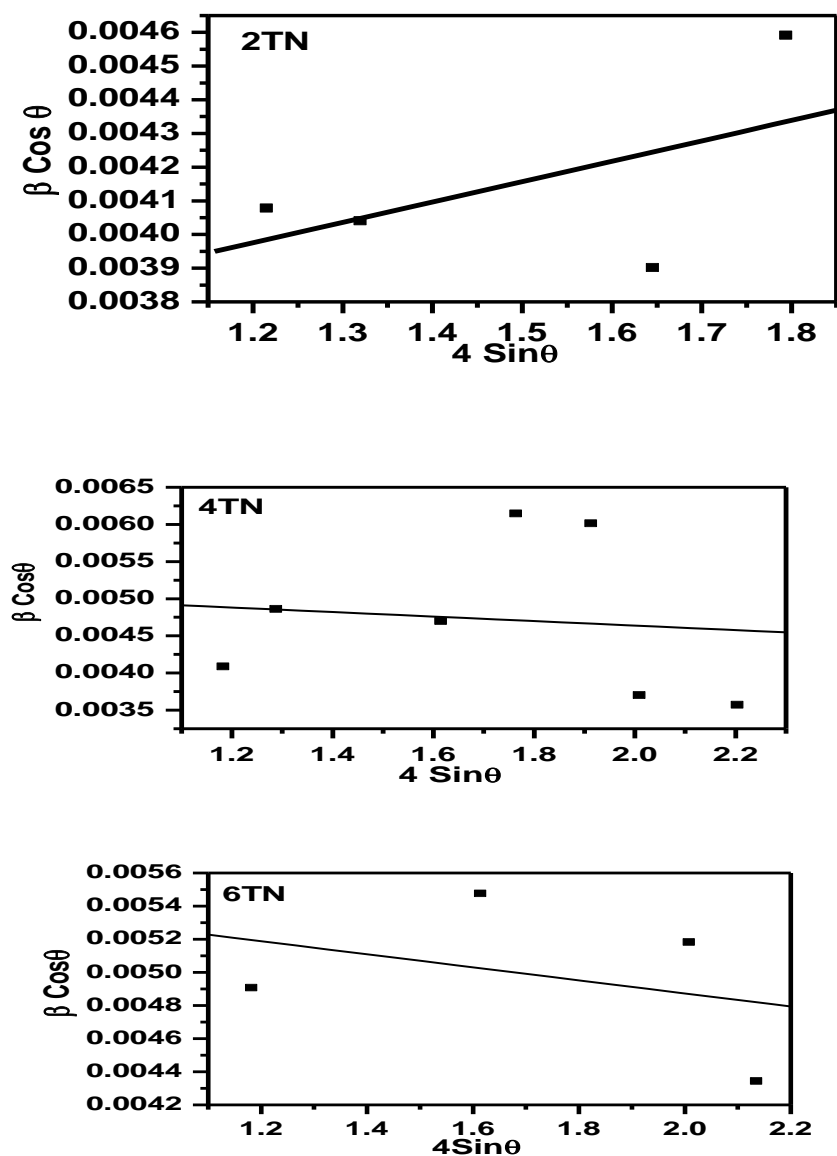


Fig.3: W-H analysis of CuO-NPs

Table 1. Measured Parameters Of CuO - NPs

Sample	Strain	Particle Size in nm		Dislocation density (m^{-2})
		Scherrer	W-H Plot	
2TN	0.00061	32.508	42.657	9.00903E14
4TN	- 0.00030	30.538	26.407	1.21073E15
6TN	- 0.00039	28.057	24.494	1.29821E15

3.4. FT-IR analysis:

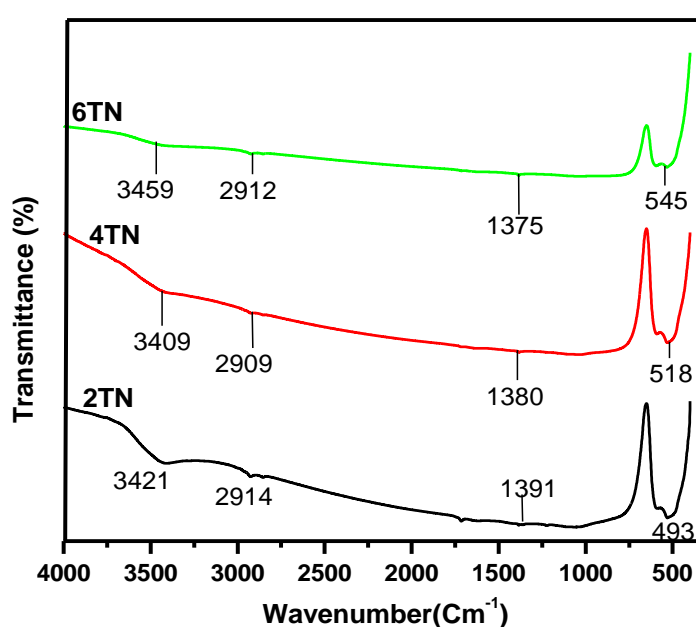


Fig . 4. FTIR Pattern Of CuO-NPs

The FT-IR spectra of as-synthesized CuO-NPs are indicated in fig.4. FTIR studies were carried out to understand the presence of functional group of any organic molecule. A peak at 3421 cm^{-1} can be attributed hydrogen bonded O-H groups of alcohols and phenols and also to the presence of amines N-H of amides on 2TN. This peak shifted to lower field at 3409 cm^{-1} in 4TN and 3459 cm^{-1} in 6TN of the synthesized CuO-NPs. Fig.4. The small peak at 2914 cm^{-1} assigned to $-\text{CH}_2$ and C-H stretching mode in alkanes in 2TN. This peak also shifted to lower field 2909 cm^{-1} in 4TN and 2912 cm^{-1} in 6TN. The small peak was seen to be 1391 cm^{-1} in 2TN, 1380 cm^{-1} in 4TN, 1375 cm^{-1} in 6TN. The peaks observed in the range of $640\text{--}1391\text{ cm}^{-1}$ have been assigned to alcohols and phenolic groups, C-N stretching vibrations of aliphatic and aromatic amines. The major peak was observed to be 493 cm^{-1} in 2TN should be a stretching of Cu-O. This peak value also shifted to higher frequency region 518 cm^{-1} in 4TN and 545 cm^{-1} in 6TN. The shifting in these bands is clearly indicating that the coordination of carboxylic acids in the protein of *O. sanctum* and *V. negundo* leaf extract with CuO-NPs play a major role on reducing, dispersing, stabilizing and capping of CuO-NPs formation^{37,38}. The FTIR spectrum of CuO-NPs suggested that CuO-NPs were surrounded by different organic molecules such as terpenoids, alcohols, ketones, aldehydes and carboxylic acid.

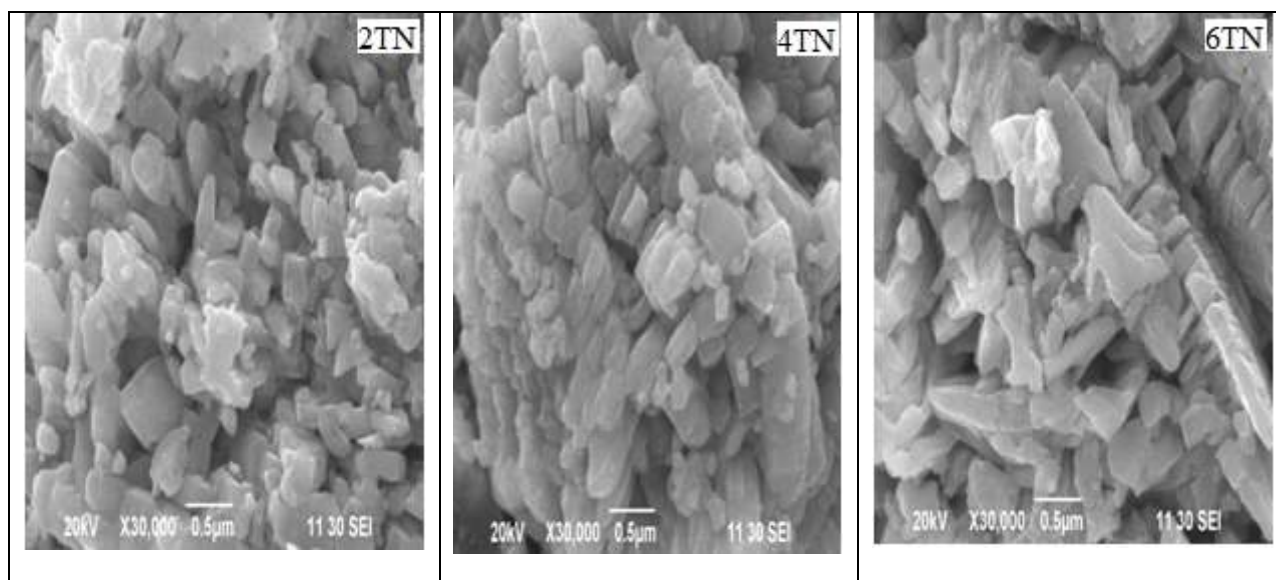
³⁷ R.Sankar, R.Dhivya, K.S.Shivasangari and V. Ravikumar "Wound healing activity of *Origanum vulgare* engineered titanium dioxide nanoparticles in *Wister albino rats*", Journal of Materials Science, Materials Medicine, Volume No.25(7), (2014), Page No. 1701-1708.

³⁸ R.Sankar, P.Manikandan, V.Malarvizhi, T. Fathima, K.S.Shivashangari, and V. Ravikumar, (2014b) "Green synthesis of colloidal copper oxide nanoparticles using *Carica papaya* and its application in photocatalytic dye degradation", Spectrochim Acta A Molecular and Biomolecular Spectroscopy, Volume No.121, (2014), Page No.746-750.

3.5. SEM:

The SEM images of CuO-NPs are shown in fig.5. The surface morphology of the synthesized copper oxide nanoparticles was examined by SEM micrographs. The prominent well-structured growth observed from the SEM micrographs of the fine particles confirms the development of the crystal structure of the copper oxide nanoparticles. The presence of aggregation and agglomeration in the higher concentration samples may be due to the occurrence of large surface energy and surface tension because of decrease in particle size³⁹. In higher concentration, the inter particle distance less and the force of attraction may dominate the repulsive force, thereby causing agglomeration of particles in 4TN and 6TN. The EDAX spectra of CuO-NPs are shown in Fig:6. The presence of Cu and O in the sample was confirmed by EDAX analysis. The chemical composition data of as-synthesized CuO-NPs are indicated in Table.2. The variation in the percentage of elements (Cu and O) may be due to the reaction conditions during the preparation of CuO-NPs. The EDX spectrum shows the characteristic copper oxide peaks on the surface of the nanoparticles, suggesting successful copper oxide nanoparticles synthesis using plant leaf extract.

Fig. 5. SEM Images Of CuO-NPs



³⁹ D. Hongve. and G.Akeson, "Spectrophotometric determination of water colour in hazen units. *Water research*", Volume No.30, (1996), 2771-2775.)

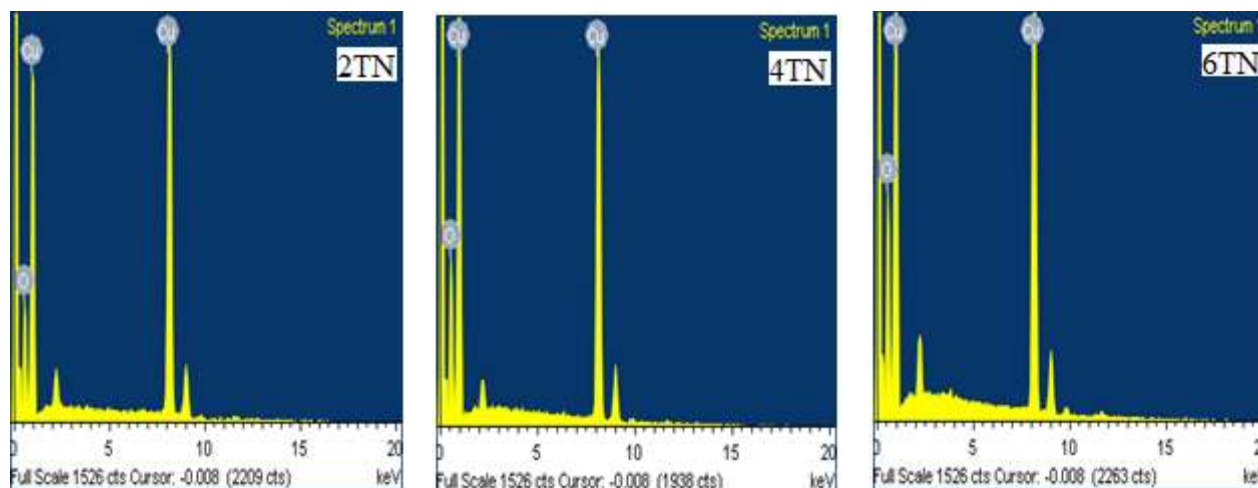


Fig.6 EDAX Pattern Of CuO NPs
Table 2 Elements of CuO-NPs

CuO-NPs	Atomic weight percentage of elements	
	Cu	O
	76.54	23.46

TEM:

TEM was employed to characterize the exact size and shape of the CuO NPs. Figure 7a. clearly indicated the presence of well dispersed nanoparticles. The selected-area electron diffraction (SAED) pattern given in Fig. 7b.exhibits a set of concentric rings with intermittent bright spots, confirm a highly crystalline nature of the produced nanoparticles. These rings can be indexed to the various diffraction from the 2.907\AA and 2.160\AA d - spacing of monoclinic copper oxide nanoparticles. These observations are reliable with the measurements made from the XRD patterns.The SAED pattern shows the well defined electron spots, confirming the crystalline nature of the monoclinic phase of copper oxide nanoparticles. SAED pattern of the synthesized CuO NPs exhibits the dotted concentric rings belong to (110), (111) planes, which matches with the result of XRD analysis.

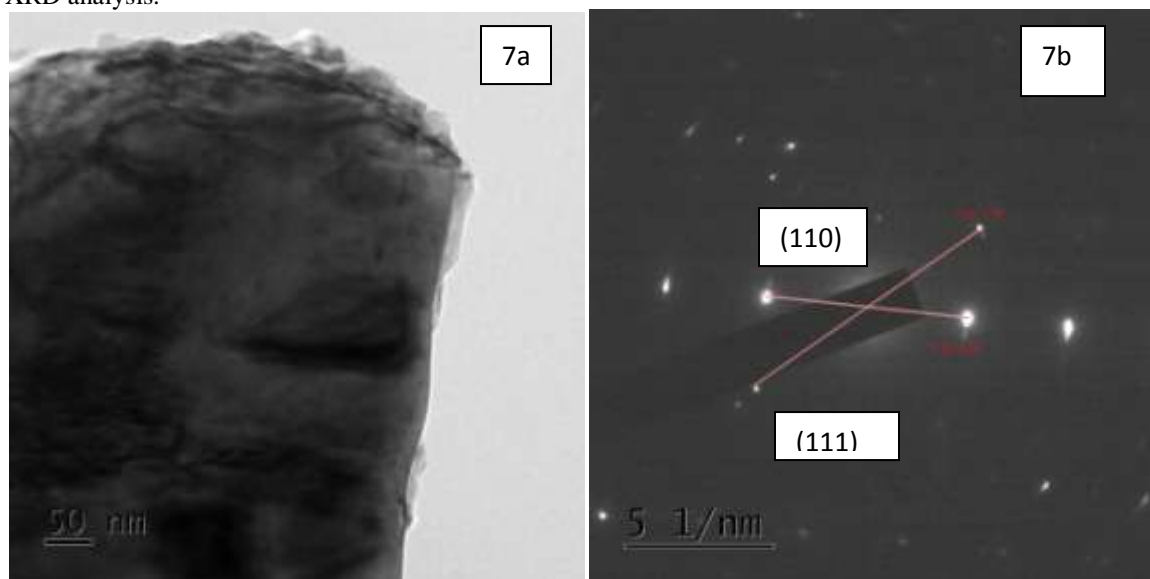
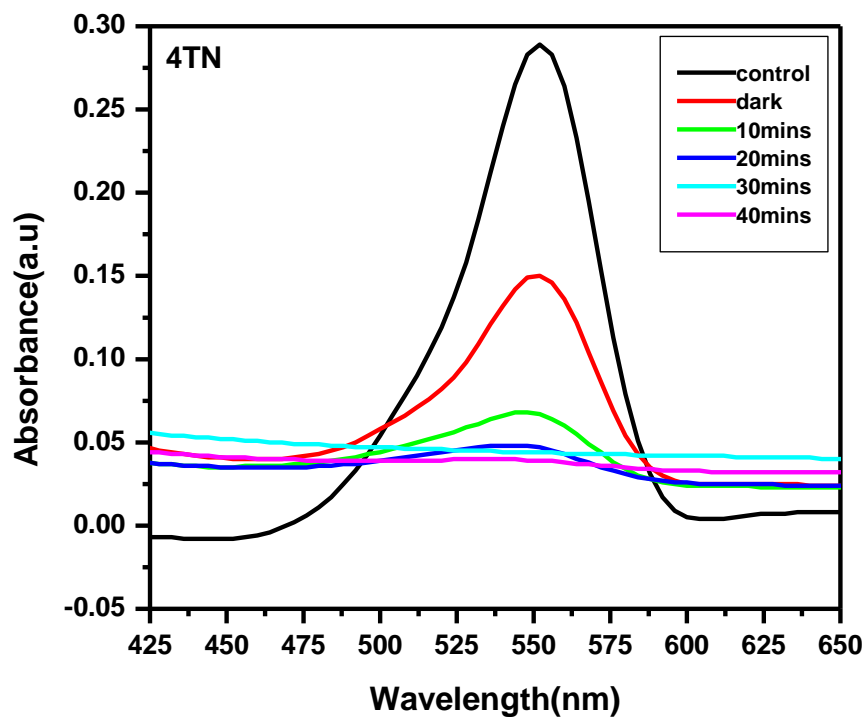
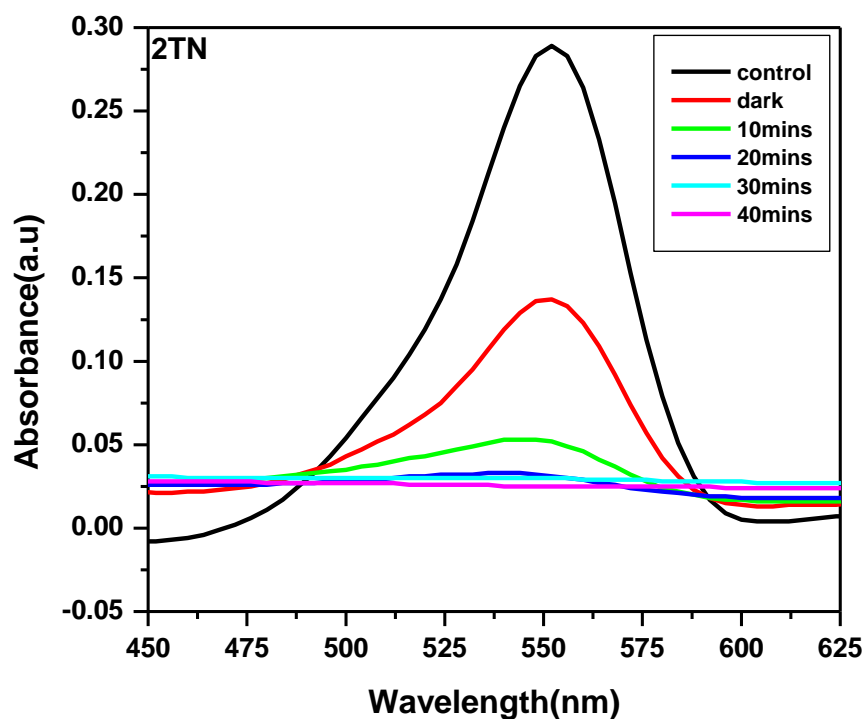


Fig. 7a.TEM Images of CuO NPs

Fig. 7b.SAED Pattern Of CuO NPs

Photocatalytic activity of CuO-NPs:



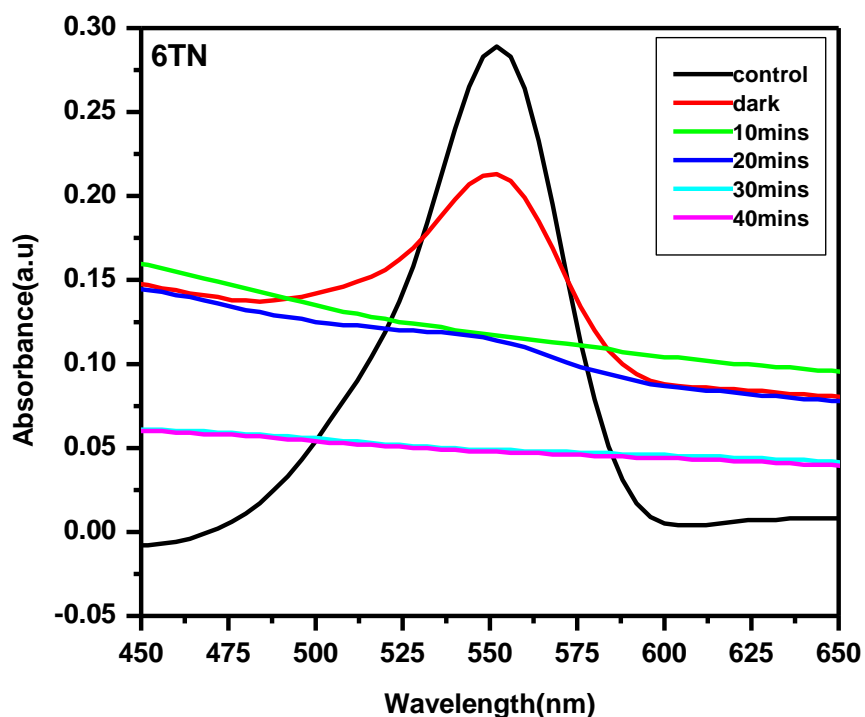


Fig.8 Degradation of CuO-NPs

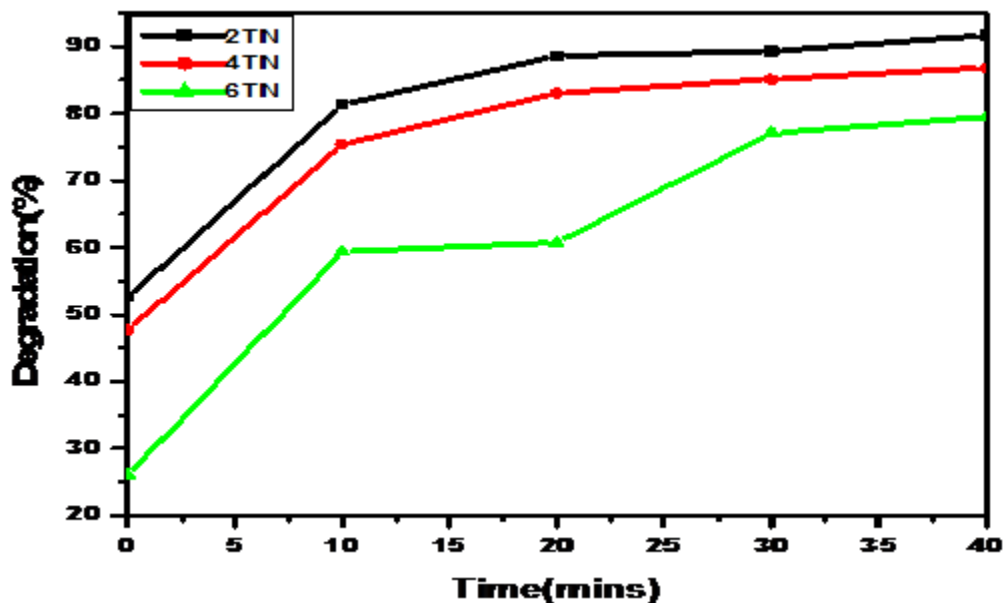


Fig. 9 Degradation percentage curve of RhB by different catalysts

Fig: 9 shows the degradation percentage curve of Cu O-NPs, was degraded rhodamine B in presence CuO-NPs irradiated under UV light. The degradation rate of rhodamine B dye without catalyst, is unchanged. In presence of CuO-
@IJAERD-2018, All rights Reserved

NPs, rhodamine B was degraded 92%, 87% and 80% for 2TN, 4TN and 6TN respectively. After exposure to UV radiation for about 40 minutes. The result has shown a good level of decrease in the absorption intensity with respect to time. The great photocatalytic activities of CuO-NPs in 2TN should be due to their large surface area which can facilitate mass transfer and increase the accessibility of active sites on CuO surface to Rh B molecules^{40,41,42}. The reduced photocatalytic activity at 4TN and 6TN indicates that the agglomeration activity due to the higher concentration of leaf extract and decrease in particle size. Since, the agglomeration accompanies the reduction of the available surface area, the photocatalytic activity should be limited by the reduced surface area. However, the exact quantification of the change in the reactive surface area of nanoparticles due to agglomeration in the aqueous suspension still remains unknown. The mass transfer of substrates to the active surface sites should be also highly hindered by the agglomerate formation. Therefore, the reduction in the surface area seems to outweigh the agglomeration decreased the photocatalytic activity in 4TN and 6TN. From the result, it was found that sample (2TN) has good photocatalytic characteristics in degrading the rhodamine B under UV light irradiation.

4. Conclusion:

Copper oxide nanoparticles were synthesized by a green synthesis method using *O.sanctum* and *V.Negundo* leaf extract. The formed CuO-NPs Powder was characterized using XRD, FTIR, SEM, EDAX, TEM and UV-visible techniques. XRD data suggested that pure monoclinic crystallite structures of CuO nanoparticles were formed. SEM images reveal that nanoparticles possess agglomeration and monoclinic structures. The average crystallite sizes were found to be 30 nm. The energy gap of synthesised CuO was around 4 eV. Thus CuO can be used as wide band gap semiconductor. The Rhodamine B was found to degrade very effectively by CuO nanoparticles in the presence of UV light. It is also concluded that the photocatalytic activity of CuO nanoparticles decreased with decrease in surface area to volume ratio due to agglomeration and decrease in particle size. The study successfully demonstrates a simple way of employing under utilized plants for the production of multifunctional CuO nanoparticles.

⁴⁰ Tong DG, Vhu W, Luo YY, Chen H, Ji XY, "Preparation and Characterization of Amorphous Co-B Catalysts with Mesoporous Structure", Journal of Molecular catalysis A: Chemical, Volume No.269, (2007), Page No.149.

⁴¹ Tong DG, Han Y, Chu W, Chen H, Ji XY (2007), "Preparation of mesoporous Co-B catalyst via self-assembled triblock copolymer templates", Materials Letters, 61(25), Volume No.4679-4682.

⁴² D.G.Tong, Y. Han Y, W.Chu, H. Chen, X.Y. Ji (2008), "Preparation of Characterization of Co-B Flowers with Mesoporous Structure", Materials Research Bulletin, Volume No. 43, Page No. 1327.