SINGLE STEP GREEN SYNTHESIS OF STABLE COPPER OXIDE NANOPARTICLES AS EFFICIENT PHOTO CATALYST MATERIAL

M. IMRAN DIN[a*], F.ARSHAD[a], A. RANI[a], A. AIHETASHAM[b],
M. MUKHTAR[b], H. A. MEHMOOD[c]
[a]*Institute of Chemistry, University of Punjab, Lahore-54590, Pakistan*
[b]*Department of Zoology, University of Punjab, Lahore-54590, Pakistan*
[c]*Department of Chemistry, GOVT.S.E College Bahawalpur, Pakistan*

By using green method, stable Copper oxide (CuO) nanoparticles (NP's) were synthesized by plant extract of *Calotropis Procera* both as capping and reducing agent. The reaction conditions containing temperature of reaction mixture, pH of reaction mixture, concentration of salt and heating time of reaction mixture were optimized in order to get the best yield and particle size of CuO NP's. The structural and optical properties of CuO NP's were studied by employing various characterization techniques including Fourier transform infrared (FTIR) spectroscopy, UV/Visible spectroscopy and XRD technique. The results of UV/Vis spectroscopy revealed that prepared NP's were mono disperse and particle size of NP's controlled by plant extract successfully. The comparison of FTIR results of both copper oxide NP's and plant extract showed that stabilization and formation of CuO NP's were due to phenolic groups and amines in plant extract. The X-ray diffraction results indicated that copper oxide NP's were mono-disperses of size 18-20 nm. The maximum yield of NP's was archived by using 20 mM salt at pH 12.0, temperature 50°C and heating time of 45 minutes of reaction mixture. Antimicrobial activity exposed that synthesized Copper oxide (CuO) nanoparticles have broad spectrum antibiotic performance against Escherichia coli bacteria. The catalytic efficiency of copper oxide nanoparticles were observed by investigating photocatalytic degradation of methylene blue (MB) dye. The degradation of MB dye followed the kinetics of first order reaction and the maximum degradation efficiency of CuO NP's obtained after 30 minutes was 81.85 %.

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1. Introduction

Semiconductor and metal nanoparticles (NP's) have drawn attention of scientists in recent years due to their shape-dependent properties and size [1, 2].The physical and chemical properties of a specific metal are much different from its bulk material [3]. The properties of NP's can be twisted both with the surface morphology and the particle size [4].Copper oxide is a semiconducting material is comparatively inexpensive as compared to other noble metals such as palladium, platinum and gold. It is the simplest compound of copper family and exhibits a range of potentially useful physical properties such as electron correlation effects, high temperature superconductivity [2] and spin dynamics. This metal plays an important role in modern electronic circuit due to relatively low costs. Metals can act as catalyst in wide range of reactions and since important factor in catalysis is surface area, metal nanoparticles with huge surface area to volume ratio have been studied. Controlling the shape, size and surface property of nanoparticles is important to discovering copper-based catalysis [5]. In future, copper oxide NP's have drawn the attention of researchers to be used in nano-electronics, nano-devices, catalytic applications, pharmaceutical materials and nano-fluids [6].

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[*] Corresponding Author: imrandin2007@gmail.com

Copper oxide nanoparticles have been synthesized by different techniques, normally categorized as chemical and physical processes [7].Physical methods, such as vacuum vapor deposition, radiation methods [8], and proton irradiation are capable of fabricating a wide range of metal nanoparticles, while physical method normally need expensive vacuum systems to create plasma [9]. In chemical synthesis we can control the growth and size of metal nanoparticles by adjusting reaction conditions which include temperature of system, pH of reaction medium, concentration of precursor salt and surfactant and by changing the reaction solvent. Micro emulsion method [10], sonochemical reduction, and chemical reduction [11], are examples of some of the chemical methods that are used for the synthesis of CuO NP's. Physical and chemical methods although produce pure NP's at large scale but they are not cost effective as well as are non eco friendly. These problems can be solved by green chemistry approach which is a booming research area whose aim is to synthesize materials by producing no or less toxic waste. This method have very minor reaction conditions, use water as nontoxic solvents, removal of harmful materials and cost effectiveness as well as compatibility for pharmaceutical and biomedical applications [12].Bio-reduction of precursor salt by the microbes or bioactive components of plants is examples of such green method which include the use of natural compounds as reductant. It is also found that plant extract can acts both as reducing and capping agents in the manufacturing process of the nanoparticles. The secondary metabolites of plant are responsible [13] for the reduction of metal salt into NP's as well as prevent the aggregation of formed NP's.

Calotropis procera is a soft woody and flowering plant belongs to aslepiadanceae family generally found Africa and Asia. Sodom apples, apple of Sodom, rubber tree or king's crown are the common names of this plant. *Calotrpi sprocera* grows to about 3 to 6 ft (0.91 to 1.83 m). Calotropis procera plant contains milky liquid is a complex mixture of chemicals as Calotropagenin, flavonoids (flavonolsand flavones) which are ketone-containing compounds [14, 15]. Aldehyde group in calotropagenin, alcoholic and keto group in flavonoland flavones are responsible for the reduction of copper ions.

The processes of advance degradation and multi-step treatment were described to a significant level in practical applications [16].The use of green synthesized CuO NPs for degradation of dye stuffs is relatively an unexplored area, since very few reports have been published which demonstrate green synthesis of copper nanoparticles and its application in photo-catalytic dye degradation. The CuO NP's shows favorable activity on the catalytic reduction of Coomassie brilliant blue R-250, and can be recycled many times without change in the catalytic activity [17].

By using green method, stable Copper oxide (CuO) nanoparticles (NP's) were synthesized by using plant extract of *Calotropis Procera* as capping agent and reducing agent.. The reaction conditions containing temperature of reaction mixture, pH of reaction mixture, concentration of salt and heating time of reaction mixture were optimized in order to get the best yield and particle size of CuO NP's. The structural and optical properties of CuO NP's were studied by employing various characterization techniques including Fourier transform infrared (FTIR) spectroscopy, UV/Visible spectroscopy and X-ray diffraction. The catalytic efficiency of copper oxide NP's were checked by showing the photo-catalysis on methylene blue (MB) dye and degradation of MB dye followed the kinetics of first order reaction.

2. Experimental methods

2.1 Preparation of *Calotropis procera* leaves extract

Fresh leaves of *Calotropis procera* were collected from Punjab university campus, Quaid-e-Azam campus, Lahore and washed several times with water to remove the dust particles and then sun dried for 5-10 min to remove the residual moisture. Known weighted of these sun dried leaves were sever into small parts and were soaked in methanol solution. In magnetic stirrer, this mixture was stirred for 24 hour at room temperature and filtered by crucible filtration apparatus.

2.2. Synthesis of copper oxide nanoparticles by *Calotropis procera* leaves extract

In conical flask 20 mL of aqueous solution of 20mM $CuCl_2.2H_2O$, 30mL of plant extract(20%), 20 mL of aqueous solution of 0.1M Urea and 10 mL of aqueous solution of sodium hydroxide(1M) were mixed and this mixture was strongly shake for 15 min in electric shaker. This mixture was then heated for 45 min in oven at 50˚C and centrifuged at 1000rpm for 15 min. The centrifuged precipitates dried in oven for 6 hour sat 60˚C.This Reaction was optimized by varying the pH of mixture, concentration of precursor salt, heating time and temperature of reaction mixture.

2.3. Characterization

The CuO NP's synthesized by green approach were characterized for their optical ability by using UV/Vis spectrophotometer with specifications (UVD-3500,Lambod, Inc., USA, Double beam and resolution is 0.1 nm). The functional group analysis was conducted using FTIR spectrophotometer with specifications (Cary 630, Agilient Technology, USA and Resolution is 0.05 cm^{-1}). The average particle size and structural analysis (grain size and phase purity) were carried out with XRD.

2.4. Photo-catalytic Degradation of methylene blue

Aqueous solution Methylene blue (MB) shows maximum absorption (wavelength) at 668 nm. In a flask 0.01 g CuO NP's, 0.6 mL of sodium borohydride (15 mM) mixed with1.6 mL of methylene blue (0.08 mM) and this mixture was diluted with 0.45 mL of water. The reaction mixture was then put to constant stirring under the revelation of sun shines. A small amount of sample was withdrawn after proper time interval from the beaker and its absorbance was determined. After each 60 sec intervals absorbance was measured.

3. Result and discussion

In UV/Vis spectrum the position of exciton absorption for CuO NPs depends on several factors including temperature, synthetic method, shape of NPs and size and because of this there is no optimum exciton peak for CuO NPs but a range of 400-420 nm is given to exciton absorption peak for CuO NPs. The UV/Vis spectrum of optimized sample of CuO NPs is shown in Fig.1 in which maximum absorption is positioned at 415 nm. This spectrum showed the formation of pure CuO NPs because there is no any other peak in this region. The amount of formed NP's is correlated with the peak intensity, so for this case large amount of NP's observer due to peak of high intensity.

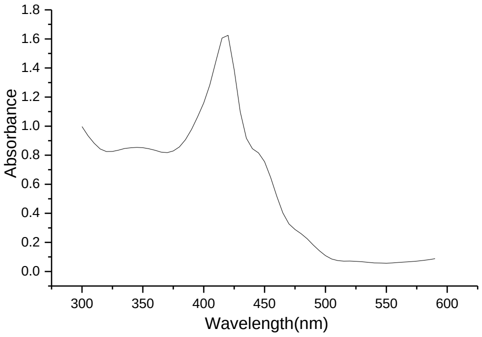
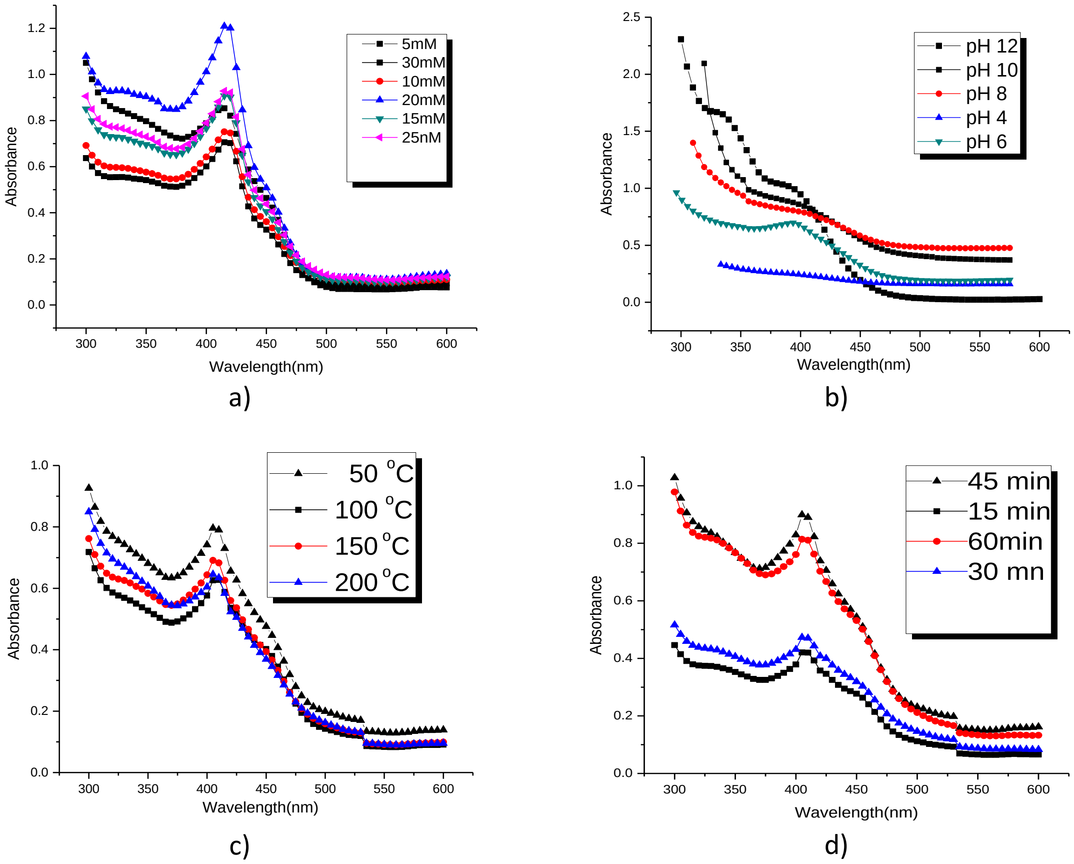


Fig.1:UV/VIS spectrum of CuO NPs

3.1. Effect of reaction parameters on the optical properties of CuO NPs

The UV/Visible spectrum of copper oxide NP's made-up by changing the concentration of salt is given in Fig. 2 (a). It can be realized from the plot that intensity of λ_{max} is highest when 20 mM salt is used which indicated that at both lower (5 mM) and higher (25 mM) concentration of salt not sufficient nuclei were shaped. In case of 25 mM salt concentration this may be due to low number of reducing agent molecules and in case of 5 mM concentration, this may be due to low number of Cu^{2+} ions which have to be reduced to Cu nuclei. By changing the pH of mixture as given in Fig. 2 (b), it can be realized that basic medium are satisfactory for the synthesis of NP's while acidic mixture is not satisfactory. Since at low pH, large quantity of the bioactive compounds are in protonated form so their complexation with metal ion is not estimated very high and under such situations they are not considered as good capping agent and reducing agent as they are at higher pH where deprotonation of many functional groups like carboxyl, amino groups and sulfhydryl occurs. Change in temperaturedoes not change that position of absorption peak as shown in Fig. 2(c);more intense peak is observed when reaction temperature is 50 ^{o}C.UV/Visible spectrum when heating time is changed, maximum intense peak detected at heating time 45 min as shown in Fig. 2(d).



a)

b)

c)

d)

Fig.2.UV/Vis Spectrum of CuO NPs synthesized by (a) varying the concentration of salt, (b) varying the pH of reaction medium, (c) by varying the concentration change in temperature and (d) by varying the heating time of reaction mixture.

FTIR-spectroscopy was used to describe the functional groups of *Calotropis procera* responsible for the stabilization and formation of NP's. In this case FTIR analysis helped to find the bioactive compounds of plant by comparison of both spectrum of formed NPs and plant extract. In Fig. 3 spectrum of plant extract shows different peaks for hydrocarbons (2833cm^{-1} and 2940cm^{-1}forCH$_2$and CH$_3$group's vibrations), 1654 cm^{-1}, halogens (peak at 1020 cm-^{1} due to C-F stretching) and ethers (at 1113cm^{-1} due to C-O stretching).In Fig. 4spectrum of CuO NP's shows that peaks 1598 cm^{-1}, 1518cm^{-1} (vibrations of N-H group of amines) suggested the role of amines in the stabilization of CuO NP sand peak for ether is slightly moved in CuO NPs spectrum, while the peak at 1020.27 of plant extract spectrum is totally missing in CuO NP's spectrum.

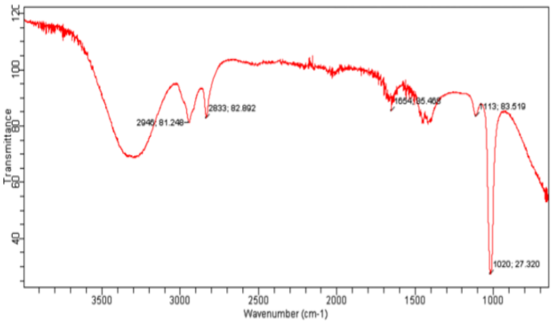


Fig.3. FTIR spectrum of Calotropisproceraleaves extract.

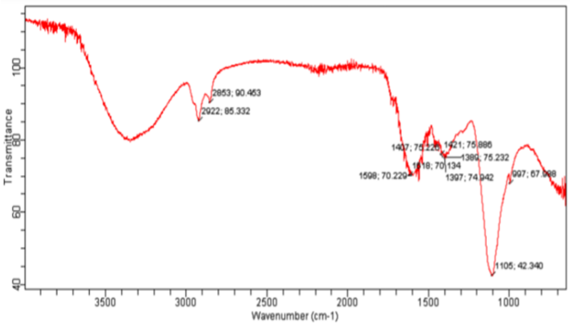


Fig.4. FTIR spectrum of CuO NPs

XRD analysis is employed to identify and quantitatively examine various crystalline forms of NPs. To accomplish this, the structure and lattice parameters of the diffracted powder specimen are analyzed by measuring the angle of diffraction. The average particle size is determined by using the Debye-Scherrer formula.

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{1}$$

Where, D = size of grain (nm), K = constant (0.98), λ = wavelength of X-rays (1.54 ^{o}A), β = full width at half maximum (FWHM) and θ = angle of diffraction. From calculation it is found that the average particle size of CuO NP's is 18-20 nm. Fig. 5 shows the XRD pattern of CuO NPs.

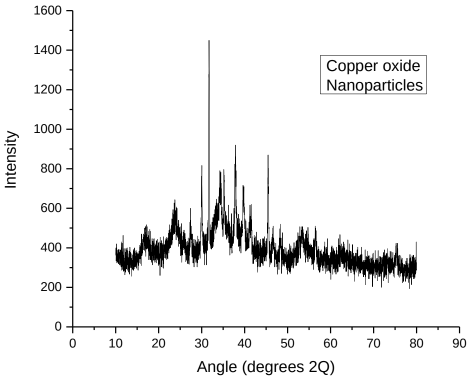


Fig.5: XRD pattern of CuO

The degradation of methylene blue follows 1st order kinetics equation (eq.2), which means that rate of reaction is only the function of initial concentration of dye present in solution. The rate of degradation is the slope of graph which is plotted between the ln of concentration of reactants versus time.

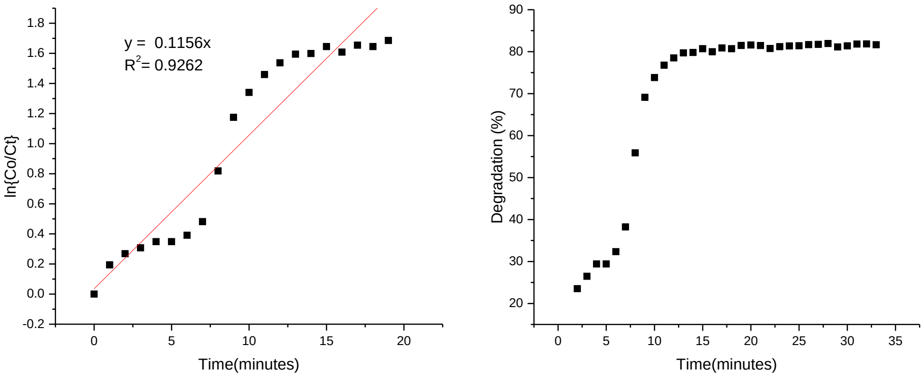
$$\ln(C_o / C_t) = k \times t \tag{2}$$

The percentage degradation can be calculated by using eq. 3.

$$\%\, degradation = \left(\frac{C_o - C_t}{C_t}\right) \times 100 \tag{3}$$

Where, C_o = initial concentration of dye (mg/L); C_t = concentration of dye after treatment (mg/L); k = rate constant (min^{-1}) and t = time (min).

Fig. 6(a) shows the plot between concentration of dye and time; from the slope of this graph the rate constant comes to be 0.115 per min (standard error: 0.001 and R^2: 0.9262), and Fig. 6(b) shows the plot between %degradation and time; it can be seen from the graph that maximum degradation occurred within 15 min and after that degradation process became slow. The maximum degradation efficiency obtained after 30 min was 81.85 %.



(a) (b)

Fig.6.(a) Degradation of methylene blue follows 1st order kinetics and (b) shows degradation efficiency rate of methylene blue dye with CuO NP's.

Fig. 7 shows that maximum absorbance of methylene blue is decreasing with time interval of 1 min which indicates that the dye is degrade with the passage of time.

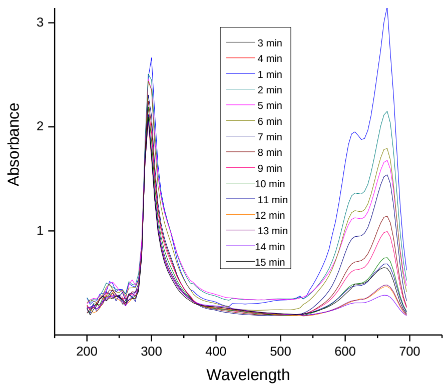


Fig.7: UV Vis-spectra for photo-catalytic dye degradation

3.2. Antimicrobial action

The antimicrobial action of CuO nanoparticles was compared with the standard drug Chloramphenicol. Results of biological tests revealed that synthesized CuO nanoparticles in case of Escherichia coli were found almost equal to Chloramphenicol. This proved that synthesized CuO nanoparticles have good ability as antimicrobial agents.

4. Conclusions

Copper oxide nanoparticles were synthesized from copper chloride in aqueous media by using leaves extract of *Calotropis Procera* as reducing agent as well as capping agent. This method provided environmental friendly, simple and efficient route for synthesis of benign nanoparticles. The optical, structural and catalytic properties of formed CuO nanoparticles were investigated. The reaction conditions including concentration of salt, pH of reaction medium, temperature of reaction system and time of heating of reaction medium were systematically optimized in order to get the best particle size and yield of nanoparticles. The best yield of nanoparticles was obtained in plant mediated fabrication at pH 12 using 20 mM salt, temperature and heating time of 50 ^{o}C and 45 minutes, respectively.

The optical and structural properties of CuO nanoparticles were investigated by employing various characterization techniques including UV/Visible spectroscopy, Fourier transform infrared spectroscopy and X-ray diffraction. The results of UV/Visible spectroscopy revealed that formed nanoparticles were monodisperse in nature and showed maximum absorption at 405 nm and 420 nm. The comparison of Fourier transform infrared spectrum of both plant and copper oxide nanoparticle revealed that amines and phenolic groups of plant were responsible for the formation and stabilization of CuO nanoparticles. The X-ray diffraction analysis showed that structure of CuO nanoparticles was [ ] while the average diameter was of 18-20 nm. Antimicrobial studies proved that synthesized CuO nanoparticles have excellent antibiotic activity against Escherichia coli.

The catalytic properties of CuO NP’s were studied by conducting their photocatalysis on methylene blue dye. The degradation of dye followed 1st order reaction kinetics and it can be seen from the graph that maximum degradation occurred within 15 min and after that degradation process became slow. From the slope of the graph between time and ln[Co/Ct] the rate constant comes to be 0.115 per min (standard error: 0.001 and R^2: 0.9262). The maximum degradation efficiency obtained after 30 min was 81.85 %.

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