Green Synthesis Of Copper Nanoparticles Using Betel Leaves: Synthesis And Characterization

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Abstract- *Bio-nanotechnology has emerged up as integration between biotechnology and nanotechnology for developing biosynthetic and greenmethods for synthesis of nanomaterials. In this study,copper nanoparticles (CuNPs) are synthesized by using betel leaves as reducing agent. Reduction of CuNPswas confirmed by UV-VIS analysis. The influenc of independent variables, i.e. temperature and reducing agent concentration on absorbance of solution and optimization of parameters was done using RSM as per central composite design (CCD). The nature of the chemical group deposited on the nanoparticles was studied using FT-IR. Particles size estimation was doneon TEM and nanoparticle size analyser. The crystalline nature of the nanoparticle formed was confirmed using XRD.The confirmation of the nanometal was performed usingEDX.*

Keywords- betel leave, central composite design, copper nanoparticles, XRD

I. INTRODUCTION

Nanotechnology is the new technologyconcerned with matter at the scale of 1 billionth of a meter (i.e., 10^{-9} m = 1 nm), and is also the study of manipulating matter at the atomic and molecular scale. A nanoparticle is the most fundamental component [1]. Metal nanoparticles (NPs) have unique characteristics because of their extraordinary chemical and physical characteristics which are at variance from their bulk counterparts [2]. Many routes are studied for the synthesis of transition metal nanoparticles [3].

Copper is the preferred material in the world due to its electrical, optical, catalytic, biomedical and antifungal, antibacterial applications. CuNPscan be used as antimicrobial agent in many fields. It is toxic to microorganism such as bacteria (E-Coli, Staphylococcus aureus, Pseudomonas aeruginosa) but non-toxic to animal cells.Due to this property it is considered to be an effective bactericidal [4]. In the modern electronic circuits copper (Cu) plays a major role as it is cost efficient [5]. CuNPspossess many useful properties as super strong materials, antibacterial, sensors and catalysts.It reacts and interacts with other particles due to their high surface-to-volume ratio [6]. CuNPs is an important semiconductor with a band gap of 2.1 eV, has been paid much attention in recent years because of its intrinsic properties and wide potential applications in many fields such as photochemical catalysis, biosensing, gas sensor, electrochemical sensing and solar/photovoltaic energy conversion [7-10].

The CuNPssynthesis has been carried out using various techniques, which include chemical reduction [11, 12], thermal decomposition [13, 14], the polyol method [15, 16], reverse micelles [17, 18], electron beam irradiation [19], micro-emulsion techniques [20], wire explosion [21] and in situ chemical synthesis [22]. Green synthesis is the most effective methods with respect to cost, eco-friendly, and no requirement ofhigh temperatures or pressures and does not involve toxic chemicals. Using the plant source for synthesizing nanoparticles is makes more sense than biological ways as it is always difficult to maintain the cell cultures. One of the green methods involves using plant extracts for their synthesis [23]. The source of the plant extract plays a major role in deciding the characteristics of the nanoparticles [24-25]. Because of different concentrations and combinations of organic reducing agents present in it [26]. A typical recipie consists of mixing the aqueous extract of the plant with relevant metal salt solution. Plant extracts are known to act both as reducing agents and stabilizing agents in the synthesis of nanoparticles [24-25].

In this work, we have made use of Response Surface Methodology (RSM) to investigate the effect of temperature and amount of betel leaveson the synthesis of CuNPsto provide a green route of nanoparticle synthesis. Synthesized nanoparticles were then characterized using different techniques.

II. MATERIALS AND METHODS

A. Materials

Copper chloridedihydrate$CuCl_2.2H_2O$ (Mol. Wt. 170.48 g)and acetic acid were of analytical grade procured from S. D. Fine-Chem Ltd (SDFCL, Mumbai, India).

B. Synthesis of CuNPs

Betel leaves were collected from the campus,washed with deionized water and cut into small pieces.0.01 M copper chloridesolutionof 100 ml was prepared in a conical flask using distilled water and the pH was adjustedto 3 with the help of acetic acid. Into this salt solution,betel leaveswere added with continuous stirring on a shaker bath machine (RossariLabtech, Mumbai, India) at 70 rpm for two hours. Experiments were carried out according to the Design of Experiment 7 by takingtemperature and amount of betel leaves as independent variables. Reduction of copper chloride into CuNPswas observed from the change in colour of the solution fromlight blueto yellowish brown. [27]Thesolution was filteredthrough nylonmesh aftercomplete reduction of the copper chloride. The residual solution containing the nanoparticles was centrifuged at 12,000 rpm for 15 minutes and washed with distilled water then dried at 80 °Cin oven.

C. Experimental Design

Parameters optimization was done using RSM as per central composite design (CCD) to study the effect of independent variables, i.e. temperature and concentration of reducing agent on absorbance of solution after each experimental run as a response which is showed in Table 1.

D. Characterization

UV-Visible spectrophotometer (UV-1800 ENG 240 V, Shimadzu, Japan) was used for the analysis of synthesized CuNPsas a function of time in the visible region. The particle size was determined using nano particle size analyser (SALD 7500 nano, Shimadzu, Japan). Surface morphology was studied with transmission electron microscopy (Phillips TEM-200 Supertwin STEM, accelerating voltage-200kV, resolution-0.23 nm). Crystallographic study of nanoparticles was carried out using X-ray diffractometer (Shimadzu XRD-6100, Japan) with CuKα radiation from 40kV/30mA using the 2θ range of 10–80º. Chemical functional group identification on CuNPswas determined using FTIR (FTIR 8400S Shimadzu, Japan) with the spectral range of 750-4000 cm^{-1} and elemental analysis was done in the Na-U channel using EDAX (EDX-720, Shimadzu, Japan).

III. RESULTS AND DISCUSSION

A. Optimization analysis

Experimental runs were conducted as per Table 1 and the values of each response was measuredas solution absorbanceat maximum wavelength of CuNPs.

Table 1: CCD experimental run of trials for the synthesis of CuNPs

No	Temp. (°C) [A]	Conc. of Reducing agent (g/100ml) [B]	Absorbance at 537nm	
			Experimental	Predicted
1	75	5	0.0718	0.083148
2	100	7.5	0.1567	0.153927
3	50	2.5	0.0127	0.019894
4	50	5	0.0648	0.050846
5	75	5	0.0974	0.083148
6	75	2.5	0.0539	0.049046
7	75	7.5	0.1122	0.108213
8	75	5	0.0807	0.083148
9	75	5	0.0755	0.083148
10	75	5	0.0815	0.083148
11	100	5	0.1206	0.125713
12	100	2.5	0.0908	0.08846
13	50	7.5	0.066	0.07276

Table 2 represents the ANOVA results. The P-values indicates the significance of each coefficient andtheinteractionstrengthofeachparameter.Inthepresent study, the F-value (25.07574) and P-values (p = 0.0002) indicated statistical significance of the model. It can be seen from the degree of significance that the quadratic effects of temperature and concentration of reducing agent are significant; meaning that they can act as limiting factors and little variation in their value will alter the reaction rate. It can be suggested from the value of adjusted-R^2 = 0.9471that total variation of 94.71% of absorbance due to the independent variables while only 5.29% cannot be explained by the model.[28]

Table 2: Analysis of Variance (ANOVA) for optimization of synthesis of CuNPsusing betel leaf

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob >F
Model	0.013792	5	0.002758	25.07574	0.0002
Pure error	0.000383	4	0.000096		
R^2	0.9471				
Adj. R^2	90.94%				

By applying the multiple regression analysis on experimental data, the second-order polynomial equation (Equation 1) that defines predicted response (Absorbance) in terms of the independent parameters was obtained.

$$\text{Absorbance} = -0.041315 + 0.0000139A + 0.015284B + 0.0000504AB + 0.0000083A^2 - 0.000723B^2 \quad \ldots\ldots\ldots(1)$$

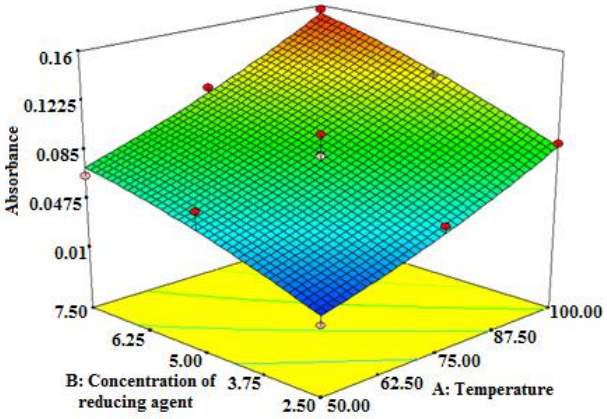


Figure 1: Response surface plot of Absorbance Vs Temperature and concentration of reducing agent

As the temperature and concentration of reducing agent is increased, absorbance of the synthesized NPsalsoincreased (figure 1) indicating increase in concentration of CuNPs. According to the RSM, the maximum value of absorbance could be achieved when the temperature and concentration of reducing agent were set at 65.32^{0}C and 4 g/100mL respectively. The maximum predicted value of absorbance was 0.0574. To confirm the optimization an experiment was conducted using the suggested conditions which gave the value of absorbance as0.0562, which was in good agreement with the predicted value.

B. Characterization

a. UV -Visible spectral analysis

The UV-vis spectra of synthesized CuNPsrecorded at optimized condition after time intervals of 15, 30, 45, 60 and 120 minutes from the start of the reaction are shown in figure 2. The absorbance peak in the region of 450-650 nm indicates the presence ofCuNPs due to the surface Plasmon resonance phenomenon. [29-30]

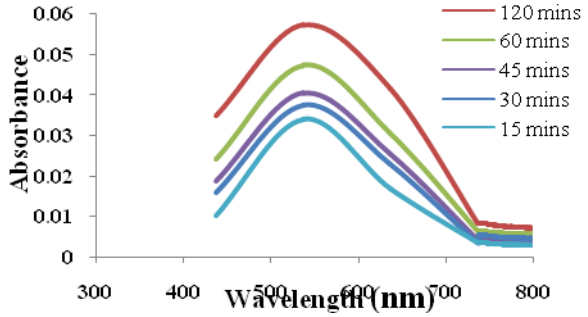


Figure 2: UV-Vis absorption spectrum of CuNPssolutions as a function of time

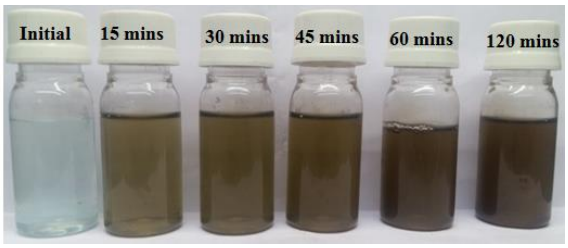
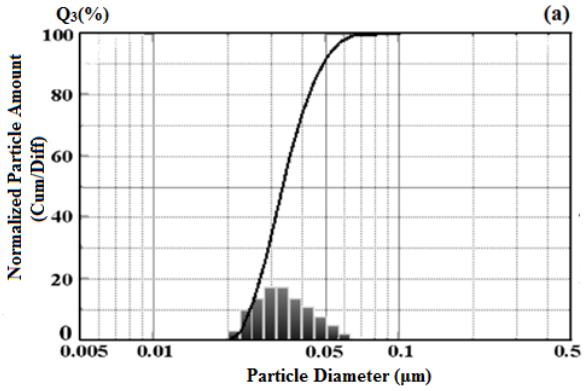


Figure 3: Images of CuNPs solutions taken out at different time intervals

Figure 3 shows, the reduction of copper chloride into CuNPs which was observed by change in colour of solution from light blue to yellowish brown with increasing reaction time. [27]

b. Particle size analysis

Figure 4-ashows particles size analysis of synthesized CuNPs. The size of the nano particle was 33 nm as determined using particle size analyser.Figure 4-b shows the TEM image of the CuNPs which were in the range of 20 nm to 50 nm with an average diameter of 32 nm.



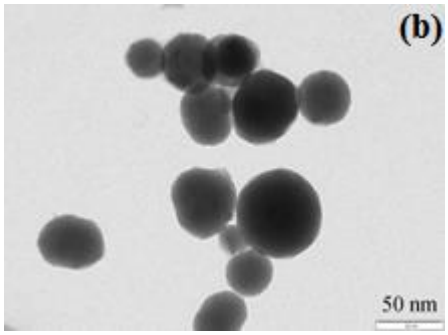


Figure 4: a) Particle size and b) TEM image of CuNPs

To prove that the synthesized particles were nanoCuO and Cu phases, XRD was performed and are shown in figure 5. The diffraction peaks at 43.8481° and 77.3144°, which can be assigned to (111) and (220) planes of Cu (JCPDS no. 71-4610) and peaks at 38.2933° and 64.2132° corresponding to (200) and (220) planes of CuO (JCPDS no. 48-1548). It showed crystallinity of 20.9520% which is also evident from the (111) plane using Scherrer's equation. [31]

Particle size calculation

The average particle size of the CuNPs was calculated using Debey–Scherrer's formula (equation 2).

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad \ldots. (2)$$

Where λ is X-ray wavelength (0.15406 nm), β is full width at half maximum (FWHM) of the diffraction peak in radians, Θ is Bragg's diffraction angle respectively. The particle size obtained was 14.51 nm. [32]

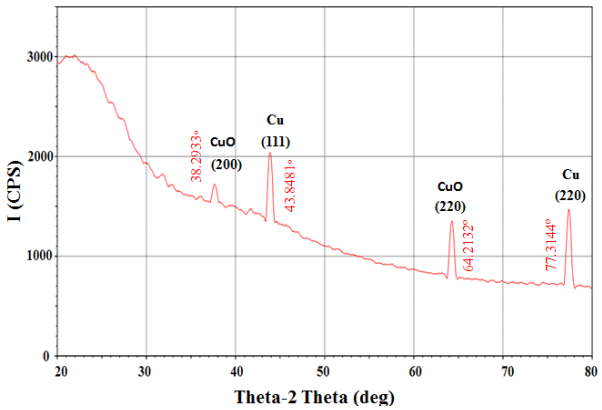


Figure5: XRD pattern of CuNPs

The calculated particle size by the XRD, TEM and Dynamic Light Scattering technique are listed in table 3. The reason for getting somewhat bigger particle size by TEM and Dynamic Light Scattering technique was could be because of agglomeration of nanoparticles.

Table 3: Particle size of CuNPsobtained by different methods

Crystallite size in nm		
Debey-Scherrer formula	Dynamic Light Scattering technique	TEM
14.51	33	32

C. Energy dispersive X-Ray analysis

The optical absorption band peak observed in EDX spectroscopy (figure 6) was in the range of 8 to 9 keV is typical for the absorption of metallic copper nanocrystallites. [33]

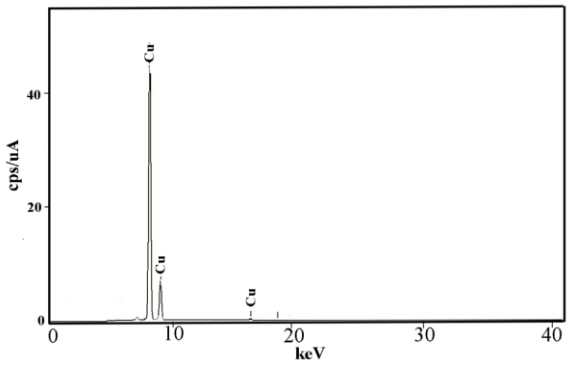


Figure 6:EDX pattern of the synthesized CuNPs

D. FTIR analysis

FTIR analysis of the CuNPwas done (Figure 7) which showed broad band around 3200cm^{-1}which are characteristics of the hydrogen bonded phenols and alcohols. The peak at 2800cm^{-1} can be attributed to the O-H stretching of carboxylic acids. The multiple bands observed around 1610.45 cm^{-1} are assigned to N-H bending as well as C=O stretching vibration of amino acids. The bands in the region 1066.56-1280.65 cm^{-1} were due to the stretching vibrations of various C–O and C–N present in the Betel leaf extract. Thus it is clear that the presence of flavones and polysaccharides in the leaf extract and the shifting of the respective bands confirms the binding of copper with the functional groups or its capping to provide further stability.[34]

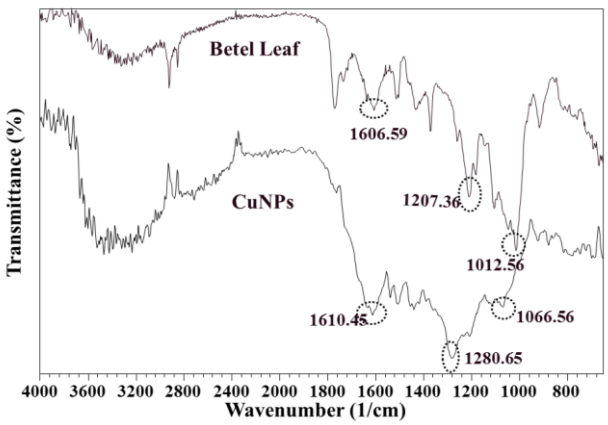


Figure7: FTIR spectrum of betel leaf and CuNPs

IV. CONCLUSION

CuNPswere successfully synthesized by using betel leaves as a reducing agent. The protein present in betel leaves was responsible for reduction of copper chloride which is also present on the surface of nanoparticle provided stability to it.The formation of nanoparticles changed colour of the solution from colourless to yellowish brown giving absorbance peak in the range of 450-650 nmin UV-visible spectroscopy. For maximum absorbance (0.0573) the optimized conditions were 65.32˚C temperature and 4 gm/100mL concentration of reducing agent as per CCD. The CuNPsformed were of predominantly spherical in shape and crystalline in nature with crystallinity of 20.9520 %. The average particle size obtained was well below 35 nm.

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REFERENCE

[1] Saliby, I.J. El, H.K. Shon, J. Kandasamy, S. Vigneswaran, water and wastewater treatment technologies-Vol-III-*Nanotechnology for Wastewater Treatment: In Brief.* Eolss Publishers Co. Ltd., (2009), UK. ISBN no. 1848262507.

[2] M. Daniels, D. Astruc, *Chem. Rev*. (2004),**104,** 293.

[3] B.L. Cushing, V.L. Kolesnichenko, C.J. O'Connor, *Chem. Rev.*(2004), **104,**3893.

[4] Abboud, Y., Saffaj, T., Chagraoui, A., Bouari, A., Brouzi, K., Tanane, O., Ihssane, B.,*Applied Nanoscience*(2013), **190**-5517.

[5] A.K. Schapter, H. Hu, A. Grenier, R. Schneider, F. Philips, *Appl. Phys. A Mater. Sci. Process.* (2004), **78,** 73.

[6] R. Narayanan, ElM.A. El-Sayed, *J. Am. Chem. Soc.* (2003), **125,** 8340.

[7] P. Zijlstra, M. Orrit, *Reports on Progress in Physics*(2011), **74,** 106401.

[8] A. Kamyshny, J. Steinke, S. Magdassi, *Open Applied Physics J.*(2011), **4**, 19.

[9] R. Gréget, G.L. Nealon, B. Vileno, P. Turek, C. Mény, F. Ott, A. Derory, E. Voirin, E. Rivière, A. Rogalev, *ChemPhysChem*(2012), **13,** 3092.

[10] R.R. Letfullin, C.B. Iversen, T.F. George, *Nanomedicine: Nanotech., Bio. and Med.*(2011), **7,** 137.

[11] G. Doria, J. Conde, B. Veigas, L. Giestas, C. Almeida, M. Assunção, J. Rosa, P.V. Baptista, *Sensors* (2012), **12,** 1657.

[12] P. Khanna, S. Gaikwad, P. Adhyapak, N. Singh, R. Marimuthu, *Materials Letters*(2007),**61**, 4711.

[13] H. Hashemipour, M.E. Zadeh, R. Pourakbari, P. Rahimi, *Inter. J. of Physical Sciences*(2011), **6,** 4331.

[14] M. Salavati-Niasari, F. Davar, *Materials Letters* (2009), **63,** 441.

[15] Y.H. Kim, D.K. Lee, B.G. Jo, J.H. Jeong, Y.S. Kang, *Colloids and Surfaces A: Physicochemical and Eng. Aspects*(2006), **284,** 364.

[16] K. Woo, D. Kim, J.S. Kim, S. Lim, *J. Moon, Langmuir*(2008), **25**, 429.

[17] B.K. Park, D. Kim, S. Jeong, J. Moon, J.S. Kim, *Thin Solid Films*(2007), **515,** 7706.

[18] M. Pileni, I. Lisiecki, *Colloids and Surfaces A: Physicochem. and Eng. Aspects*(1993), **80,** 63.

[19] E. Egorova, A. Revina, *Colloids and Surfaces A: Physicochem. and Eng. Aspects*(2000),**168**, 87.

[20] R. Zhou, X. Wu, X. Hao, F. Zhou, H. Li, W. Rao, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* (2008), **266,** 599.

[21] J.N. Solanki, R. Sengupta, Z. Murthy, *Solid State Sciences*(2010), **12**, 1560.

[22] P. Dash, *Research J. of Nanoscience and Nanotech.*(2010), **1,** 25.

[23] Mohammad Mansoob Khan, ShafeerKalathil, Jintae Lee, Moo Hwan Cho, Bull.*Korean Chem. Soc.* (2012), **33**, 2592.

[24] Kumar V, Yadav SK.,*J ChemTechnolBiotechnol* (2009), **84**, 151–157.

[25] Kumar V, Yadav SC, Yadav SK.,*J ChemTechnolBiotechnol* (2010), **85**, 1301–1309.

[26] Mukunthan K, Balaji S.,*Int J Green Nanotechnol* (2012), **4**, 71–79.

[27] Shikha Jain, Niharika Nagar and Vijay Devra, *Advances in Applied Science Research* (2015), **6**(6), 171-180.

[28] HamedBarabadi, SoheilaHonary, PounehEbrahimi, Milad Ali Mohammadi, AhadAlizadeh, FarzanehNaghibi, *Brazilian Journal of Microbiology* (2014), 45(4), 1493-1501.

[29] Priya Banerjee, MantoshSatapathy, AniruddhaMukhopahayay and Papita Das, *Bioresources and Bioprocessing*(2014), 1-3.

[30] E. Alzahrani, R. A. Ahmed,*Int. J. Electrochem. Sci. (*2016*)*,**11**,4712 – 4723.

[31] K. Cheirmadurai, Soma Biswas, R. Murali and P. Thanikaivelan, *The Royal Society of Chemistry* (2014), **4,** 19507–19511.

[32] Y.T. Prabhu , K. Venkateswara Rao , V. SeshaSai, TamburPavani, *Journal of Saudi Chemical Society*(2017), **21** (2), 180-185.

[33] Mustafa Biçer, İlkayŞişman, *powder Technology*(2010),**198,** 279–284.

[34] Huimei Chen , JingWang , DengpoHuang, XiaoerChen, JiajiaZhu, DaohuaSun , Jiale Huang, Qingbiao Li, *Materials Letters* (2014), **122,** 166–169.