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Green Synthesis and Structural Characterisation of CuO Nanoparticles Prepared by Using Fig Leaves Extract

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Abstract. In this study, copper oxide nanoparticles (CuO) were prepared by a simple method from the corresponding salt using Fig (*Ficus carica*) leaves extracts. The particles were characterised using XRD, SEM, TEM, and AFM techniques. XRD spectra revealed that the particle size obtained was around (7.31 nm), which agreed fairly well with those estimated from SEM and TEM. Surface morphology of the nanoparticles was studied by SEM, TEM and AFM.

Keywords: copper oxide, nanoparticles, fig leaves, characterisation, green synthesis

Introduction

Metal oxide nanoparticles is a highly valuable material with various applications in optical, electrical and mechanical devices, catalysts, gas sensors, sunscreens and cosmetics (Rajendran and Sengodan, 2017). Several chemical and physical methods have been used for their synthesis such as sol-gel, precipitation, sonochemical, electro thermal synthesis, vapour deposition, electro-chemical methods, combustion, colloid-thermal synthesis process and microwave irradiation and pulsed wire explosion methods (Hariprasad *et al*., 2016; Ahamed *et al*., 2014). Most of these methods are complicated and have drawbacks like use of hazardous organic solvents, expensive reagent, toxic by-products, drastic reaction condition, difficult to isolate nanoparticles and longer time required etc. (Devi and Singh, 2014), therefore there is an essential need to develop environment friendly methods for synthesis of metal oxides nanoparticles (Geraldes *et al*., 2016).

Nowadays, varieties of nanoparticles with well-defined chemical composition, size and morphology have been synthesised by different methods and their applications in many innovative technological areas have been explored (Yu *et al*., 2016; Khademi-Azandehi and Moghaddam, 2015). The renewable nature of plant extracts, eco-friendly aqueous medium and mild reaction conditions make the method advantageous over other hazardous methods (Saif *et al*., 2016). In the last years, different kinds of plant extracts and their products have received attention due to their low cost, energy-efficient and nontoxic behaviour in approach for synthesis of metal nanoparticles (Prasad *et al*., 2017). Green synthesis of nanoparticles using plant extracts is an emerging area of research and is potentially advantageous over chemical or microbial synthesis as it eliminates the elaborate process and can also meet large-scale production with green synthesis being low cost (Nagajyothi *et al*., 2017) where the role of the extract is reduction and conversion of the salts to its corresponding oxide nanoparticles. Regarding biological synthesis different nanoparticles have been prepared using plants such as neem, alfalfa, lemon grass, tamarind bark extract, leaf extract, fruit, tea and coffee powder, peel extract and flower extract ect. (Awwad *et al*., 2015). In addition to biological synthesis methods of nanoparticles reported using *Escherichia coli* (Ajay *et al*., 2010) and *Pseudomonas fluorescens* (Shantkriti and Rani, 2014) and by *Ixora coccinea* leaf extract (Yedurkar *et al*., 2017).

Copper oxide is an important metal oxide which has attracted recent researchers because of its low cost, abundant availability as well as its particular properties (Nithya *et al*., 2014). It is a semiconductor material and gains considerable attention due to its excellent optical, electrical, physical, and magnetic properties. Its crystal structures possess a narrowband gap, giving useful photocatalytic and photovoltaic properties (Ijaz *et al*., 2017). Different nano-structures of CuO are synthesised in form of nano-wire, nano-rod, nano-needle, nano-flower and nano-particle (Phiwdang *et al*., 2013).

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Nanoparticles application for removal of pollutants has come up an interesting area of research. The unique properties of nanosorbents are providing unprecedented opportunities for the removal of metals in highly efficient and cost-effective approaches (Hassan and Mahdi, 2017).

The aim of the present work is to synthesise CuO nanoparticles using environmentally friendly green method from copper salt and fig (*Ficus carica*) leaves extract and characterise their structure.

Materials and Methods

Material. Analytical grade materials were used without any further purification in addition to deionised water, fig leaves, copper (II) chloride dihydrate ($CuCl_2.2H_2O$), sodium hydroxide (NaOH) and absolute ethanol (C_2H_2OH).

Preparation of fig leaves extract. Fig leaves were collected from a tree in a house garden, cleaned from the suspended dirt and washed with distilled water several times and dried in shade. They were then ground with an electric grinder and stored away from wet, (5 g) of this powder was added to (400 mL) of deionised water and boiled for (30 min) until the colour of solution change to brown–yellow. The obtained solution cooled to room temperature and filtered, centrifuged the filtrate at 1200 rpm for 2 min to remove biomaterials and stored the extract at room temperature until use.

CuO nanoparticles preparation. Copper chloride dihydrate ($CuCl_2.2H_2O$) (0.27 g) was dissolved in (400 mL) of deionised water with continuous stirring and then (10 mL) of fig leaves extract was added gradually with continuous stirring also at room temperature where the colour changed from light blue to light green, adjusted the pH of the mixture by adding sodium hydroxide (1 M) where precipitate with a brown- dark colour was formed, It was then filtered and washed with deionised water several times and with ethanol absolute to remove impurities and finally dried in an oven at (60 °C) for 2 h. The steps are shown in Fig. 1 as flow diagram showing the steps for preparing copper oxide nanoparticles using fig leaves extract.

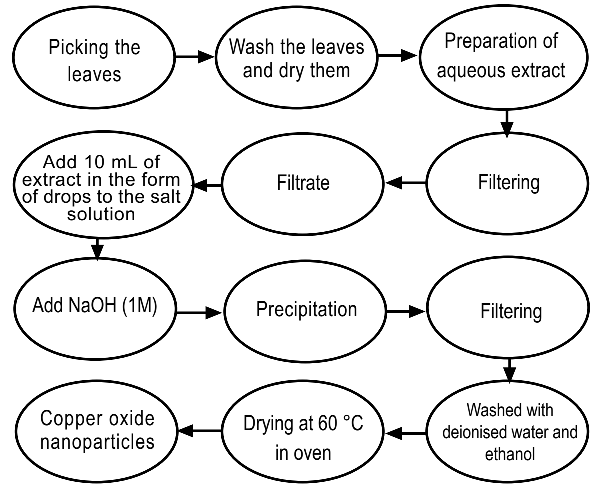

Fig. 1. Flow diagram showing the steps for preparing copper oxide nanoparticles using fig leaves extract.

Characterisation of copper oxide nanoparticles. The X-ray diffraction pattern of the prepared oxide were recorded using XRD-6000 with Cukα (λ=1.5406A°) that have an accelerating voltage of 220/50 Hz which is produced by SHIMADZU Company. The scanning electron microscope (SEM) used in imaging the nanoparticles was a scanning electron microscope AIS2300C. Atomic force microscopy (AFM) used to study surface morphology of the samples was AFM model AA 3000 SPM 220 V- angstrom Advanced INC, USA, and finally transmission electron microscope (TEM) images were recorded using a JEOL 2100 Plus instrument operated at 200kV.

Results and Discussion

Preparation of copper oxide nanoparticles. The fig leaves extract acts as a reducing agent (Rajendran and Sengodan, 2017) by containing a high amount of polyphenols and other organic groups which take part in reaction mechanism involving reduction of precursor to metal nano-particle in two steps (Gottimukkala, 2017); first precursor forms a complex by breaking the OH bond and forming a partial bond with a metal ion. Secondly, there is breakage of the partial bond and the transfer of electrons to form the metal hydroxide which is then reacted with OH^{-1} of sodium hydroxide to copper oxide nanoparticles and liberated H_2O and thus itself get oxidised to ortho-quinone.

X-ray diffraction analysis. The XRD technique was used to determine and confirm the crystal structure of the prepared nanoparticles. XRD pattern of prepared copper (II) oxide nanoparticles is shown in Fig. 2 with the data of strongest three peaks shown in Table 1. The peak positions exhibited the monoclinic structure and single phase of CuO nanoparticles and are in a good agreement with those reported in JCPDS file (NO. 48-1548), no other impurity peak was observed in the XRD patterns. The broadening of the diffraction peaks indicates that the crystal size is small.

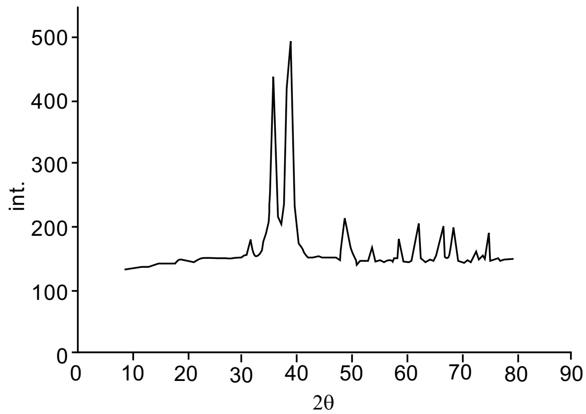

Fig. 2. XRD pattern of prepared copper oxides nanoparticles.

Table 1. The peaks in XRD spectrum of prepared CuO nanoparticles

No.	2θ (deg.)	d (Å)	FWHM (deg.)	Intensity (counts)
1	34.2786	2.6138	0.5600	20
2	35.5665	2.5221	1.1283	186
3	38.6473	2.6473	1.2450	214
4	48.7888	1.8650	1.1283	47
5	53.4417	1.7131	0.8100	19
6	57.6651	1.5973	0.9200	21
7	61.6338	1.5036	1.1000	16
8	67.9818	1.3778	1.0600	30
9	68.8016	1.3634	0.2400	9
10	75.0099	1.2652	0.7000	15

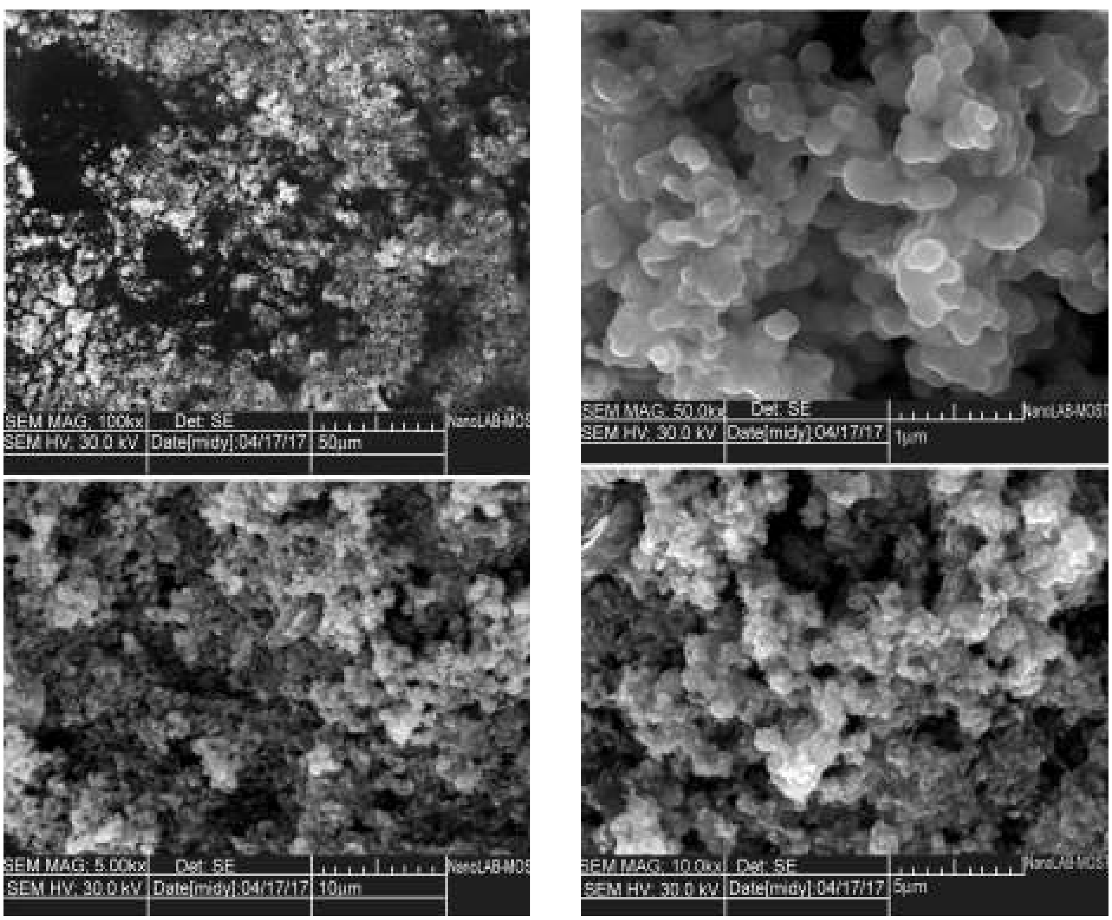

Fig. 3. SEM image of prepared copper oxide nanoparticles.

Particle size calculation of copper oxide nanoparticles. The particle sizes were calculated from formula given by Ghidan *et al*. (2016):

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad \text{..} \; 1$$

where:

D = the crystallite size, λ = the wave length of radiation, θ = the Bragg's angle, β = the full width at half maximum (FWHM).

The calculated particle size is (7.31 nm) which represents the smallest particle size; the presence of sharp peaks in XRD and particle size being less than 100 nm refers to the nano-crystalline nature.

Scanning electron microscope. The surface morphology of the prepared copper oxide nanoparticles (CuO) were revealed through the SEM image shown in Fig. 3. It shows a homogeneous distribution of spheroidal nanoparticles with irregular distribution. From the SEM images it is confirmed that the particles having size in

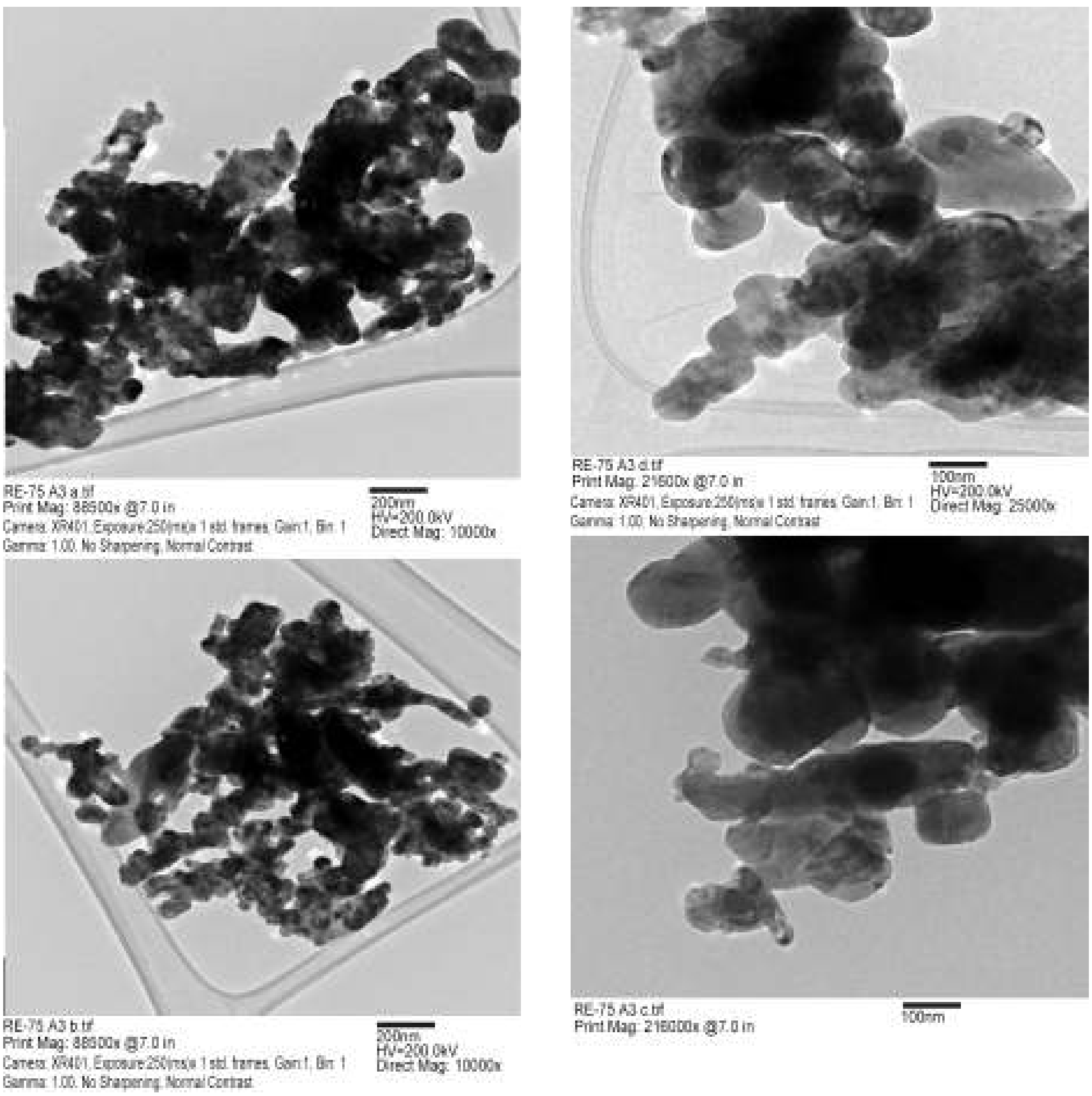

Fig. 4. Transmission Electron Microscope (TEM) images of prepared copper oxide nanoparticles.

between 34.57 nanometers as calculated by Image-J programme which again confirmed the nanostructure nature of the oxide (Maruthupandy *et al*., 2017).

Transmission electron microscope. TEM (Transmission Electron Microscope) of copper oxide nano-particles are shown in Fig. 4. The estimated particle size is found to be 7.5 nm for the smallest and 35 nm for the largest one which is similar to those calculated from XRD and calculated from SEM (Naika *et al*., 2015; Kumar *et al*., 2015).

Atomic force microscope. The surface morphology average grain size of prepared copper oxide nanoparticles was studied utilizing atomic force microscope (Hassan and Mahdi, 2016). Figure 5 is typical AFM image of the CuO nanoparticles, it shows images measured with size = 2032 × 2027 nm, and ability analytical pixel = 392, 39. Figure 5a is AFM image in three dimensions (3D), it explains structure shape for grain and Fig. 5b is AFM image in two dimensions (2D), it is found that average roughness is (0.311 nm). The root mean square (RMS) is (0.3581 nm), and average diameter being (71.28) nm. Table 2 and Fig. 6 show the granularity cumulating distribution and average diameter data.

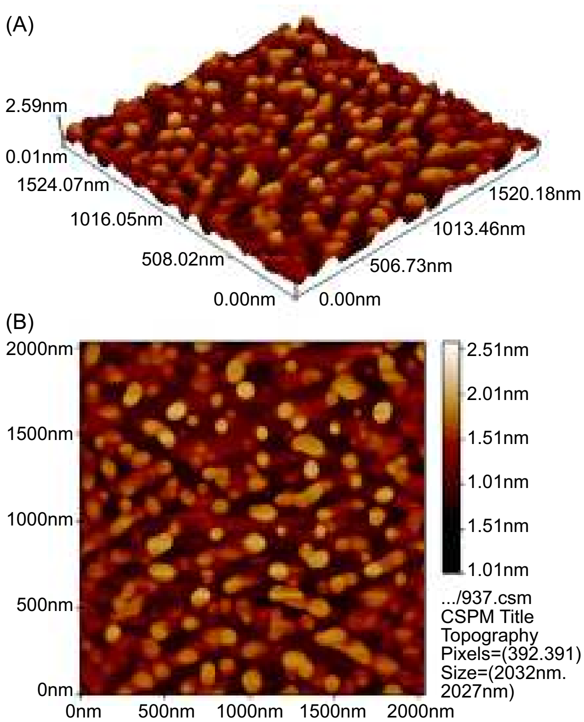

Fig. 5. AFM images of prepared copper oxide nanoparticles.

Table. 2. Granularity cumulating distribution and average diameter of prepared copper oxide nanoparticles

Avg.Diameter :71.28 nm		
Diameter (nm)<	Volume (%)	Cumulation (%)
15.00	0.47	0.47
20.00	0.93	1.40
25.00	1.63	3.03
30.00	4.43	7.46
35.00	2.80	10.26
40.00	3.26	13.52
45.00	5.13	18.65
50.00	5.13	23.78
55.00	8.62	32.40
60.00	6.76	39.16
65.00	8.39	47.55
70.00	6.53	54.08
75.00	6.76	60.84
80.00	5.83	66.67
85.00	4.20	70.86
90.00	4.43	75.29
95.00	4.20	79.49
100.00	3.26	82.75
105.00	2.80	85.55
110.00	3.03	88.58
115.00	1.40	89.98
120.00	1.86	91.84
125.00	2.56	94.41
130.00	1.17	95.57
135.00	1.63	97.20
140.00	0.23	97.44
145.00	0.70	98.14
150.00	0.93	99.07
155.00	0.70	99.77
160.00	0.23	100.00

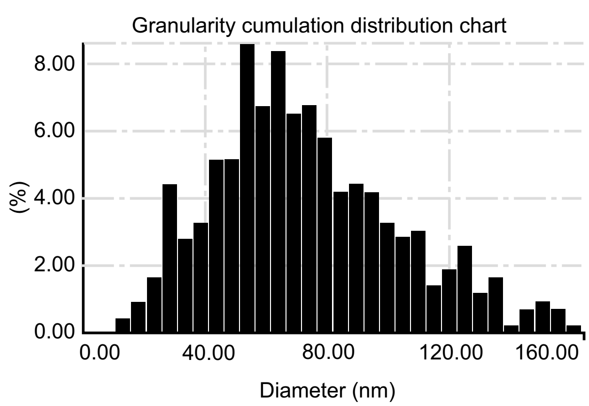

Fig. 6. Granularity cumulating distribution of prepared copper oxide nanoparticles.

Conclusion

In this study copper oxide nanoparticles were prepared well by using fig leaf extract method. X-ray diffraction results explain that the calculated particle size is (7.31) nm. The SEM results indicated that the average particle size of CuO nanoparticles was found to be (34.57) nm while those calculated from TEM seems to be (7.5-35) nm. From AFM the average particle size observed in the nano scale (71.28) nm, so SEM, TEM and AFM analysis of the CuO showed that the diameters of the particles are in a nanometer range.

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References

Ahamed, M., Alhadlaq, H.A., Khan, M.A.M., Karuppiah, P., Al-Dhabi, N.A. 2014. Synthesis, characterization, and antimicrobial activity of copper oxide nanoparticles. *Journal of Nanomaterials*, **2014:** 1-4.

Ajay, V.S., Patil, R., Anand, A., Milani, P., Gade, W.N. 2010. Biological synthesis of copper oxide nanoparticles using Escherichia coli. *Current Nanoscience*, **6:** 365-369.

Awwad, A.M., Albiss, B.A., Salem, N.M. 2015. Antibacterial activity of synthesized copper oxide nanoparticles using *Malva sylvestris* leaf extract. *SMU Medical Journal*, **2:** 91-101.

Devi, H.S., Singh, T.D. 2014. Synthesis of copper oxide nanoparticles by a novel method and its application in the degradation of methyl orange. *Advances in Electronic and Electrical Engineering*, **4:** 83-88.

Geraldes, A.N., Alves, A., Leal, J., Estrada-Villegas, G.M., Lincopan, N., Katti, K.V. 2016. Green nanotechnology from plant extracts: synthesis and characterization of gold nanoparticles. *Advances in Nanoparticles*, **5:** 176-185.

Ghidan, A.Y., Al-Antary, T.M., Awwad, A.M. 2016. Green synthesis of copper oxide nano-particles using *Punica granatum* peels extract: effect on green peach aphid. *Environmental Nanotechnology, Monitoring & Management*, **6:** 95-98.

Gottimukkala, K.S.V. 2017. Green synthesis of iron nanoparticles using green tea leaves extract. *Journal of Nanomedicine & Biotherapeutic Discovery*, **7:** 1-7.

Hariprasad, S., Bai, G.S., Santhoshkumar, J., Madhu, C.H., Sravani, D. 2016. Green synthesis of copper nanoparticles by Arevalanata leaves extract and their anti-microbial activites. *International Journal of Chem-Tech Research*, **9:** 98-105.

Hassan, K.H., Mahdi, E.R. 2017. Preparation and characterization of copper oxide nanoparticles used to remove nickel ions from aqueous solution. *Diyala Journal for Pure Sciences*, **13:** 217-234.

Hassan, K.H., Mahdi, E.R. 2016. Synthesis and characterization of copper, iron oxide nanoparticles used to remove lead from aquous solution. *Asian Journal of Applied Sciences*, **4:** 730-738.

Ijaz, F., Shahid, S., Khan, S.A., Ahmad, W., Zaman, S. 2017. Green synthesis of copper oxide nanoparticles using *Abutilon indicum* leaf extract: Antimicrobial, antioxidant and photocatalytic dye degradation activities. *Tropical Journal of Pharmaceutical Research*, **16:** 743-753.

Khademi-Azandehi, P., Moghaddam, J. 2015. Green synthesis, characterization and physiological stability of gold nanoparticles from *Stachys lavandulifolia* Vahl extract. *Particuology*, **19:** 22-26.

Kumar, P.V., Shamee, U., Kollu, P., Kalyani, R.L., Pammi, S.V.N. 2015. Green synthesis of copper oxide nanoparticles using *Aloe vera* leaf extract and its antibacterial activity against fish bacterial pathogens. *BioNanoScience*, **5:** 135-139.

Maruthupandy, M., Zuo, Y., Chen, J.S., Song, J.M., Niu, H.L., Mao, C.J., Zhang, S.Y., Shen, Y.H. 2017. Synthesis of metal oxide nanoparticles (CuO and ZnO NPs) via biological template and their optical sensor applications. *Applied Surface Science*, **397:** 167-174.

Nagajyothi, P.C., Muthuraman, P., Sreekanth, T.V.M., Kim, D.H., Shim, J. 2017. Green synthesis: *In-vitro* anticancer activity of copper oxide nanoparticles against human cervical carcinoma cells. *Arabian Journal of Chemistry*, **10:** 215-225.

Naika, H.R., Lingaraju, K., Manjunath, K., Kumar, D., Nagaraju, G., Suresh, D., Nagabhushana, H. 2015. Green synthesis of CuO nano-particles using *Gloriosa superba* L. extract and their antibacterial activity. *Journal of Taibah University for Science*, **9:** 7-12.

Nithya, K., Yuvasree, P., Neelakandeswari, N., Rajasekaran, N., Uthayarani, K., Chitra, M., Kumar, S.S. 2014. Preparation and characterization of copper oxide nanoparticles. *International Journal of Chem Tech*

Research, **6:** 2220-2222.

Phiwdang, K., Suphankij, S., Mekprasart, W., Pecharapa, W. 2013. Synthesis of CuO nanoparticles by precipitation method using different precursors. *Energy Procedia*, **3:** 740-745.

Prasad, K.S., Patra, A., Shruthi, G., Chandan, S. 2017. Aqueous extract of *Saraca indica* leaves in the synthesis of copper oxide nanoparticles: finding a way towards going green. *Journal of Nanotechnology*, **2017:** 1-6.

Rajendran, S.P., Sengodan, K. 2017. Synthesis and characterization of zinc oxide and iron oxide nanoparticles using *Sesbania grandiflora* leaf extract as reducing agent. *Journal of Nanoscience 2017*, pp. 1-7.

Saif, S., Tahir, A., Asim, T., Chen, Y. 2016. Plant mediated green synthesis of CuO nanoparticles: comparison of toxicity of engineered and plant mediated CuO nanoparticles towards *Daphnia magna*. *Nanomaterials*, **6:** 1-15.

Shantkriti, S., Rani, P. 2014. Biological synthesis of copper nanoparticles using *Pesudomonas fluorescens*. *International Journal of Current Microbiology and Applied Sciences*, **3:** 374-383.

Yedurkar, S.M., Maurya, C.B., Mahanwar, P.A. 2017. A biological approach for the synthesis of copper oxide nanoparticles by *Ixora coccinea* leaf extract. *Journal of Materials and Environmental Sciences*, **8:** 1173-1178.

Yu, J., Xu, D., Guan, H.N., Wang, C., Huang, L.K. 2016. Facile one-step green synthesis of gold nanoparticles using *Citrus maxima* aqueous extracts and its catalytic activity. *Materials Letters*, **166:** 110-112.