GREEN SYNTHESIS OF COPPER OXIDE NANO PARTICLES FROM ALOE VERA EXTRACT AND ITS CATALYTIC APPLICATIONS IN OXIDATION OF 3-INDOLE DERIVATIVES: A KINETIC STUDY

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Abstract

In the present work green synthesis of copper oxide nano particles was carried out in the presence of aloe vera plant extract in aqueous medium at 45°C. Copper oxide nanoparticles in the as-synthesised conditions were size characterised by PXRD,HR-TEM and FE-SEM and was found to fall in the range 15± 2.0 nm and such values coincided with reported values. The nano particles executed high stability and narrow polydispersity. The catalytic activity in the oxidation reactions of organic substrates was verified utilising 3-Indole derivatives.It was shown by many researchers that various indole derivatives have considerable anti-inflammatory, anti-microbial and anti-tumor activities which find potential therapeutic applications especially in the treatment of lung cancer. 3- indole carboxylic acid (ICA) and 3-(hydroxy acetyl) indole (IHA) were used as successful chemotherapeutic agents. However the results towards the shelf life ,longevity and in vitro activity stand needful. In this work oxidation reactions of 3-indole carboxylic acid (ICA) and 3-(hydroxylacetyl) (IHA) in presence of sodium peroxomono sulfate ($Na_2S_2O_5$) as oxidant and CuO nps as the catalyst have been carried out at 25 ^{0} C. Using the time variance UV absorption spectra recorded for each of the organic substrates ICA and IHA, the progress of the reactions were kinetically monitored and parameters such as half life period ($t_{½}$) and rate co-efficient (k) values were determined. The catalytic efficiency of CuO nps and IHA and ICA substrates were studied. It was found that CuO nps efficiently catalyzed the chosen indole derivatives and IHA reacted rapidly under oxidation stress more than ICA.

Index Terms: Metal oxide nano particle catalysis, CuO nano particles, 3-Indole derivatives.

I. INTRODUCTION

Nanopraticles (nps) of transition metals and metal oxides have emerged as potential reaction catalysts via boosting up of the reactivity of the substrates, rapidity of the reactions, product selectivity, % yield controls and eco-friendlier reaction conditions (1-5). The uniqueness of nps has been attributed to the increase in surface area to mass ratio. In this work CuO nps are chosen as green reaction catalysts due to their cost effectiveness, abundance and suitable precursors for environment benign reaction conditions (6-11)

In the present study CuO nps are prepared using the Aloe vera (Aloe barbadensis Miller) extract as stabilising agent as it contains about 75 potentially active ingredients which possess anti inflammatory,antiparasitic and

wound healing properties(12-15), in the aqueous medium maintained at alkaline pH which are enviro friendly conditions. The class of indoles and their derivatives possess wide applications in the synthetic organic chemistry and as well as in protective bio medical therapeutic capacities (16,17). Oxidation of indole and its derivatives forms an important route for the formation of oxindoles which serve as synthetic precursors for numerous chemotherapeutics (18-20). Popular and synthetic routes of oxidation of indoles involve oxidants like N- halo succinimides, t-BuOCl, etc which evolve eco-deadlier by products. In the present study sodium peroxomono sulfate ($N_2S_2O_5$) has been chosen as the oxidant which produces enviro benign by products in aqueous medium. Indole derivatives such as Indole-3- carboxylic acid (ICA) and 3- hydroxyl acetyl indole (IHA) are chosen (Fig.1) for the oxidation reaction with $Na_2S_2O_5$ in presence of CuO nps in aqueous medium.

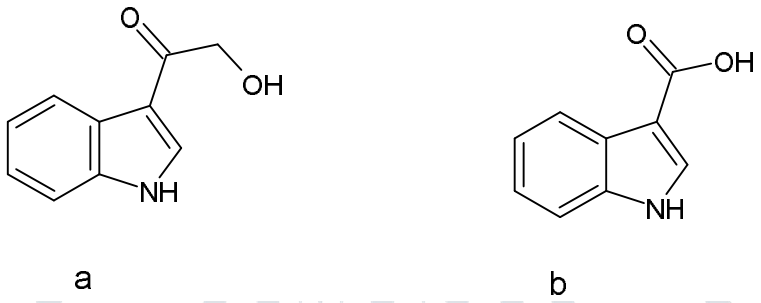


Fig.1.a. Molecular structure of 3-hydroxyl acetyl indole 1.b. Indole-3-carboxylic acid

The indole derivatives are well exploited as potential anticancer agents and show anti-proliferative capacity in liver, breast, ovaries, colon, lung etc.(21,22) Also, these indole substrates show protective therapeutic activity against cisplatin induced injury in various organs during anticancer treatments (23,24).The oxidation reactions of IHA and ICA are conducted in vitro aqueous medium at 25°C with CuO nps as catalysts and peroxomonosulfate as the oxidant adopting pseudo first order reaction conditions. The kinetic parameters such as the overall pseudo first order rate coefficient (k), % yield and half life period are found out from the time variance absorbance data of the substrate in the UV region spectra during the progress of the reaction. From the results, the catalytic performance of the Aloe vera extract stabilized CuO nps as catalysts, and the relative reactivities of ICA and IHA under oxidation stress conditions are found out. A plausible reaction mechanism of oxidation reaction has been put forth.

II. MATERIALS AND METHODS

2.1 Chemicals:

$Cu(NO_3)_2$ hydrated , $Na_2S_2O_5$, ICA, IHA and NaOH samples used were analytical grade and supplied by sigma – Aldrich India. The chemicals were used as such without further purification. Fresh triple distilled water was used wherever necessary.

2.2 Synthesis of CuO nps:

Fresh and skin peeled AloeVera slices (50gms) were ground to a fine paste adding 50ml of alkaline NaOH solution at pH=3.0. The thick slimy solution was filtered and the clear filtrate was used as the nano particle stabilizing agent. 20ml of 1mM $Cu(NO_3)_2$ solution was added to alkaline aqueous medium at pH = 1.5 to 1.8 maintaining 1:2 mole ratio of metal ion to hydroxyl ions in soultion. Into this , 50ml of aloe vera solution was added drop wise, simultaneously maintaining 45°C as the medium temperature with constant vigorous

stirring. Formation of black solution indicates the completion of reaction. Black CuO nps were collected by ultra centrifugation with repeated washings. The residues collected were vacuum dried and subjected to size analysis, and further use.

2.3 Particle Size characterization:

The as-synthesized CuO nps are analyzed by Powder XRD using Philips PW 1050/37 model diffractometer operating at 40KV and 30mA.CuKα radiation with 1.54A wavelength and step size of 0.02° in 20 degree ranges was used. FE – SEM of the nps are measured using SU6600, Hitachi model operating at an accelerating voltage of 100 KV and for HR-TEM CM20 PHILIPS model operating at 200 KV accelerating voltage instruments respectively.

2.4 Oxidation reaction Kinetics:

One pot batch reactor type reaction setup was adopted. 1 mg of the nanometal oxide, catalyst was added to aqueous solution containing mixture of 20ml of 0.1 mM ICA and 20ml of 1 mM oxidant dissolved in water. Near neutral pH and 25°C of the reaction mixture was maintained along with vigorous stirring for one hour to ensure completeness of the reaction. From the time of addition of catalyst, at regular intervals of time small aliquots of the reaction mixture were drawn out and UV spectra was recorded. The completion of the reaction was indicated by the reduction of the UV absorbance peak at the characteristic wave length to near zero value. Similar oxidation procedure was adopted for IHA also. All the kinetic experiments were repeated several times until concordant data are obtained.

III. RESULTS AND DISCUSSION

Morphology and size analysis of the synthesized nps are deduced from PXRD (Fig .2.) and HR TEM and FE – SEM (Fig .3.). The peak patterns of PXRD are assigned by JCPDS data file 48- 1548 (25). Utilizing the Scherrer formula, the average sizes of CuO nps are deduced to be 15± 2.0 nm. In Fig.3. the HR – TEM results show the average size of particles to fall in the range 15 ± 2.0nm while the FE – SEM photo indicate the particle morphology to be spherical and nearly monodisperse. The size values are in agreement with PXRD results. These results indicate that use of Aloevera extract in the place of other synthetic capping agents, has proved to produce spherical CuO nps with nearly monodisperse form within the size range 15± 2.0nm.(26).

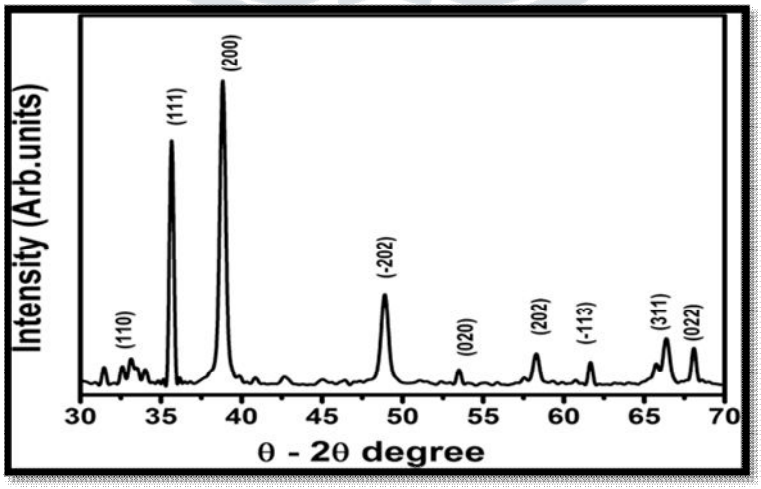


Fig 2. XRD pattern of CuO nps.

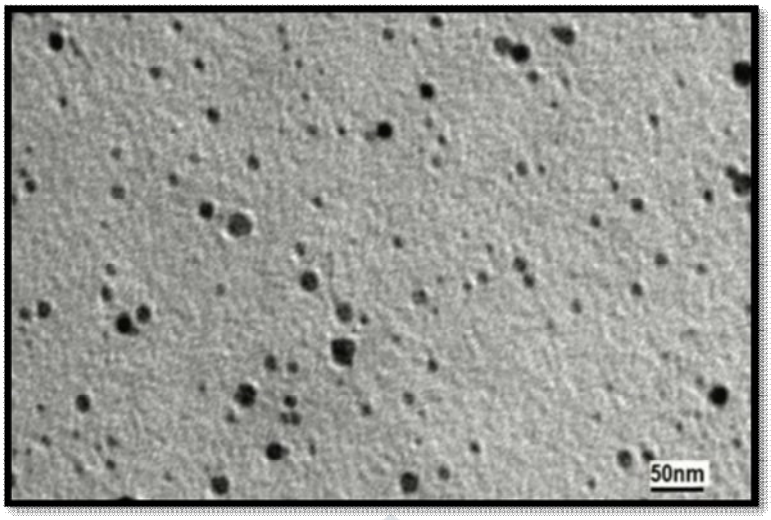
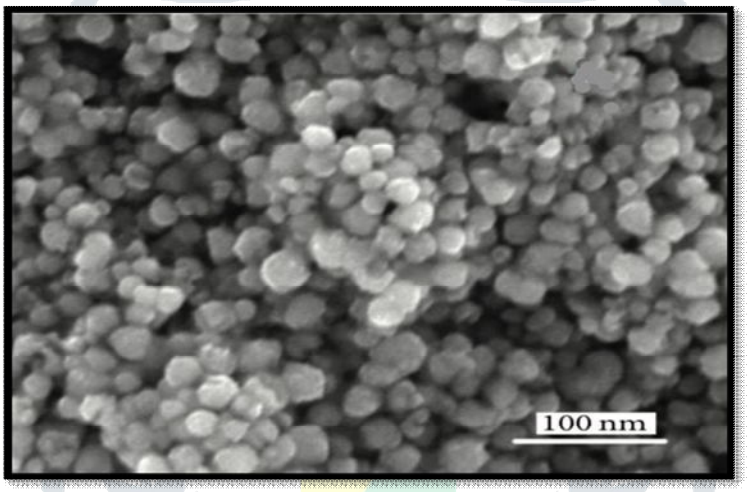


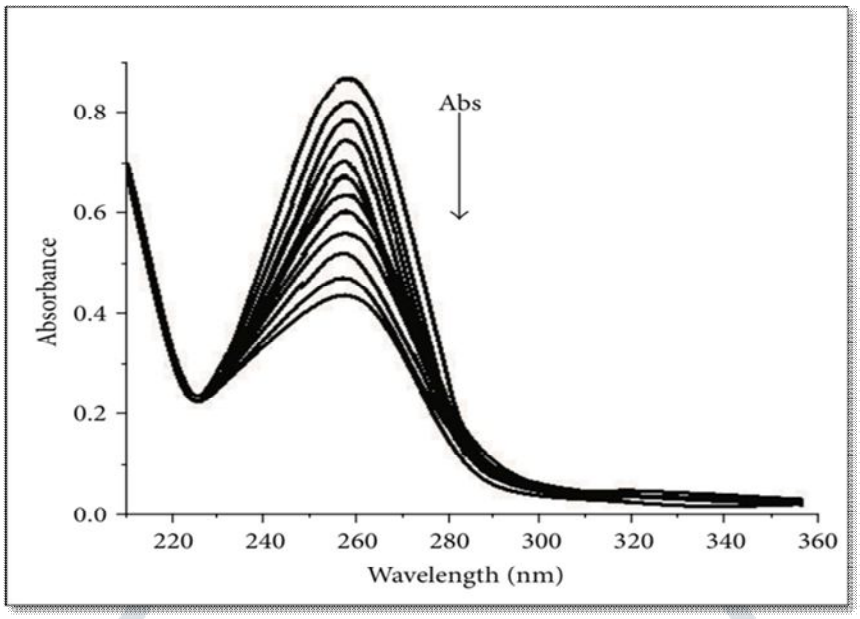
Fig. 3.a. HR-TEM image of CuO nps



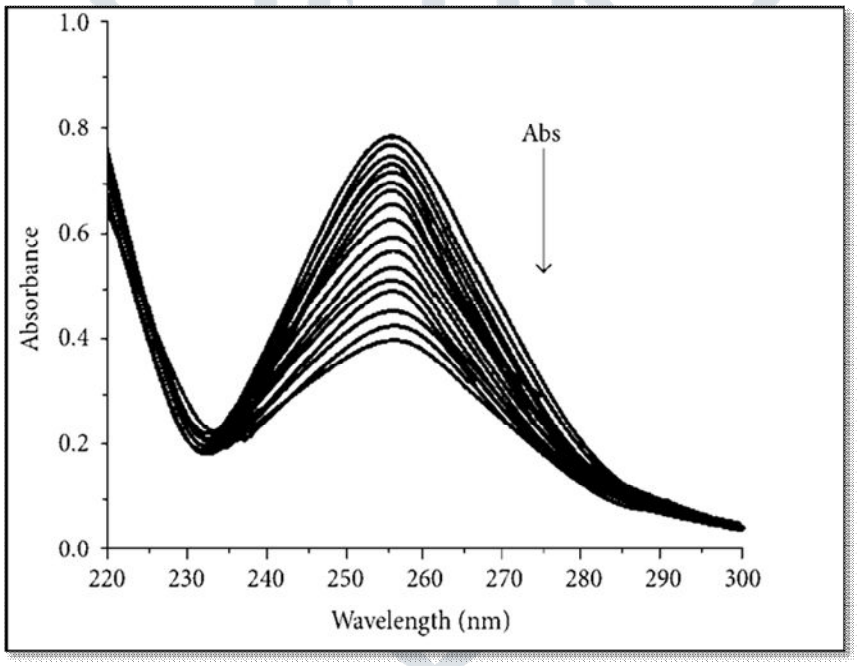
.Fig. 3.b. FE-SEM image of CuO nps.

When the oxidation reactions of ICA and IHA are carried out adopting identical experimental conditions but in the absence of CuO nps catalyst, the progress of the reactions are quite slow and completion of the reaction took more than 8 hrs.

The UV spectra variance with time of the progress of the oxidation reactions of ICA and IHA in the presence of CuO nps shown in Fig.4. indicate the completion of the reaction occurred in 1 hour time period.



(a) ICA

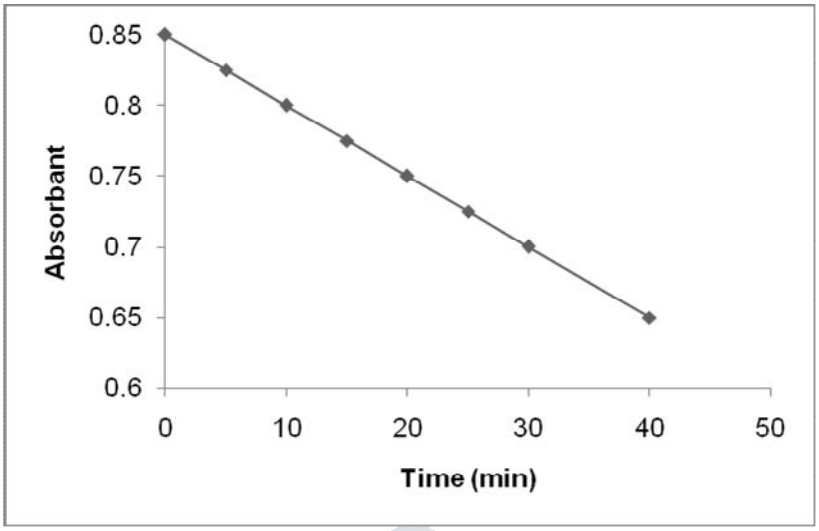


(b)IHA

Fig 4. Time dependant UV spectra of oxidation of (a) ICA and

(b)IHA by peroxomono sulfate in presence of CuO nps at 25°C

The absorbance time dependence plots deduced from the UV- spectra variations with time, in the presence of CuO nps separately for ICA and IHA are given in Fig.5 . The composition of the oxidant was maintained in excess and no intermediate product was isolated. From the slopes of the linear plots Fig. 6, the overall pseudo first order rate co- efficient values are determined and listed in Table 1.



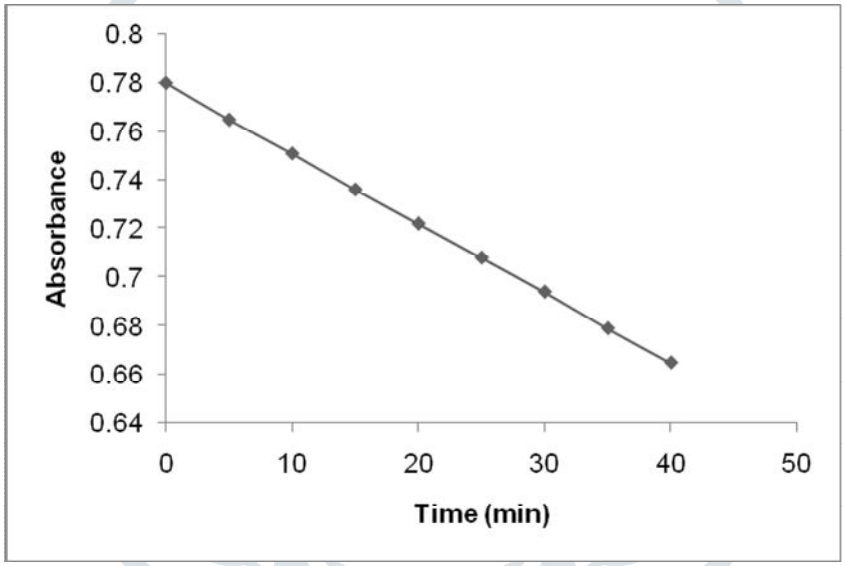


Fig 5. Absorbance – time dependence plots for the oxidation reactions of

(a) IHA and (b) ICA by peroxomono sulfate in presence of CuO nps.

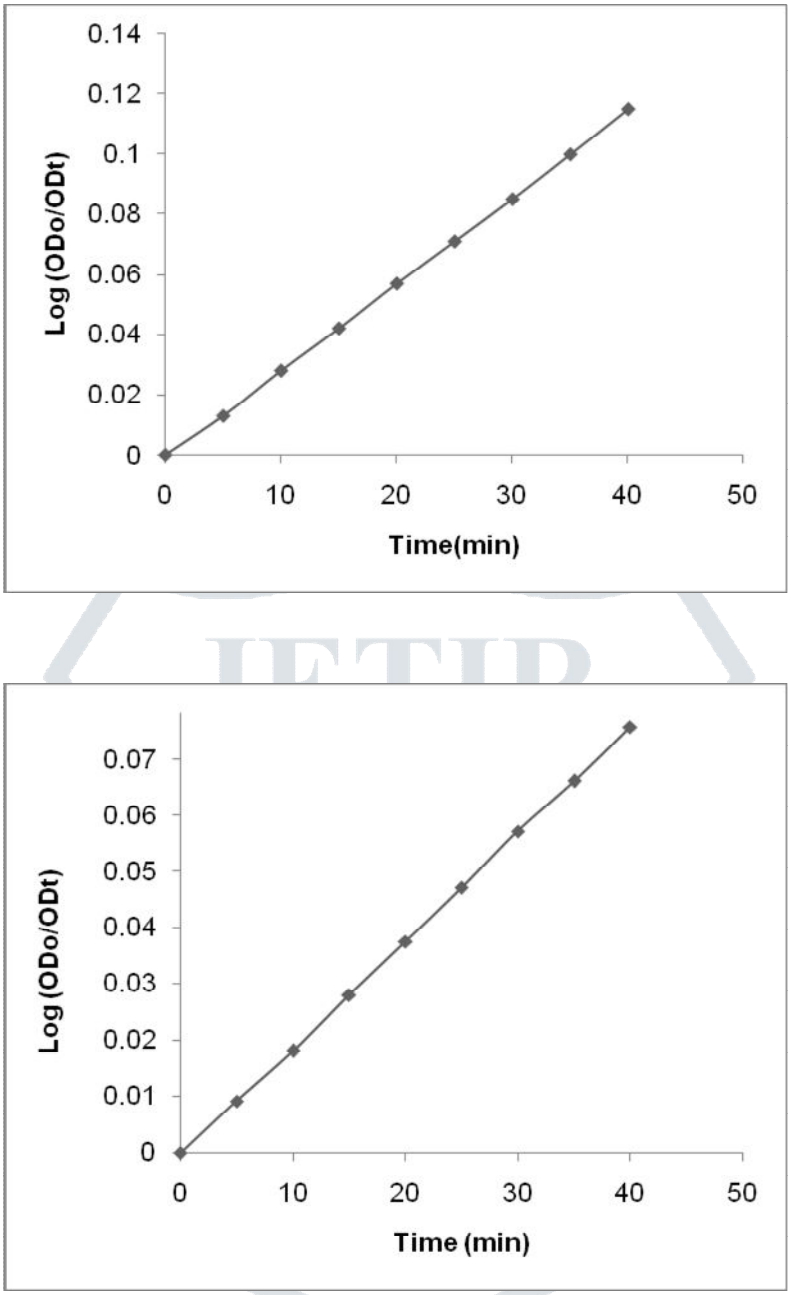


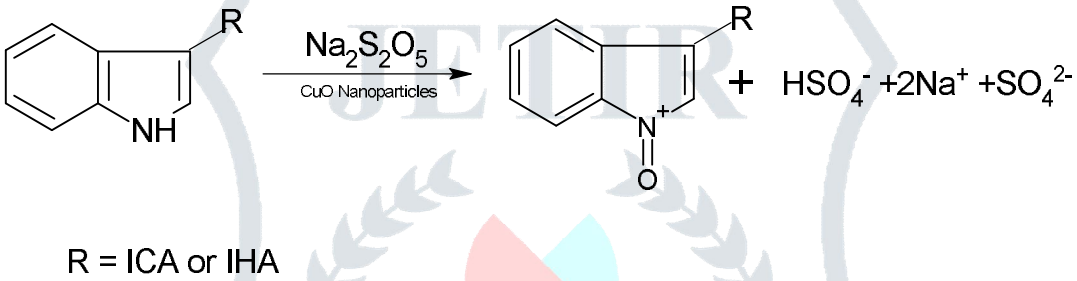
Fig. 6. Kinetic plots for the overall rate coefficient values under pseudo first order condition for oxidation of (a) IHA and (b)ICA by peroxomonosulfate in presence of

Cuo nps at 25°C.

Table 1. The overall pseudo first order rate coefficient ($kx10^{-4}$ sec^{-1}) values for the oxidation reactions of IHA and ICA using peroxomono sulfate and CuO nps as catalyst at 25°C.

Substrate	k	t ½ (min)	% mineralisation
IHA	4.74	24.54	93.0
ICA	3.21	36.22	89.6

After the completion of the reaction the mixture was filtered to remove the catalyst and the filtrate was analysed. Only the mineralized products of indole substrates and the oxidant were found. The possible reaction mechanism of the oxidation step is shown in scheme 1



Rate determining step of oxidation reaction of 3-indoles by peroxomono sulphate

scheme – 1

The rate determining step involves the ionization of the electron rich nitrogen by the oxidant followed by rapid oxidative mineralization reactions. The rate coefficient values half life period and % yield (Table 1) indicate that the reactivity in oxidative stress and the catalytic activity of CuO nps are found higher for IHA than ICA, which may be due to the overall electronic effects imparted by carboxylic acid and hydroxyl acetyl substituents. % yield refers to the total mineralization of substrate oxidised. Among the two indole derivatives ICA and IHA investigated in this study, the antioxidant behaviour of ICA is found to be more than IHA, which agrees with literature reports (27).

IV. CONCLUSION

CuO nps synthesised from Aloe vera extract proved to be a better catalyst for oxidation reactions and the nanoparticles are detected to have appreciable stability. After the completion of the reaction the catalyst were filtered out, repeatedly washed vacuum dried and used again as catalyst .The activity of the catalyst remained the same for five recycling reactions. Such an appreciable impact may be attributed to the aloe vera extract serving as the stabilising agent. Larger half life period of the oxidation reaction and the percent mineralised at the completion of the reaction shown in (Table 1) indicate that ICA could exhibit anti ageing property better than IHA. However, in - vivo data is required to validate this.

V. ACKNOWLEDGEMENTS

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REFERENCES

[1] Y.Suresh, S.Annapurna, A.K.Singh, G.Bhikshamaiah, "Green Synthesis and Characterization of Tea Decoction Stabilized Copper Nanoparticles", International Journal of Innovative Research in Science, Engineering and Technology, 3(4), (2014) 11265-11270.

[2] S.Ashokkumar, S.Ravi, V. Kathiravan, S.Velmurugan, "Synthesis of silver nanoparticles using A.indium leaf extract and their antibacterial activity",Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, (2015)

[3] H.Bar, D.K.Bhui, G.P.Sahoo, P.Sarkar, S.P.De, A.Misra "Green synthesis of silver nanoparticles using latex of Jatropha curcas", Colloid Surf, (2009), A 339, 134-139.

[4] T.Tuutijarvi, J.Lu, M.Sillanpaa, G.Chen "As(V) adsorption on magnemite Nanoparticles" J. Hazard. Mater. 166, (2009) 1415-1420.

[5] T.Tuutijarvi, J.Lu, M.Sillanpaa, G.Chen, "Adsorption mechanism of arsenate on crystal gamma - Fe2O3 nanoparticles", J. Environ.Eng. 136, (2010), 897-905.

[6] V.Vinod Kumar, S. Anbarasan, L.R.Christena, N.SaiSubramanian, S.P.Anthony, "Bio-funtionalized silver nanoparticles for selective colorimetric sensing of toxic metal ions and antibacterial studies", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy". 129, (2014), 35-42.

[7] S.P.Chandran, M.Chaudhary, R.Pasricha A.Ahmad, M.Sastry, "Synthesis of Gold nanotriangles and silver nanoparticles using Aloe Wera plant extract", Biotechnol. Prog,22, (2006), 277-583.

[8]. S.Jafarirad, M.Mehrabi, and E.R.Pur, "Biological Synthesis of Zinc Oxide and Copper Oxide Nanoparticles", International Conference on Chemistry, Biomedical and Environment Engineering, (2014), 62-64.

[9]. P.Raveendran, J.Fu, S.L.Wallen, "Completely "green" synthesis and stabilization of metal nanoparticles", J. Am. Chem. Soc. 125, (2003), 13940–13941.

[10]. K.Kalimuthu, R.S.Babu, D.Venkataraman, B.Mohd, S.Gurunathanm, "Biosynthesis of silver nanocrystals by Bacillus licheniformis", Colloids Surf. B 65, (2008), 150–153.

[11] A.V.Simakin, V.V.Voronov, N.A. Kirichenko,G.A Shafeev, "Nanoparticles Produced by laser ablation of solids in liquid environment", Appl. Phys. A 79,(2004),1127-1132.

[12] S.Gunalan, R. Sivaraj, R.Venckatesh, "Aloe barbadensis Miller mediated green Synthesis of mono-disperse copper oxide nanoparticles: Optical properties" Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy, 97, (2012), 1140-1144.

[13] A.Surjushe, R. Vasani, D.G.Saple, "Aloe vera", Indian Journal of Dermatology, 53,(2008), 163–166.

[14] A. Pugazhendhi, S.S. Kumar, M. Manikandan, M. Saravanan, "Photocatalytic properties and antimicrobial efficacy of Fe doped CuO nanoparticles against the pathogenic bacteria and fungi", Microb. Pathog., 122, (2018), 84-89.

[15] S.Vasantharaj, M.Sathiyavimal, P. Saravanan, K. Senthilkumar, M. Gnanasekaran, E. Shanmugavel, A.Manikandan, Pugazhendhi "Synthesis of ecofriendly copper oxide nanoparticles for fabrication over textile fabrics: characterization of antibacterial activity and dye degradation potential"

J. Photochem. Photobiol. B Biol., 191, (2019), 143-149.
[16] M. Bernart and W.H. Gerwick, Phytochemistry, 29, (1990), 3697.
[17] M.A. Ashour, E.S. Elkhayat, R. Ebel, R. Edrada and P. Proksch, ARKIVOC, 225, (2007).
[18] Chenhao Zhang, Sanliang Li, Filip Bures, Richmond Lee, Xinyi Ye and Zhiyong Jiang, "Visible Light Photocatalytic Aerobic Oxygenationof Indoles and pH as a Chemoselective Switch"Catal, 6 (2016) 10, 6853-6860.
[19] Junxu, Lixin Liang, Rongbiao Tong, "Green oxidation of insoles using halide catalyst", Nature communications 10, (2019) , 4754
[20] Lvin Zheng, Kailiang Tao, Wei Guo, "Recent developments in Photo catalyzed / promoted synthesis of Indoles and their functionalization : Reactions and Mechanisms" Wiley online Library,30 october, 2020.
[21] X. Han, X.F. Bao, C.X. Wang, J. Xie, X.J. Song, P. Dai, G.D. Chen, D. Hu, X.S. Yao, H. Gao, Nat. Prod. Res. (In press) (2019).
[22] M. Chen, X. Liu, Y. Shan, S. Xu, X. Feng and Q.Z. Wang, Nat. Prod. Res., 35, (2021), 222.
[23] P. Chalorak, P. Jattujan, S. Nobsathian, S.T. Poomtong, P. Sobhon and K. Meemon, "Nutr. Neurosci", (2018), 427.
[24] J. Liao, C. Yuan, Y. Di, H. He and X. Hu, Asian J. Chem., 26, (2014), 4504.
[25] M.I.Amal, H.M.Ghaida, M.Laila, "A Copper (11) oxide nano catalyst preparation and characterization green chemistry route", Bull Nat. Res, Cent., 42(2018),6.
[26] J.Santhanalakshmi- L.Parimala, "The copper nanoparticles catalysed reduction of substituted nitrobenzenes: effect of nanoparticle stabilizers",J.Nanopart Res 14, (2012),1090.
[27] Preeyanuch Manohong, Krai Meemon, Montakan Tamtin, Tirapast Sichaem, " Isolation of 3-(Hydroxyacetyl) indole and Indole-3-carboxlic acid from Red Alga Halymenia durvillei: Their Anti-lung Cancer Cell and in vivi Anti-aging Activity", Asian Journal of Chemistry, Vol.33, No.4, (2021),775-780.