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Research Article

Synthesis, Characterization and Catalytic Application of Copper Nanoparticles on Oxidation of Alanine in Acid Aqueous Medium

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Abstract

In this paper, we report on the synthesis of copper nanoparticles (Cunps) through a single route of chemical reduction method. The effect of different concentration of precursor salt and temperature on the morphology of Copper nanoparticals was investigated. The synthesized copper nanoparticles were characterized by UV-Visible spectrophotometer, Fourier Transform Infrared (FTIR) Spectrophotometer, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) analysis. The average size of copper nanoparticles was found to be 12 nm and spherical in shape at the optimal experimental conditions. The catalysis by colloidal copper nanoparticles was studied kinetically in the oxidation of L-Alanine (Ala) by peroxodisulphate (PDS) in acid aqueous medium. The copper nanoparticles catalyst exhibited very good catalytic activity and the kinetics of the reaction was found to be first order with respect to peroxodisulphate and independent of alanine concentration. The effects of catalyst concentration, ionic strength and temperature on the reaction were also investigated.

Keywords: *Copper nanoparticles, L-alanine, Peroxodisulphate, Oxidation, Kinetics.*

1. Introduction

The field of nanocatalysis has undergone an explosive growth during the past decades, both in homogeneous and heterogeneous catalysis (Bradley and Scmided, 1994), (Thomas, *et al*, 2003). Since nanoparticles have a large surface to volume ratio compared to bulk materials, they are attractive to use as catalyst (Bruss, *et al*, 2006), (Firooz, *et al*, 2011). Metal nanoparticles with high specific catalytic activity are ubiquitous in modern synthetic organic chemistry during the recent decades (Jansat, *et al*, 2004). However how to reduce their dosage is one of the most exciting challenges due to the limiting reserves of noble metals. Some selective oxidation reactions are reported involving transition metal ions of Ag, Rh, Cr, Ru, Mn etc. are reported to act as catalyst for amino acids oxidations (Devra and Yadav, 2012), (Singh and Singh, 1992), (Bilehal, *et al*, 2005), (Seregar, *et al*, 2007), (Berlett, *et al*, 1990) with the emergence of metal nanoparticles possessing appreciable stability and high surface area per particle, their potential use as catalyst for organic biochemical relevant reactions (Sanathanlakshmi and Vankatesan, 2012), (Huang, *et al*, 2005). Amongst them Copper nanoparticles are paid more attention due to their low cost and easy availability. Copper nanoparticles have also been considered (Hoover, *et al*, 2006), (Niu and Crooks, 2003) as an alternative for noble metals in many applications such as heat transfer and microelectronics (Eastman, *et al*, 2001). In this study, highly stable colloidal dispersion of copper nanoparticles has been synthesized by chemical reduction method, using ascorbic acid as a reducing agent as well as capping agent. The particle size has been effectively controlled by the variation of precursor salt and temperature during the synthesis. The synthesized Cunps were characterized by UV-Visible Spectrum, FTIR, SEM, TEM etc. techniques.

The kinetics of the oxidation of inorganic and organic substrates by peroxodisulphate under both catalyzed and uncatalyzed conditions have received considerable attention (Wilmarth and Haim, 1961), (House, 1962). The peroxodisulphate ion is one of the strongest oxidizing agents known in aqueous solution. The standard oxidation reduction potential for the reaction is estimated to be -2.01V.

$$2\ SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$$

The reaction involve this ion are generally very slow in the absence of suitable catalysts (Chandra and Srivastava, 1971).The transition metal ion catalysis oxidation of amino acid by peroxodisulphate was reported in aqueous acidic medium (Chandra and Srivastava, 1973), (Zelechonok and Silverman, 1992), (Khalid, 2008). The oxidation of amino acids is of the

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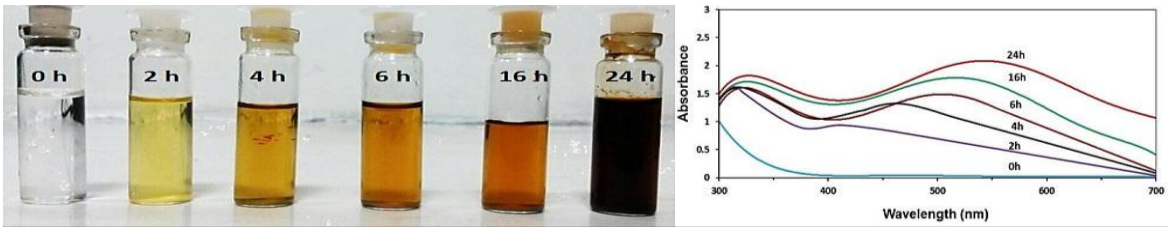


Figure 1 The time evolution of the dispersion photographs and the UV-Visible spectra

utmost importance, both from a chemical point and in view of its bearing on the mechanism of amino acid metabolism. It has been observed that there is not enough information in the literature on the kinetics of oxidation of amino acid by peroxodisulphate in presence of copper nanoparticles. The present investigation is a part of a broad programme of study of the catalytic effect of copper nanoparticles on the oxidation of alanine by peroxodisulphate in acid aqueous media.

2. Experimental

2.1 Material

For the present work, we used analytical grade chemicals such as copper chloride dihydrate ($CuCl_2.2H_2O$-97%), L-ascorbic acid (vitamin C-98%), L-Alanine and Peroxodisulphate were obtained from E. Merck. A fresh solution of peroxodisulphate was prepared before starting the experiments. All chemicals were used as received without further purification. Double distilled water was employed throughout the study.

2.2 Synthesis of Copper Nanoparticles

The one step synthesis scheme for copper nanoparticles initiates with dissolving copper chloride dihydrate (0.02 mol L^{-1}) in deionized water to obtain a blue solution. L-ascorbic acid (0.01 mol L^{-1}) drop wise added to the aqueous solution of copper salt while vigorously stirring at 353 K in oil bath. With the passage of time, the colour of dispersion gradually changed from white, yellow, orange, brown finally dark brown with a number of intermediate stages. The appearance of yellow colour followed by orange colour indicated the formation of fine nanoscale copper particles from L-ascorbic acid assisted reduction. The resulting dispersion was centrifuged for 15 minutes. The supernatant was placed under ambient conditions for 2 months. The studies were performed at different concentration of $CuCl_2.2H_2O$ and temperature to investigate the morphology of copper nanoparticles.

2.3 Characterization

UV-Visible spectroscopy from a double beam spectrophotometer (U.V. 3000+ LABINDIA) was used for preliminary estimation of copper nanoparticles synthesis. FTIR (ALPHA-T –Bruker) provided information about oxidation product of the reaction. Morphological study of the copper nanoparticles was carried out with scanning electron microscope (SEM) (EVO 18 carlzeiss) and Transmission electron microscope (TEM) (FEI Techni G2S2 Twin). TEM and SEM images were recorded to confirm size distribution and shape homogeneity of synthesized copper nanoparticles.

2.4 Kinetic Measurements

The reaction was carried out in glass-stoppered Pyrex round bottom flask. Appropriate amount of the amino acid solution in acidic form, potassium sulphate, and water (to keep the total volume constant for all runs) were taken in the round bottom flask and thermostatted at 308 K for thermal equilibrium. A measured amount of peroxodisulphate was rapidly added to the mixture. The progress of the reaction was monitored by iodometric determination of unreacted peroxodisulphate in a measured aliquot of the reaction mixture at different intervals of time (Khalid and Kheir, 2008). The rate constants were computed from the linear plots of log [PDS] against time. The course of the reaction was followed for at least 80% of the reaction.

3. Results and Discussion

3.1(a) Metal Nanoparticles Characterization Results

UV-Visible absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak position and shapes are sensitive to particle size. During the synthesis of copper nanoparticles in aqueous solution, the UV-Visible spectra of samples were recorded at different time intervals for every colour change presented in (Figure 1).

The spectacular colour change correlates with large shift of UV-Visible spectra. The first absorption peak of different curves is at 335 nm corresponding to oxidation product of L-ascorbic acid (Xiong, *et al*, 2011). The second absorption peak is increasingly broadening with an increasing concentration of L-ascorbic acid. The absorption peak of copper nanoparticles has been reported at around 560 nm of

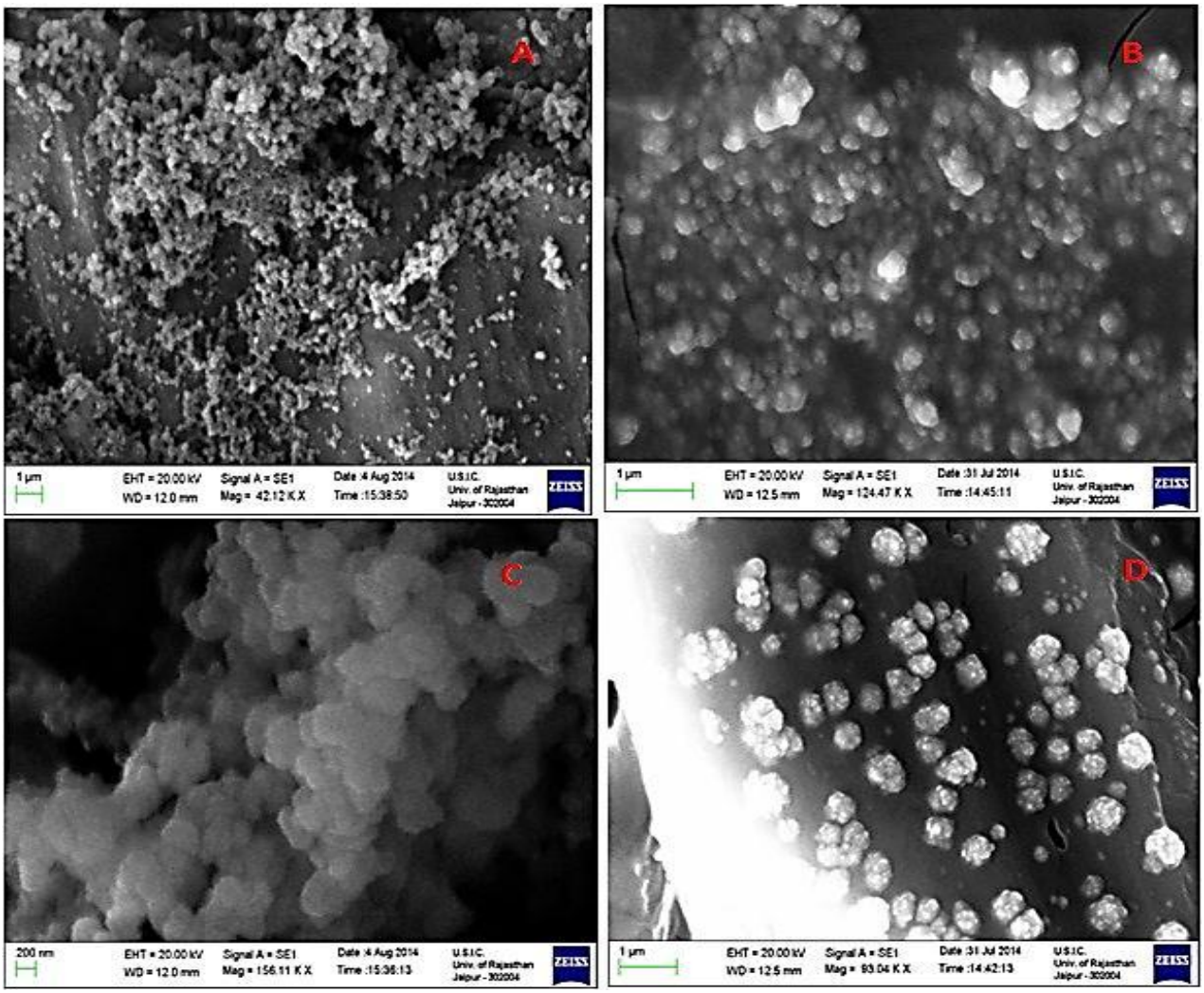


Figure 2 SEM images of the synthesized copper nanoparticles with various concentration of the precursor salt ($CuCl_2.2H_20$) (A) 0.01 mol L^{-1}, (B) 0.015 mol L^{-1}, (C) 0.02 mol L^{-1}, (D) 0.03 mol L^{-1}

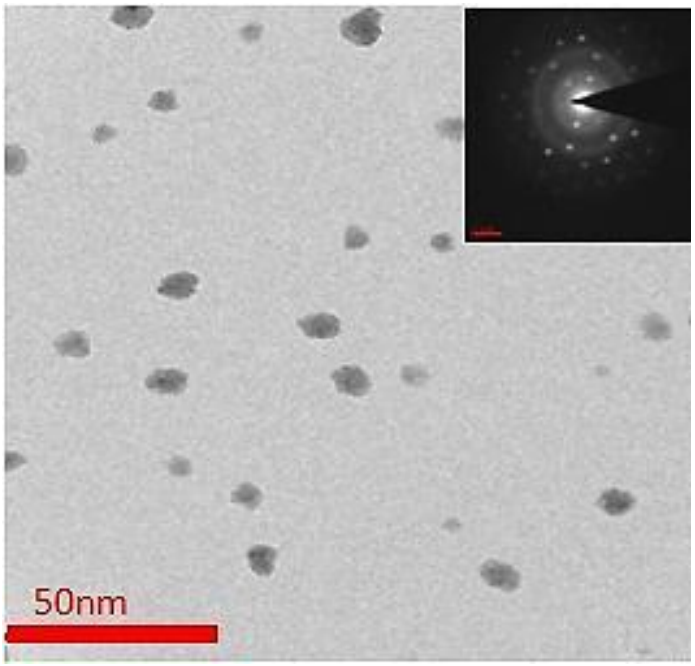


Figure 3 TEM image of synthesized copper nanoparticles at the optimal experimental conditions

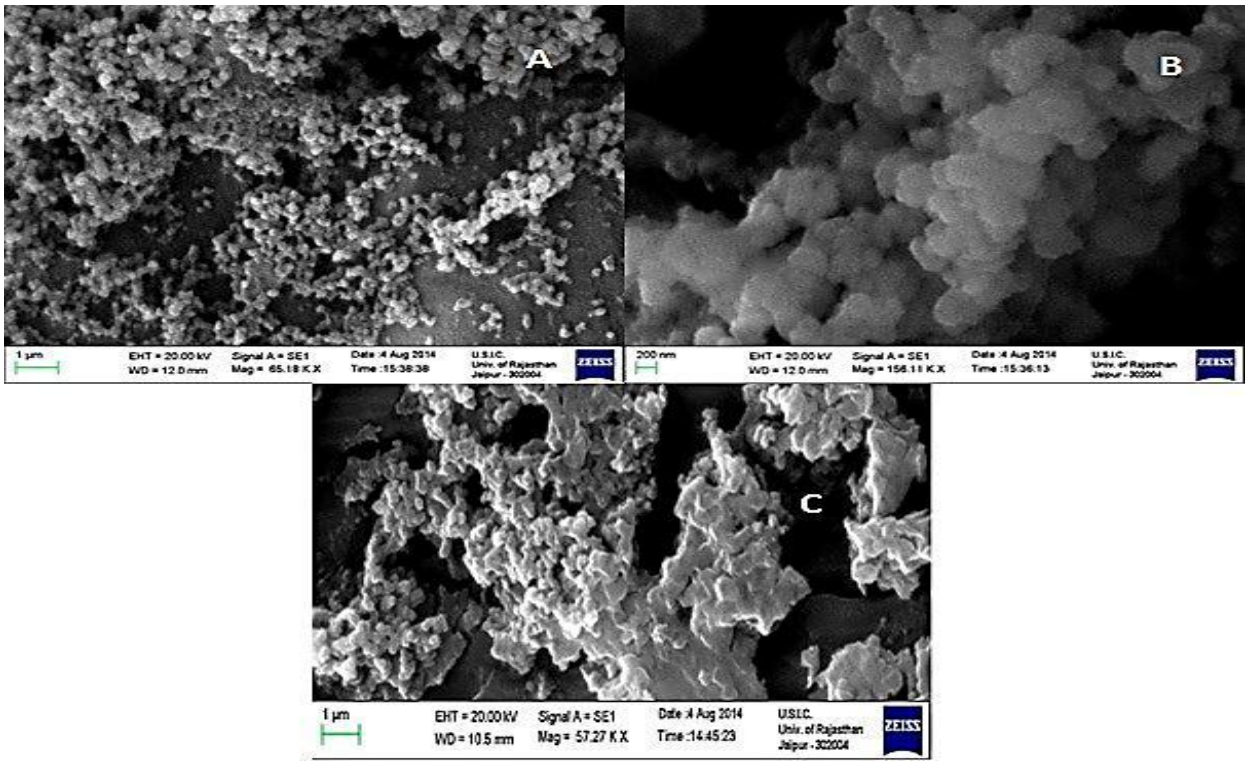


Figure 4 SEM images of synthesized copper nanoparticles with variation of temperature (A) 343 K, (B) 353 K, (C) 363 K

UV-Visible wavelength which proves the formation of copper nanoparticles (Kapoor, *et al*, 2002), (Zhang, *et al*, 2009).

3.1(b) Effect of initial concentration of precursor salt

The effect of initial concentration of precursor salt on synthesis of copper nanoparticles was studied at four different concentrations $CuCl_2.2H_20$ viz. 0.01, 0.015, 0.02, 0.03 mol L^{-1}. There are two stages in the synthesis of copper nanoparticles, the first stage is to generate copper nuclei and second stage is the growth of copper (Liu, *et al* 2010). So it is important to control preparation process that copper nuclei must generate faster and grow up slower which requires better control of the initial concentration of Cu^{+2}. It can be seen that reaction rate increases with increases the concentration of Cu^{+2}. With the increasing reaction rate, the amount of copper nuclei rises and smaller particle size are obtained correspondingly which is shown in SEM images A, B, C of (Figure 2) further increases the concentration of Cu^{+2}, the result is the agglomeration of the nuclei and growing the particle size as shown in SEM image D of (Figure 2). This may be due to collision between small particles, which leads to particle growth (Dang, *et al*, 2011). So the optimal concentration of precursor salt is 0.02 mol L^{-1} and 0.1 mol L^{-1} of L-ascorbic acid at 353 K. In this experimental condition, the TEM image of the synthesized copper nanoparticles is shown in (Figure 3). It can be seen that the nanoparticles are spherical in shape and monodispersed with size 12 nm ± 0.5 nm.

3.1(c) Effect of reaction temperature

The present investigation reveals that nanoparticles did not form below the temperature 333 K in any conditions. Therefore reaction temperature higher than 333 K with appropriate concentration of the reactants should be inserted to the synthesis of copper nanoparticles. In (Figure 4), SEM images A, B, C of copper nanoparticles synthesized at 343 K, 353 K, 363 K respectively, shown that at higher temperature (363 K), the nanoparticles were agglomerated, while at 353 K are well dispersed with an average size at about 12 nm.

Basically, the reduction of Cu^{+2} were increase by increasing the reaction temperature. Therefore the synthesis rate is too high to control particle size at high temperature. When reducing agent adds to precursor solution at 363 K, rate of growth and agglomeration as well as nucleation of copper nanoparticles accelerated almost coincidently. These phenomena result in the formation of copper nanoparticles were precipitated. Therefore moderate temperature (353 K) should be selected for synthesis of the copper nanoparticles with appropriate controlling on size.

3.1(d) Stability of nanoparticles dispersion

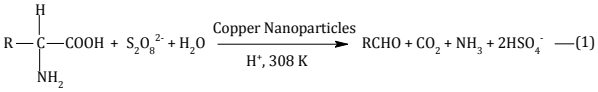
The stability of nanoparticles dispersion is key factor in their application. In this study L-ascorbic acid was used as both reducing and capping agent without any other special capping agent. The photographs of dispersion before and after the storage (2 months) are shown in

(Figure 5). The antioxidant properties of L-ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules (Wu, *et al*, 2006) accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid and finally converted into polyhydroxyl structure through hydrolysis (Kerber, 2008). Therefore L-ascorbic acid plays dual role as reducing agent and antioxidant of copper nanoparticles. Thus reaction can complete without any protective gas.

Figure 5 The photos of dispersion of Cunps (A) before (B) after 2 months of storage

3.2 Stoichiometry

Attempts were made to determine the stoichiometry, the reaction mixture containing an excess of peroxodisulphate (PDS) over Alanine (Ala) were allowed for 24 hours to react is a temperature controlled water bath. The excess of PDS was determined iodometrically. The identification of product by IR (Infra red spectrum) and formation of 2, 4-dinitrophenyl hydrazone derivative indicate the stoichiometry as represented by equation (1).



—(1)

Where R represents -CH_3

Ammonia identified by nessler's reagent, brownish colour was observed indicating deamination reaction, carbon dioxide was identified by freshly prepared lime water and the solution turned milky indicating decarboxylation reaction. The product aldehyde was identified by qualitative test and further 2, 4-dinitrophenyl hydrazone derivative was also obtained which is confirmed by FTIR spectrum in (Figure 6). The IR peaks at 3343 cm^{-1}, 2901 cm^{-1}, 1610 cm^{-1} are attributed to –NH, –CH and –C=N stretching respectively. The deamination of the L-Alanine by persulphate in presence of copper nanoparticles was shown in UV- Visible absorption spectrum (Figure 7).

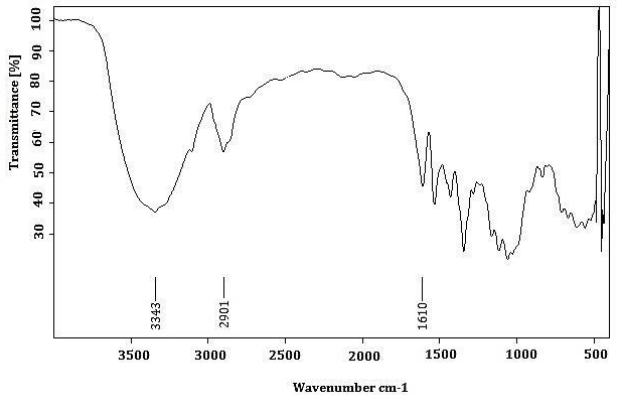


Figure 6 The FTIR Spectra of the oxidation product of alanine oxidation

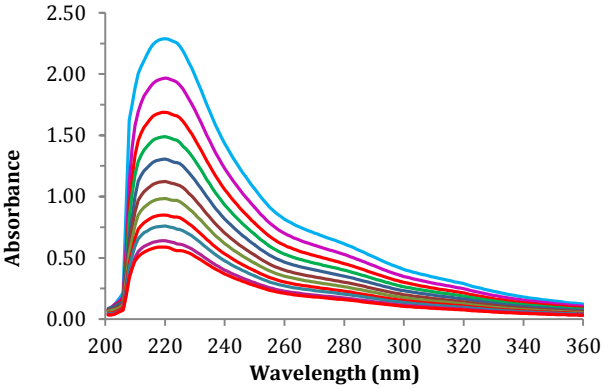


Figure 7 UV absorption spectra for the deamination of L-alanine (time 0-40 min.) in the presence of the copper nanoparticles

3.3 Peroxodisulphate dependence

Kinetic runs were carried out by varying concentration of peroxodisulphate from 1×10^{-3} – 7.5×10^{-3} mol L^{-1} at fixed concentration of [Ala] = 5×10^{-2} mol L^{-1}, [H^+] = 0.1 mol L^{-1}, I = 0.2 mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1} at 308 K temperature. The plot of log [PDS] versus time was linear for each initial concentration of peroxodisulphate. The observed pseudo first order rate constant (k_{obs}) were independent of the concentration of peroxodisulphate which is given in Table-1.

3.4 Alanine dependence

Reaction were carried out at constant concentration of all reactants [PDS] = 5×10^{-3} mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1}, [H^+] = 0.1 mol L^{-1}, I = 0.2 mol L^{-1} and by varying initial concentration of alanine from 1×10^{-2} – 7×10^{-2} mol L^{-1} at 308 K temperature. Plot of log k_{obs} versus log [Ala] gave straight line parallel to log [Ala] axis indicating zero order dependence with respect to alaine as shown in Table 1.

Table 1: Effects of variation of [PDS], [Ala], [Cunps], [H^+] on the oxidation of Alanine by Peroxodisulphate at fixed Ionic Strength (I) = 0.2 and Temperature 308 K

S. No.	10^3 [PDS] mol L^{-1}	10^2 [Ala] mol L^{-1}	10^5 [Cunps] mol L^{-1}	10^1 [H^+] mol L^{-1}	10^4 k_{obs} sec^{-1}
1	1	5	1	1	5.7
2	2	5	1	1	5.7
3	3	5	1	1	5.7
4	4	5	1	1	5.73
5	5	5	1	1	5.73
6	6	5	1	1	5.75
7	7.5	5	1	1	5.73
8	5	1	1	1	5.7
9	5	2	1	1	5.72
10	5	3	1	1	5.7
11	5	4	1	1	5.7
12	5	5	1	1	5.73
13	5	6	1	1	5.73
14	5	7	1	1	5.7
15	5	5	0	1	1.5
16	5	5	0.1	1	1.95
17	5	5	0.2	1	2.35
18	5	5	0.3	1	2.8
19	5	5	0.4	1	3.2
20	5	5	0.5	1	3.65
21	5	5	0.6	1	4.15
22	5	5	0.7	1	4.5
23	5	5	0.8	1	4.9
24	5	5	0.9	1	5.3
25	5	5	1	1	5.73
26	5	5	1	1.1	4.5
27	5	5	1	1.2	3.2
28	5	5	1	1.3	2.3
29	5	5	1	1.4	1.6
30	5	5	1	1.5	1.2
31	5	5	1	1.6	0.95
32	5	5	1	1.7	0.85
33	5	5	1	1.8	0.8
34	5	5	1	1.9	0.8
35	5	5	1	2	0.79

3.5 Copper Nanoparticles dependence

The concentration of copper nanoparticles were varied from 1×10^{-6} – 1×10^{-5} mol L^{-1} at fixed concentration of all reactants [PDS] = 5×10^{-3} mol L^{-1}, [Ala] = 5×10^{-2} mol L^{-1}, [H^+] = 0.1 mol L^{-1}, I = 0.2 mol L^{-1} at three temperature (303 K, 308 K, 313 K). The rate of reaction increases with increasing concentration of copper nanoparticles (Table-1). In order to show the catalytic activity, a graph is plotted between the concentration of copper nanoparticles and rate constants at different temperature. The plot obtained is straight lines showing direct dependence of reaction rate on copper nanoparticles concentration (Figure 8). As these straight lines do not pass through origin, it is evident that the uncatalysed oxidation of alanine by peroxodisulphate is also possible.

The activation parameters were also calculated from the observed constants at three temperatures (Table-2).

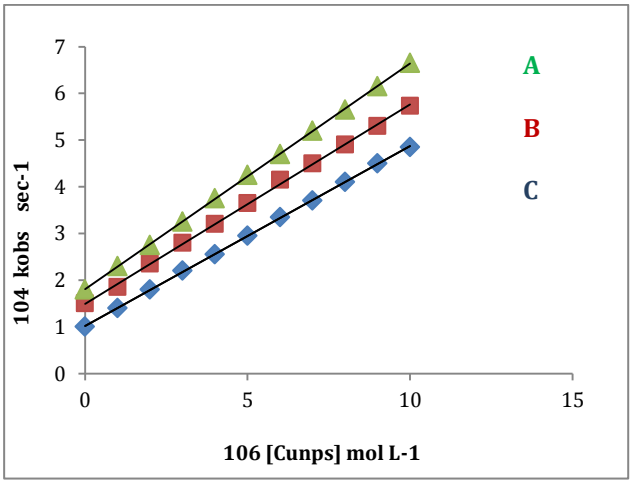


Figure 8 The effect of [Cunps] at different temperature (A) 303, (B)308, (C) 313 K at fixed [PDS] = 5.0×10^{-3} mol L^{-1}, [Ala] = 5.0×10^{-2} mol L^{-1}, [H^+] = 0.1 mol L^{-1}, I = 0.2 mol L^{-1}

Table-2 [PDS] = 5×10^{-3} mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1}, [Ala] = 5×10^{-2} mol L^{-1}, [H^+] = 0.1 mol L^{-1}, I = 0.2 mol L^{-1}

Temperature (K)	10^4 K_{obs} (sec^{-1})	E_a (KJ/mol)	ΔS (J/K/mol)	ΔH (KJ/mol)	ΔG (KJ/mol)
303	4.85	23.846	-238.17	21.29	94.651
308	5.73				
313	6.65				

The high positive values of free energy of activation (ΔG) and enthalpy of activation (ΔH) indicated that the transition state was highly solvated while the negative values of entropy of activation (ΔS) suggested the formation of rigid transition state with reduction in the degree of freedom of molecules.

3.6 Hydrogen ion dependence

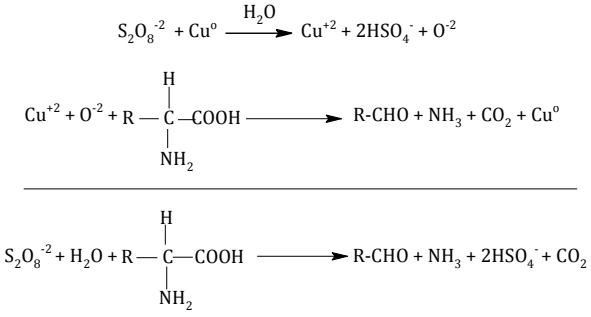
Hydrogen ion variation was made by varying the concentration of sulphuric acid from 0.1 to 0.2 mol L^{-1} at fixed concentration of [PDS] = 5×10^{-3} mol L^{-1}, [Ala] = 5×10^{-2} mol L^{-1}, [Cunps] = 1×10^{-5} mol L^{-1}, I = 0.2 mol L^{-1} and temperature 308 K. The rate of the reaction decreases with increasing concentration of H^+ and then tends towards a limiting value at higher concentration (Table-1). Since rate does not depend upon the concentration of alanine, hydrogen ion dependence cannot be related to the amino acid. However, decrease in rate with increasing H^+ concentration accounts for the higher reactivity of the molecular form of the acid.

3.7 Effect of ionic strength

The effect of ionic strength on the rate of reaction was studied by varying the concentration of potassium sulphate at constant concentration of reactants and conditions. The change in the k_{obs} with increase in the ionic strength is found to be very small. This indicates that unionized molecular forms are involved in the reaction.

3.8 Mechanism

The definite mechanism of the homogeneous metal nanoparticles catalysed oxidation is not clear. Although identify the formation of transition species through certain physical measurements but it is very difficult to isolate and characterize from homogeneous mixture. Since in the present study, the rate of reaction does not depend upon the concentration of alanine, oxidative deamination of alanine occurs in presence of peroxodisulphate only upon addition of copper nanoparticles while peroxodisulphate converted to hydrogen sulphate ion. The plausible mechanism in support of the observed kinetics is given in scheme-1.



Scheme-I The plausible route of copper nanoparticles catalyzed oxidation of alanine

Conclusion

In the present work, highly stable dispersed copper nanoparticles were prepared by low cost, environment friendly and can be prepared in simple lab equipment in ambient condition. The synthesized nanoparticles are highly stable and do not show sedimentation even after storage for 2 months. The catalytic activity of copper nanoparticles was investigated through the oxidation of alanine in aqueous acid medium. The reaction is four times faster in the presence of very small copper nanoparticles concentration (10×10^{-6} mol L^{-1}). The results of the study indicate the reaction between alanine and peroxodisulphate in the presence of Cunps was first order. The study will be helpful in the biochemical and medical fields.

References

Berlett, B. S., Chock, P. B., Yim, M. B., Stadtman, E. R. (1990), Manganese(II) catalyzes the bicarbonate-dependent oxidation of amino acids by hydrogen peroxide and the amino acid-facilitated dismutation of hydrogen peroxide, *Proc. Natl. Acad. Sci.,* 87**,** 389-393.

Bilehal, D., Kulkarni, R., Nandibewoor, S. (2005), Comparative study of the chromium(III) catalysed oxidation of l-leucine and l-isoleucine by alkaline permanganate: A kinetic and mechanistic approach , *Journal of Molecular Catalysis A: Chemical,* 232, 21-28.

Bradley J. S., Scmided G. (1994), Clusters and Colloids: From Theory to Application VCH, New York *Cluster Colloids,* 459

Bruss A.S., Gelesky M.A., Machado G., Dupont. J. (2006), Rh(0) nanoparticles as catalyst precursors for the solventless hydroformylation of olefins*, J. Of Molecular Catalysis A: Chemical*, 252, 212-218.

Chandra, G. and Srivastava, S. N. (1971), Kinetics of Ag(I) ion catalyses oxidation of glycine by peroxy disulphate ion, *Bull. Chem. Soc.,* 44, 3000-3003.

Chandra, G. and Srivastava, S. N. (1973), Kinetics of Ag(I) catalysed peroxydisulphate oxidation of glycine, alanine and valine, *Ind. J. Chem.,* 11, 773-776.

Devra, V., Yadav, M. B. (2012), Kinetics and Mechanism of Osmium (VIII) Catalysed Oxidation of Valine by Hexacyanoferrate (III) in Alkaline Medium, *Rasayan J. Chem*., 5**,** 67-73.

Dang, T. M. D., Le, T. T. T., Fribourg-Blanc, E. and Dang, M. C. (2011), The Influence of Solvents and Surfactants on the Preparation of Copper Nanoparticles by a Chemical

reduction Method, *Adv. Nat. sci. Nanosci. Nanotechnol*., 2, 015009-015021.

Eastman, J. A., Choi, S. U. S., Li, S., Yu, W. and Thompson, L. (2001), Anomalously increased effective thermal conductivities of ethylene glycol based nano fluids containing copper nanoparticles, *J. Appl. Phy. Lett,* 78, 718-720.

Firooz A. A., Mahjoub A. R. and Khodadadi A. A. (2011), World Academy of Science,Engineering and Technology, 5, 118-120.

Hoover, N. N., Auten, B. J., Chandler, B. D. (2006), Tuning supported catalyst reactivity with dendrimer-templated Pt−Cu nanoparticles, *J. Phys. Chem. B*, 110**,** 8606-8612.

House, D. A. (1962), Kinetics and Mechanism of Oxidations by Peroxydisulfate, *Chem. Rev.,* 62, 185-203.

Huang, X., El-Sayed, I. H., Yi, X., El-Sayed, M. A. (2005), Gold nanoparticles: Catalyst for the oxidation of NADH to NAD^+, *J. Photochem. Photobiol. B*, 81, 76-83.

Jansat, S., Gomez, M., Philippot, K., Muller, G., Guiu, E., Claver, C., Castillon, S., Chaudret, B. (2004), A Case for Enantioselective Allylic Alkylation Catalyzed by Palladium Nanoparticles*, J. Am. Chem Soc.,* 126, 1592-1593.

Kapoor, S., Joshi, R., Mukherjee, T. (2002), Influence of I-anions on the formation and stabilization of copper nanoparticles, *Chemical Physics Letters***,** 354, 443-452.

Kerber, R. C. (2008), As simple as possible, but not simpler-the case of dehydroascorbic, *J. Chem. Educ.,* 85**,** 1237-1242.

Khalid, M. A. A. (2008), Oxidative Kinetics of Amino Acids by Peroxydisulphate: Effect of Dielectric Constant, *The Arabian Journal for Science and Engineering,* 33, 199-210.

Khalid, M. A., Kheir, A. M. (2008), Kinetics and Mechanisms of Amino Acids-Peroxodisulphate Reaction, Part I, *Sudan Journal of Basic Sciences*, 15, 69-83.

Liu, Q. M., Zhou, De-bi., Nishio, K., Ichino, R., Okido, M. (2010), Effect of Reaction Driving Force on Copper Nanoparticle Preparation by Aqueous Solution Reduction Method, *Materials Transactions*, 51**,** 1386-1389.

Niu, Y., Crooks, R. M. (2003), Preparation of dendrimer-encapsulated metal nanoparticles using organic solvents, *Chem. Mater.,* 15, 3463-3467.

Sanathanlakshmi, J., Vankatesan, P. (2012), Kinetic of oxidation of L-leucine by mono- and bimetallic gold and silver nanoparticles in hydrogen peroxide solution, *Chinese Journal of Catalysis*, 33, 1306-1311.

Seregar, V., Veeresh, T. M., Nandibewoor, S. T. (2007), Ruthenium (III) catalysed oxidation of L-leucine by a new oxidant, diperiodatoargentate(III) in aqueous alkaline medium, *Polyhedron*, 26**,** 1731-1739.

Singh, B. K., Singh, R. P. (1992), Mechanism of Rh(III) Catalysis in Oxidation of Glutamic Acid by Alkaline Solution of Hexacyanoferrate(III), *Asian J. of Chem.,* 4, 508-510.

Thomas, J. M., Johnson, B. F. G., Raja, R., Sankar, G., Midgley, P. A. (2003), High-Performance Nanocatalysts for Single-Step Hydrogenations, *Acc. Chem. Res*., 36, 20-30.

Wilmarth, W. K. & Haim, A. (1961), Mechanism of Oxidation by Peroxodisulphate ion, edited by J. O. Edwards (Interscience, London), 175.

Wu, C. W., Mosher, B. P., Zeng, T. F., Yin, Z. L. (2006), one step green route to narrowly dispersed copper nanocrystals, *J. Nanopart. Res.,* 8, 965-969.

Xiong, J., Wang, Y., Xue, Q. and Wu, X. (2011), Synthesis of highly stable dispersion of nanosized copper particles using L-ascorbic, *Green Chemistry***,** 13, 900 - 904.

Zhang, H. X., Siegert, U., Liu, R. and Cai, W. B. (2009), Facile fabrication of ultrafine copper nanoparticles in organic solvent, *Nanoscale Research Letter***,** 4, 705-708.

Zelechonok, Y. and Silverman, R. B. (1992), Silver(I)/Peroxydisulfate-Induced oxidative decarboxylation of aminoacids: A chemical model for a possible intermediate in the monoamine oxidize-catalysed oxidation of amine, *J. Org. Chem.,* 57, 5787-5790.