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Synthesis of copper nanoparticles and their catalytic activity in oxidation of threonine

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Abstract

Present study describes the fabrication of CuNPs (copper nanoparticles) by chemical reduction method and L-AA (L-ascorbic acid) use as a reducing as well as capping agent. Size of CuNPs was depending on the various concentration of L-AA. The synthesized CuNPs have resistance to oxidation by atmospheric oxygen for two months. The copper nanoparticles were studied by spectrophotometric techniques. The average sizes of copper nanoparticles were found to be 28, 16, 12 nm at increasing concentrations of L-ascorbic acid respectively. Interestingly, it was observed that, the activity depends on the size of particles. The catalysis by colloidal copper nanomaterials was studied kinetically with the oxidation of L-threonine (Thr) by peroxodi sulfate (PDS) at neutral pH. The copper nanoparticles are expected to be play important role in the field of catalysis and reduce water pollution.

Keywords: Copper nanoparticles, L-Ascorbic acid, peroxodisulfate, threonine, catalysis.

Introduction

Research on nanoparticles has received considerable attention since they have unique properties and numerous applications in different areas[1-3]. Metallic nanomaterials are of great interest due to their good chemical, physical and catalyticproperties[4]. Among colloidal transition metal nanomaterials, copper nanomateials receive considerable attention since they are used as an advanced material with electronic, optical and thermal properties[5]. CuNPs were assumed to be cheaper than noble metals. Hence, they are widely use in the field of catalysis and conductive links[6]. Among various methods, the chemical reduction process is potentially selected for the synthesis of CuNPs due to their low price, high efficiency and no need special equipments. It is simple and control of size and shape of particles obtained under controlled conditions is seen[7]. Although the fabrication of CuNPs has been done by different methods, very few studied reported about the size effective NPs as a catalyst[8].

The major problem in fabrication of CuNPs are stability towards the air oxidation and coagulation. So many approaches relevant to the coagulation and oxygen resistance which needs to the remove before use. Some studies reveal that to secure CuNPs by the oxygen, ascorbic acid is use as anantioxidant[9-11]. Therefore this experiment was carried out without inert atmosphere.

Metallic ions play an important role in the oxidative kinetic studies of amino acids by the different oxidants like hexacyanoferrate (III), peroxomonosulfate, peroxodisulfate, cerium (IV), chromium (VI) in the presence of metal catalysts as well as hexacyanoferrate (III), hydrogen peroxide, peroxomonosulfate in the presence of transition metal nanoparticles in aqueous medium have been studied[12-19]. However, different kinds of reaction mechanisms have been suggested but the specific details are yet to be found out.

The peroxodisulphate ion is strong oxidizing agents known in aqueous solution. The standard oxidation reduction potential is calculated to be -2.01V.

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

The reactions of these ions are slowest in absence of any catalyst[20]. The most thoroughly investigated catalyst is Ag(I) ion although reaction involving Cu(II) and Fe(III) ions also have been studied[21].

Decarboxylation of amino acids by peroxo oxidants is an area of demanding research because peroxo oxidants are environmentally benign oxidants and do not produce toxic compounds during their reduction. The applications of metal nanoparticles as catalyst for organic conversion include hydrogenation, hydrosilation and hydration reaction of unsaturated organic molecules as well as redox and other electron transfer process[22-26]. Though studies on kinetic study of amino acid with peroxodisulphate have been extensively done, but in the present study, the universal nature of CuNPs as catalysts was highlighted by employing highly efficient copper nanoparticles for the oxidation of threonine by peroxodisulphate in aqueous medium[14,27].

Materials and methods

Material: For this work, used chemicals are cuprous chloride dihydrate ($CuCl_2.2H_2O$-97%), L-ascorbicacid (vitamin C-98%), threonine and peroxodisulphate were obtained from E. Merck. A freshly prepared solution of peroxodisulphate was prepared before starting the experiments. All chemicals were used as received without further purification. Throughout the study double distilled water was used.

Fabrication of CuNPs: The single step fabrication process for CuNPs starts, when requires amount of copper chloridedihydrate dissolving in 50 ml double distilled water. L-AA (0.01 mol L^{-1}) mixed drop wise in to the solution of copper chloride while at 353 K temperature in oil bath and stirring vigorously. During the reaction, the colour of reaction mixture was progressively changed from white, yellow, orange, brown finally dark brown. The yellow colour changed into orange colour shows the synthesis of CuNPs from L-AA reduction, finally changed into brown color the resulting dark brown solution was centrifuged for 15 minutes. This supernatant was stored for 2 months at ambient conditions.

Characterization: UV-Visible spectroscopy (U.V. 3000^{+}LABINDIA) and FT-IR (ALPHA-T –Bruker) techniques are used for characterization of synthesized CuNPs and information about oxidative product of the reaction. Transmission electron microscope (TEM) (FEI Techni G2S2 Twin) and scanning electron microscope (SEM) (EVO 18 carlzeiss) techniques are used for study of morphology of CuNPs.

Kinetic measurements: All reactions were carried out in Erlenmeyer flasks painted black from the outside to check photochemicalde composition. Calculated volumes of CuNPs and threonine were taken in a reaction vessel and were put in a thermostat maintained at 308K. To start the reaction the calculated quantities of potassium peroxodisulphate solution were mixing in the reaction flasks. The reaction was studied by estimating the remaining peroxodisulphate iodometrically at different interval of time. Since the concentration of amino acid is ten times more than that of the peroxodisulphate, a pseudo first order plots is drawn from which the values of k_{obs} is determined.

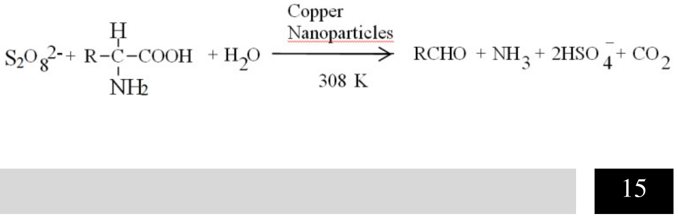
Results and discussion

Metal nanoparticle characterization results: The solution became colorless when L-ascorbic acid wasadded, then gradually turned to yellow, orange, brown and finally dark in 24 h (Figure-1). The fabrication of CuNPs by L-AA is identified by yellow color change in orange color. The peak obtained at 335 nm relevant to the L-AA oxidative product[28]. The second absorption peak of CuNPs was obtained at around 560 nm of UV–Visible wavelength which proves the formation of CuNPs[29,30]. We investigated the dependence of L-AA concentration (0.10, 0.09 and0.08 mol L^{-1}) on the synthesis of copper nanoparticles by UV–Visible spectrophotometer. The absorption peak is increasingly broadening with an increasing concentration of L-AA. These results indicate that a higher L-AA concentration leads to a more effective capping capacity of L-AA and then formed smaller CuNPs. The SEM images are used to identify the shape of CuNPs, which is spherical (Figure-2). The size of CuNPs decreases with the increases the concentration of L-AA, it is identified by results of TEM images and histograms analysis (Figure-3, 4, 5, 6, 7, 8). The size of CuNPs obtained at different concentrations (0.10, 0.09 and 0.08 mol L^{-1}) of L-AA is12, 16, and 28 nm respectively. Since, L-AA molecules encapsulate Cu^{+2} and reduce Cu^{+2} into Cu (0), then the oxidation products adsorb on the resulting CuNPs surfaces, preventing the particles from growing further. As a result, smaller CuNPs can be obtained.

Figure-1: The time evolution photograph of copper nanoparticles formation.

Stability of nanoparticles: The characterization results reveals that reducing and capping agent was L-AA. The antioxidant properties of L-AA came from its ability to scavenge free radicals and reactive oxygen molecules, accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid hydration of 2-carbonyl is also reported and finally converted into polyhydroxyl structure through hydrolysis[28,31,32]. Therefore L-AA plays dual role as reducing agent and antioxidant of CuNPs. As a result, the reaction can be done without any protective inert gas and the dispersion of CuNPs is stable for 2 months after storage.

Stoichiometry: Under the kinetic conditions, the reaction was carried out with excess of peroxodisulphate over threonine in presence of nanoparticles in a thermostat water bath at 308K for 24 hours. The excess of peroxodisulphate was determined iodometrically. An addition of 2, 4-dinitrophenyl hydrazine in the reaction mixture yield brown precipitate of hydrazone derivative of aldehyde[33]. The product aldehyde was confirmed by its FT-IR spectrum (Figure-9). The IR peaks at 3343 cm^{-1}, 2901cm^{-1}, 1607 cm^{-1} are attributed to –NH, –CH, –C=N stretching respectively. From observations of different sets, the stoichiometry of the reaction can therefore be presented by equation-1.



$$S_2O_8^{2-} + R-\underset{NH_2}{\overset{H}{C}}-COOH + H_2O \xrightarrow[308\ K]{\text{Copper Nanoparticles}} RCHO + NH_3 + 2HSO_4^{-} + CO_2$$

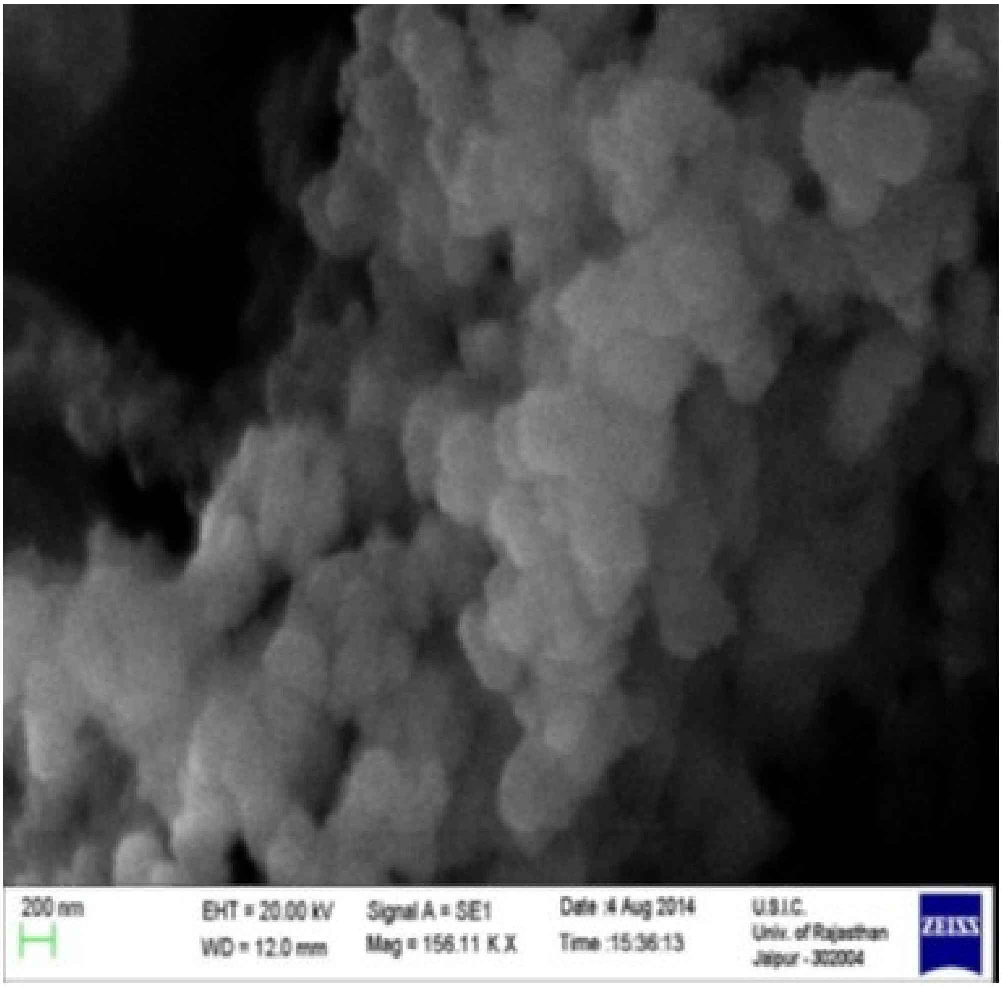


Figure-2: SEM image of copper nanoparticles.

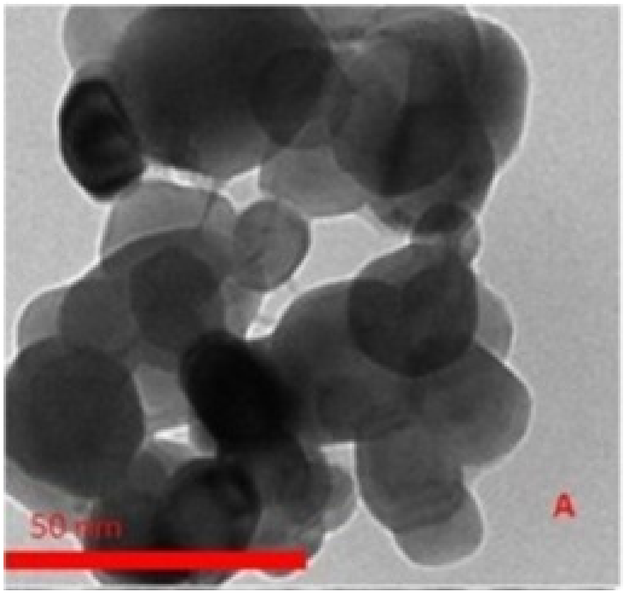


Figure-3: TEM images of the fabrication CuNPs at 0.08 mol L^{-1} concentrations of L-AA: the average diameter of particle is: d= 28 nm.

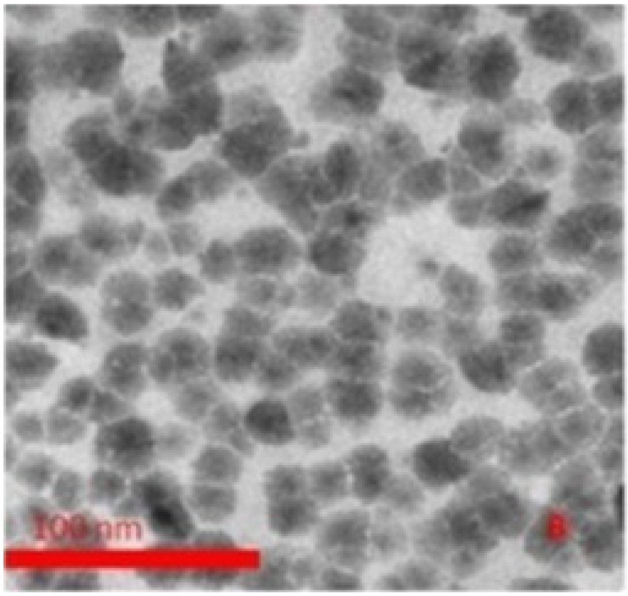


Figure-4: TEM images of the fabrication CuNPs at 0.09 mol L^{-1} concentrations of L-AA: the average diameter of particle is: d= 16 nm.

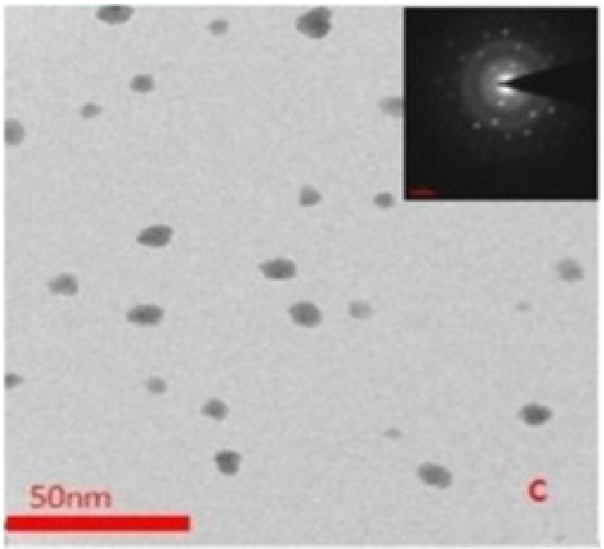


Figure-5: TEM images of the fabrication CuNPs at 0.10 mol L^{-1} concentrations of L-AA: the average diameter of particle is: d= 12 nm.

Ammonia identified by nessler′s reagent, brownish color was observed indicating deamination reaction, carbondioxide was identified by freshly prepared lime water and the solution turned milky indicating decarboxylationreaction.

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 [Thr] = 5×10^{-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 PDS (Figure-10), indicating that the reaction is first order with respect to [PDS].

Threonine 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} and by varying initial concentration of threonine from1×10^{-2}– 7×10^{-2}mol L^{-1} at 308 K temperature. Plot of log k_{obs} versus log [Thr] give straight line parallel to log [Thr] axis indicating zero order dependence with respect tothreonine.

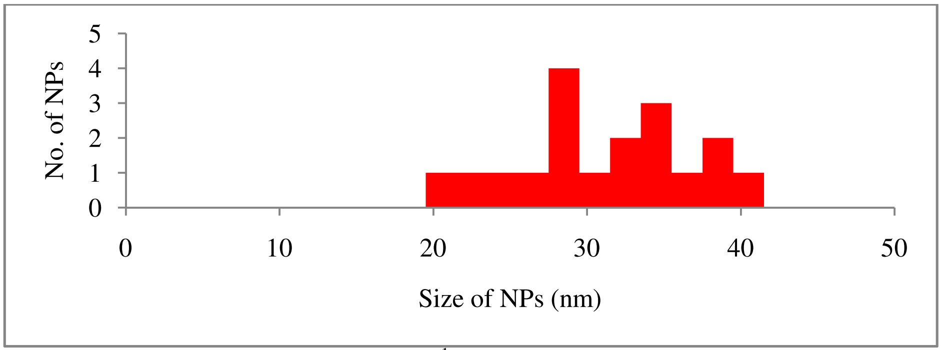


Figure-6: Histograms of the fabrication CuNPs at 0.08 mol L^{-1} concentrations of L-AA: the average diameter of particle is: d= 28 nm.

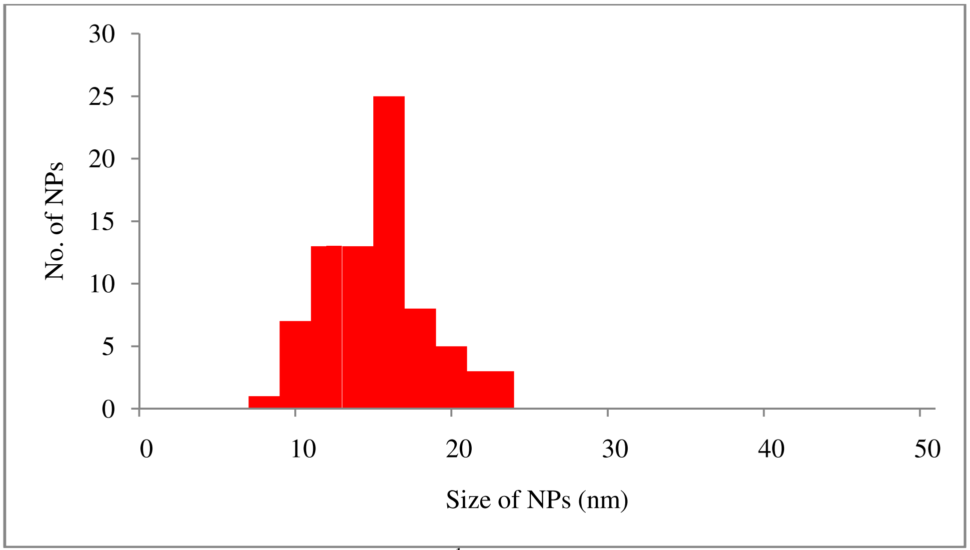


Figure-7: Histograms of the fabrication CuNPs at 0.09 mol L^{-1} concentrations of L-AA: the average diameter of particle is: d= 16 nm.

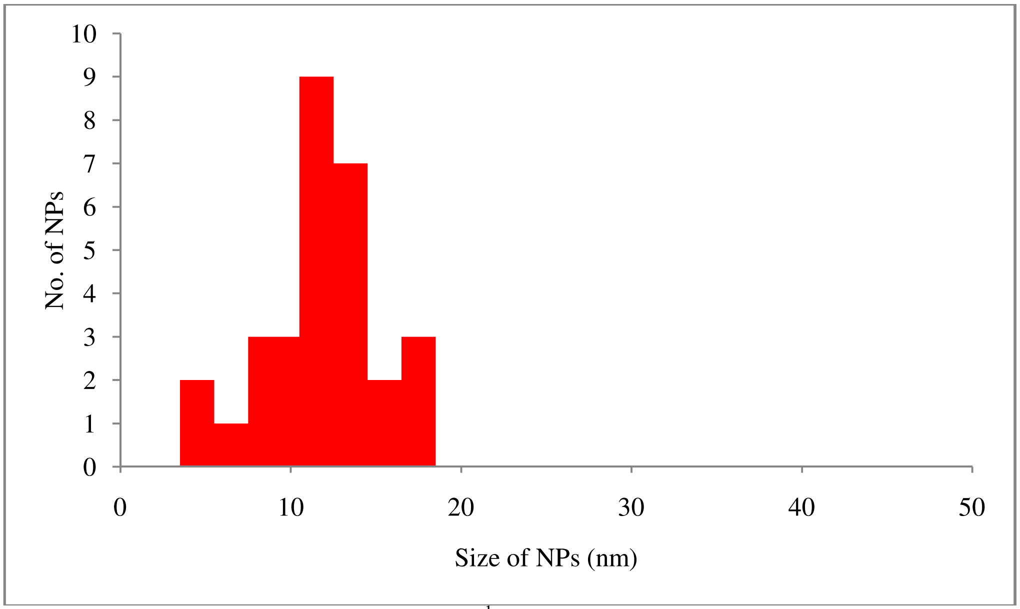


Figure-8: Histograms of the fabrication CuNPs at 0.10 mol L^{-1} concentrations of L-AA: the average diameter of particle is:d= 12 nm.

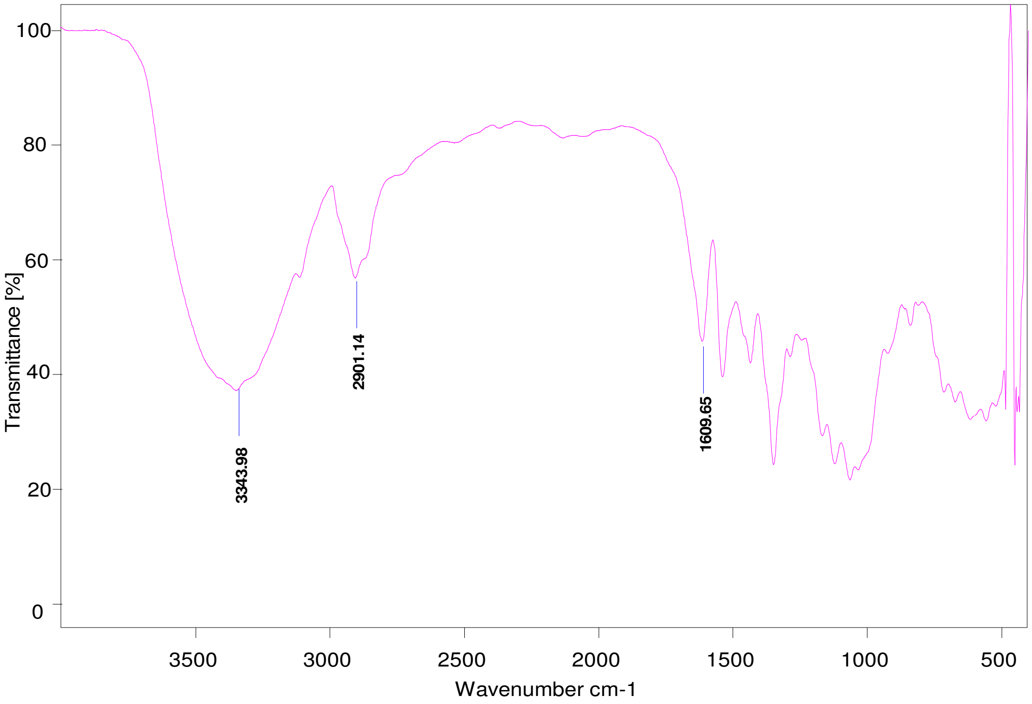


Figure-9: The FTIR Spectra of the oxidation product of threonine oxidation.

Copper nanoparticles dependence: The dependence of CuNPs on the reaction rate of threonine has been calculated with different concentration of CuNPs 1×10^{-6}- 1×10^{-5}mol L^{-1} at three different size of nanoparticles (28, 16 and 12 nm), synthesized at three concentration (0.10, 0.09, 0.08 mol L^{-1}) of L-AA respectively, other chemicals used in reaction and reaction parameters were no changed. When the concentration of copper nanoparticles was increases then rate of reaction were also increases. The size dependence of CuNPs shows when concentration of L-AA is changed from 0.07 to 0.1mol L^{-1}, rate of reaction increases. The variation in rate can be attributed to the diameter changed in the resulting CuNPs. The direction in the calculated K_{obs} being 12>16>28nm (Figure-11). This observation can be apply on the nanoparticles size that as size decreases surface area increases and the active center are also increases.

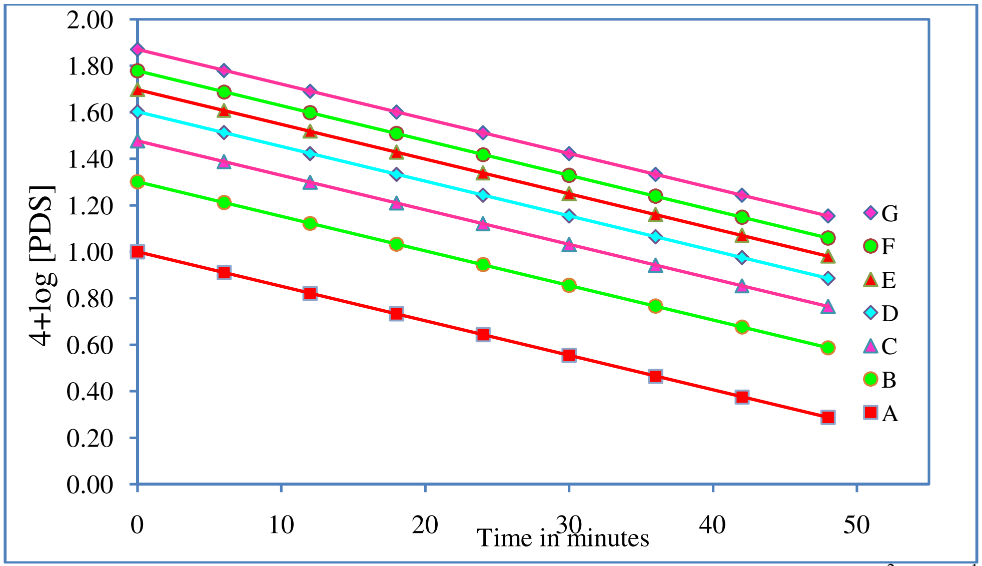


Figure-10: First order plots of the variation of peroxodisulphate concentration at 308 K[Thr]= 5.0×10^{-2} mol L^{-1}, [Cunps] = 1.0×10^{-5} mol L^{-1}, [PDS]$\times10^{-3}$ mol L^{-1} = (A) 7.5, (B) 6.0, (C) 5.0, (D) 4.0, (E) 3.0, (F) 2.0, (G) 1.0.

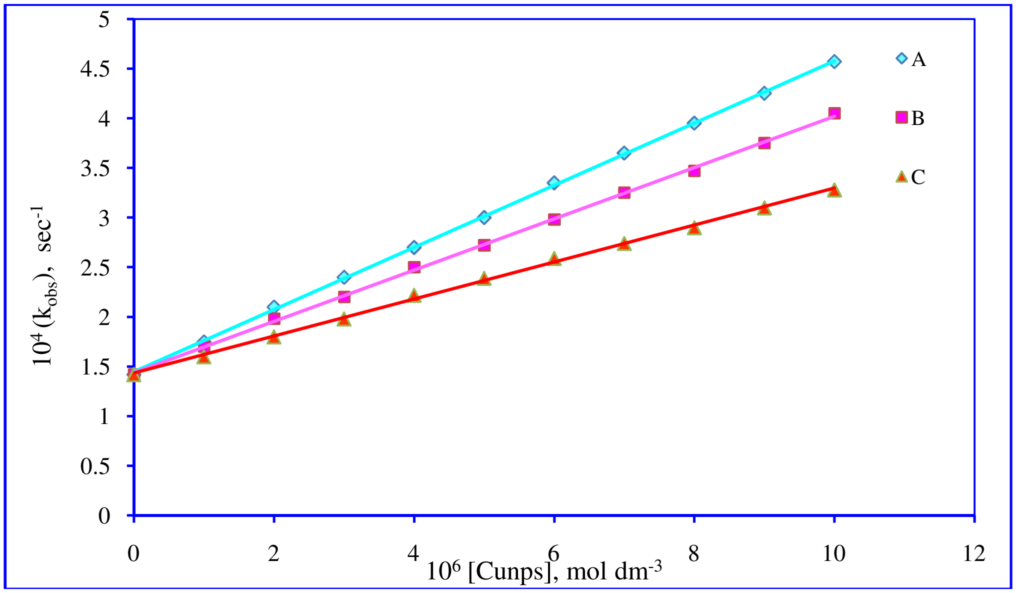
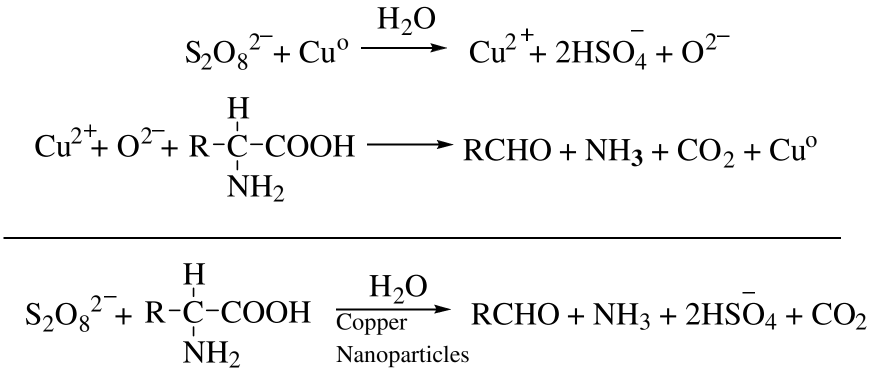


Figure-11: The effect of [CuNPs] at different size of CuNPs in nm (A) 12, (B)16, (C) 28 at fixed [PDS] = 5.0×10^{-3} mol L^{-1}, [Thr] =5.0×10^{-2} mol L^{-1} at 308K.

Temperature dependence: The effect of temperature on the rate of reaction was studied at three temperature 303 K, 308 K, 313 K respectively at constant concentration of other reaction ingredients. A plot of log k_{obs} was made against 1/T, yielded a straight line. The energy of activation (E_a), entropy of activation ($\Delta S\neq$), enthalpy of activation ($\Delta H\neq$), free energy of activation (ΔG) were obtained 22.69 KJ mol^{-1}, -207.32 JK^{-1} mol^{-1}, 22.13 KJ mol^{-1}, 95.226 KJ mol^{-1}respectively. 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) was suggested the formation of rigid transition state with reduction in the degree of freedom of molecules.

Mechanism: The definite mechanism of the homogeneous metal nanoparticles catalyzed 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 threonine, oxidative deamination of threonine occurs in presence of peroxodisulphate only upon addition of CuNPs while peroxodisulphate converted to hydrogen sulphate ion.

The plausible mechanism in support of the observed kinetics is given in Scheme-1.



$$S_2O_8^{2-} + Cu^o \xrightarrow{H_2O} Cu^{2+} + 2HSO_4^- + O^{2-}$$

$$Cu^{2+} + O^{2-} + R-\underset{NH_2}{\overset{H}{C}}-COOH \longrightarrow RCHO + NH_3 + CO_2 + Cu^o$$

$$S_2O_8^{2-} + R-\underset{NH_2}{\overset{H}{C}}-COOH \xrightarrow[\text{Copper Nanoparticles}]{H_2O} RCHO + NH_3 + 2HSO_4^- + CO_2$$

Scheme-1: The plausible route of copper nanoparticles catalyzed oxidation of threonine.

Conclusion

In the present study, highly stable dispersed CuNPs were synthesized in aqueous medium without employing any protecting inert gas. By this green method, synthesis of monodispersed CuNPs (ranging from 12 to28 nm) was obtained using different concentrations of reducing agent. L-AA is used as a reducing agent and antioxidant. The activeness of fabricated CuNPs was explored by rate of decay of threonine at natural pH. Increasing the diameter of CuNPs decreases the activeness of CuNPs. The report indicates that reaction between peroxodisulpfate and threonine in the presence of CuNPs was first order.

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