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A KINETIC STUDY ON COPPER NANOCATALYSIS IN THE OXIDATION OF SERINE BY PEROXOMONOSULPHATE

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Abstract: *Highly stable dispersion of nanosized copper nanoparticles (Cunps) was prepared successfully by chemical reduction method. The synthesized copper nanoparticles were characterized by UV-Visible spectrophotometer, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) analysis. The catalysis by colloidal copper nanoparticles was studied kinetically in the oxidation of L-serine by peroxomonosulphate (PMS) in acidic 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 serine and peroxomonosulphate. The effects of catalyst concentration, ionic strength and temperature on the reaction were also investigated.*

Keywords: *Copper nanoparticle, L-serine, Peroxomonosulphate, Perchloric acid, Oxidation, Kinetics.*

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1. INTRODUCTION

Amino acids act not only as the building blocks in the protein synthesis but they also play a significant role in metabolism. The specific metabolic role of amino acid includes the biosynthesis of polypeptides, proteins and synthesis of nucleotides [1]. Several kinetic studies on the oxidation of amino acids both in acid and alkaline medium and also in presence of metal and non-metal ions catalysts have been reported [2-5]. The study of amino acids becomes important of their biological significance and selectivity towards the oxidant to yield different product [6, 7]. Aqueous solutions of amino acids have been oxidized by Mn(II) [8], ($[Fe(CN)_6]^{3-}$) [9], Chloramines T [10], Peroxomonosulphate [11] etc. in both acid and alkaline media. Very few reports are available on the kinetics of oxidation of serine by peroxomonosulphate [12]. Peroxomonosulphate is a derivative of hydrogen peroxide, replacing one of the hydrogen atoms in H_2O_2 by sulphate group. Peroxomonosulphate is one of the strong oxidizing agents compared to other peroxo oxidants [13, 14]. The predominant reactive species of peroxomonosulphate in acidic medium is HSO_5^-. The HSO_5^- frequently act as a two electron oxidant in redox reactions that involve heterolytic cleavage of peroxo bond [15, 16], oxidative decarboxylation of amino acids is a known and documented in biochemical reaction. Kinetics and mechanism of decarboxylation of amino acids by peroxo oxidants is an area of intensive research because peroxo oxidants are environmentally benign oxidants and do not produce toxic compounds during their reduction.

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 [17-21], 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 [22, 23]. Amongst them copper nanoparticles are paid more attention due to their low cost and easy availability. Copper nanoparticles have also been considered [24, 25] as an alternative for noble metals in many applications such as heat transfer and microelectronics [26]. In the present work, copper nanoparticles were prepared by chemical reduction method, in which L-ascorbic acid is used as reducing and capping agent in aqueous medium. The prepared copper nanoparticles are highly stable and do not show sedimentation even after storage for two months. Therefore, it is of great interest to study metal nanoparticle catalyzed

oxidation of serine using peroxomonosulphate. In this study, we demonstrate the efficiency of synthesized nanoparticles catalyst on the oxidation of serine under a range of different experimental conditions.

2. EXPERIMENTAL

2.1 Material

Peroxomonosulphate (PMS) was obtained from Sigma-Aldrich under the trend name "Oxone". The purity of the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ was estimated by iodometry and found to be 98%. However, the presence of H_2O_2 in the oxone sample was tested and it shows negative results, thus eliminating the chances of hydrolysis of oxone. A fresh solution of oxone was prepared before starting the experiments. Copper Chloride dihydrate ($CuCl_2.2H_2O$-97%), L-ascorbic acid (vitamin C-98%), L-Serine and Perchloric acid were obtained from E. Merck. All other chemicals used in this study were of Analar grade and used as such without any further treatment. Double distilled water was employed throughout the study.

2.2 Synthesis of Copper Nanoparticles

In a synthetic procedure, copper nanoparticles were obtained via a wet chemical reduction route. $CuCl_2.2H_2O$ aqueous solution was prepared by dissolving $CuCl_2.2H_2O$ (0.02 mol L^{-1}) in 50 ml deionized water. The flask containing aqueous solution of $CuCl_2.2H_2O$ was heated to 353 K in oil bath with magnetic stirring. 50 ml of L-ascorbic acid aqueous solution (0.1 mol L^{-1}) was added drop wise into the flask while stirring. With the passage of time, the color of dispersion gradually changed from white, yellow, orange, brown finally dark brown with a number of intermediate stages. The appearance of yellow color followed by orange color 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. Various optimization studies were performed to investigate the size and shapes 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 were carried out with desired concentration of reactants in a 250 ml blackened iodine flask and kept in a thermostat at 308 K. A known volume of peroxomonosulphate solution, thermostatted at the same temperature separately, was pipetted out into the reaction mixture, and simultaneously a timer was started. Consumption of peroxomonosulphate was monitored by iodometric method [27]. The rate of the reaction was studied under pseudo first order condition i.e., [amino acid] » [PMS]. The rate of the reaction followed first order kinetics and the rate constant k_{obs} was calculated from the linear plots of log [PMS] versus time.

3. RESULTS AND DISCUSSION

3.1 Metal Nanoparticles Characterization Results

The UV-Visible absorbance spectrum of synthesis of copper nanoparticles was recorded at different interval of time at every color change as shown in Figure 1. The spectacular color 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 [28]. 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 UV-Visible wavelength which proves the formation of copper nanoparticles [29, 30].

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 [31]. 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

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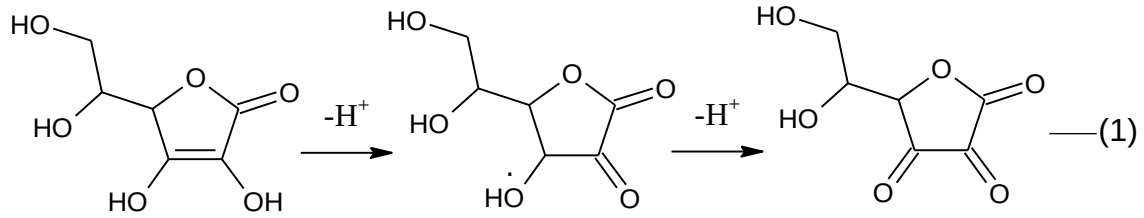
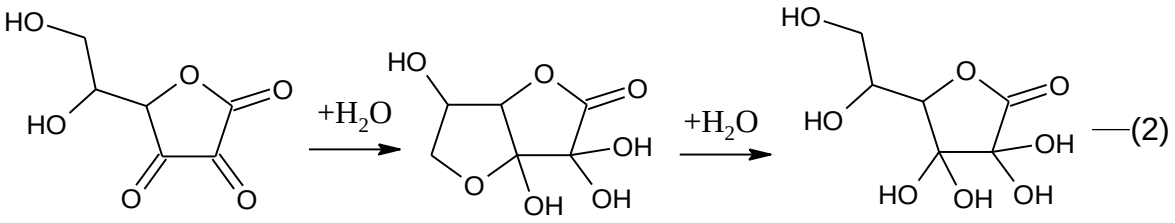
image D of Figure 2. This may be due to collision between small particles, which leads to particle growth [32]. So the optimal concentration of precursor salt is 0.02 mol L^{-1} and 0.1 mol L^{-1} of L-ascorbic acid at 353 K. In this experimental condition, the TEM image of the synthesized copper nanoparticles 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.

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 antioxidant properties of L-ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules [33], accompanying the donation of electrons to give semi-dehydroascorbate radical and dehydroascorbic acid. (Equation-1)



L-Ascorbic acid Semi-dehydroascorbate radical dehydroascorbic acid

The dehydroascorbic acid has three carbonyl groups in its structure. The 1, 2, 3 tricarbonyl is too electrophilic and finally converted into polyhydroxyl structure through hydrolysis [34]. (Equation-2)

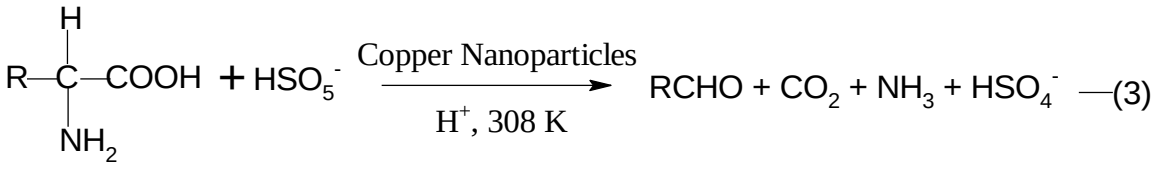


Hydrolysis of dehydroascorbic acid

Therefore L-ascorbic acid plays dual role as reducing agent and antioxidant of copper nanoparticles. Thus reaction can complete without any protective gas.

3.2 Stoichiometry

The Stoichiometry of the reaction was determined for copper nanoparticles catalyzed reaction mixtures containing a large excess of [PMS] over [amino acid]. The reaction mixtures were kept at 308 K for 48 hours and the excess of PMS was estimated iodometrically. The Stoichiometry of the oxidation of serine by an oxygen transfer from peroxomonosulphate in presence of copper nanoparticles was presented by equation (3).



Where R represents -CH_2OH

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 4. The IR peaks at 3367.24 cm^{-1}, 2936 cm^{-1} and 1618 cm^{-1} are attributed to –NH, –CH, –C=N stretching respectively. The deamination of the L-serine in presence of copper nanoparticles was shown in UV- Visible absorption spectrum which is presented in Figure 5.

3.3 Effect of Peroxomonosulphate Concentration

The copper nanoparticles catalyzed oxidation of serine was studied at different concentration of peroxomonosulphate varying from 1×10^{-3} - 7×10^{-3} mol L^{-1} at 308 K temperature, at fixed concentration of [Serine] = 5×10^{-2} mol L^{-1}, [H^+] = 0.01 mol L^{-1}, I = 0.02 mol L^{-1}, [Cunps] = 5×10^{-6} mol L^{-1}. The plot of log [PMS] versus time was linear which was shown in Figure 6, indicating that the reaction is first order with respect to [PMS]. The observed pseudo first order rate constant (k_{obs}) were independent of the concentration of peroxomonosulphate which is given in Table-1.

3.4 Effect of Serine Concentration

The effect of Serine concentration was studied by varying its concentration in the range of 2×10^{-2} – 7×10^{-2} mol L^{-1} at 308 K temperature, keeping all other reactant concentration and conditions constant. The rate of reaction increases with increasing concentration of serine is given in Table -1. Plot the graph between k_{obs} versus concentration of serine, straight line obtained with zero intercept confirm the first order with respect to serine as shown in Figure 7.

3.5 Effect of Copper Nanoparticles Concentration

The effect of copper nanoparticles on the oxidation of serine has been studied by varying its concentration from 1×10^{-6} – 1×10^{-5} mol L^{-1}. The result show the reaction rate increases as copper nanoparticles concentration increases as given in Table-1.

3.6 Effect of $[H^+]$ and Ionic Strength

The rate of reaction was decreases with increasing concentration of $[H^+]$ ion by the variation of concentration of $HClO_4$ at constant other reactants concentration and conditions as given in Table1. The rate of reaction was unaffected by the variation of ionic strength. The ionic strength adjusted by different concentration of $NaClO_4$, which indicates that in our experimental conditions, HSO_5^- and serine (Neutral) to be reactive form of peroxomonosulphate and serine respectively.

3.7 Effect of Temperature

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 which is shown in Figure 8. The energy of activation (E_a) was calculated from the slope of the line to be 21.02 $KJmol^{-1}$. The entropy of activation was calculated by employing the relationship [35],

$$k=\frac{k_B T}{h}\times e^{-\Delta H^{\neq}/RT}.e^{\Delta S^{\neq}/R}$$

Where $\Delta S^{\neq}$ is entropy of activation and other terms have their usual significance. Thus entropy of activation was calculated to be -240.67 JK^{-1} mol^{-1}.

3.8 Mechanism

Serine is neutral amino acid, the probability of initial interaction in between serine and peroxomonosulphate is weak. The deamination of the amino group in serine to NH_3 occurs in the presence of copper nanoparticles by peroxomonosulphate, while peroxomonosulphate is change into hydrogen sulphate ion. Although the definite mechanism of homogenous metal nanoparticles catalyzed oxidation of serine is not clear, based on previous report[12] and present observation the catalytic cycle shown in scheme-1.

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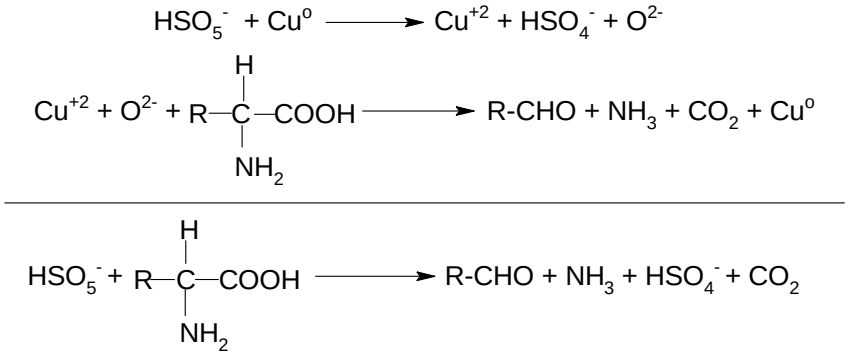

Scheme-I The plausible route of copper nanoparticles catalyzed oxidation of serine

4. CONCLUSION

The 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 serine in aqueous acid medium. The reaction is 10 times faster in the presence of copper nanoparticles. The oxidation study revealed that the reaction was pseudo first order with respect to serine and peroxomonosulphate. The study will be helpful in the biochemical and medical fields.

FIGURES

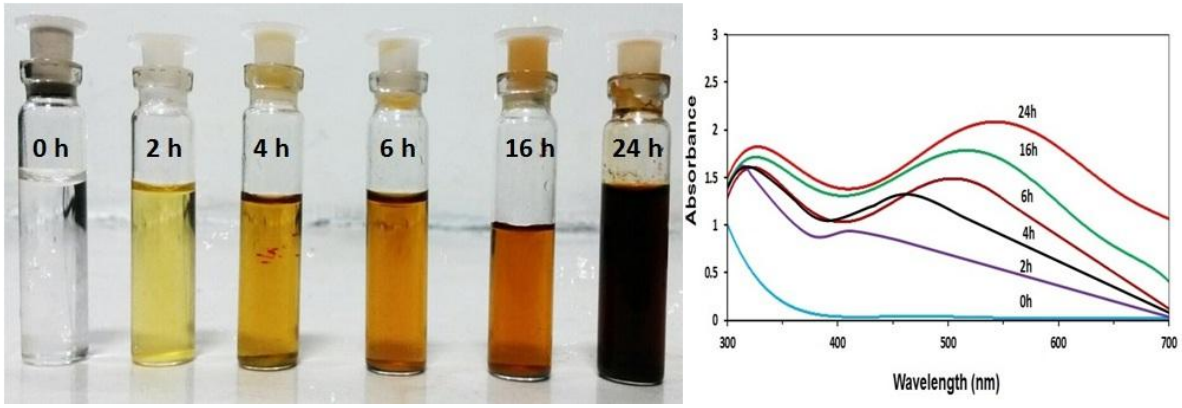

Figure 1. The time evolution of the dispersion photographs and the UV-Visible spectra

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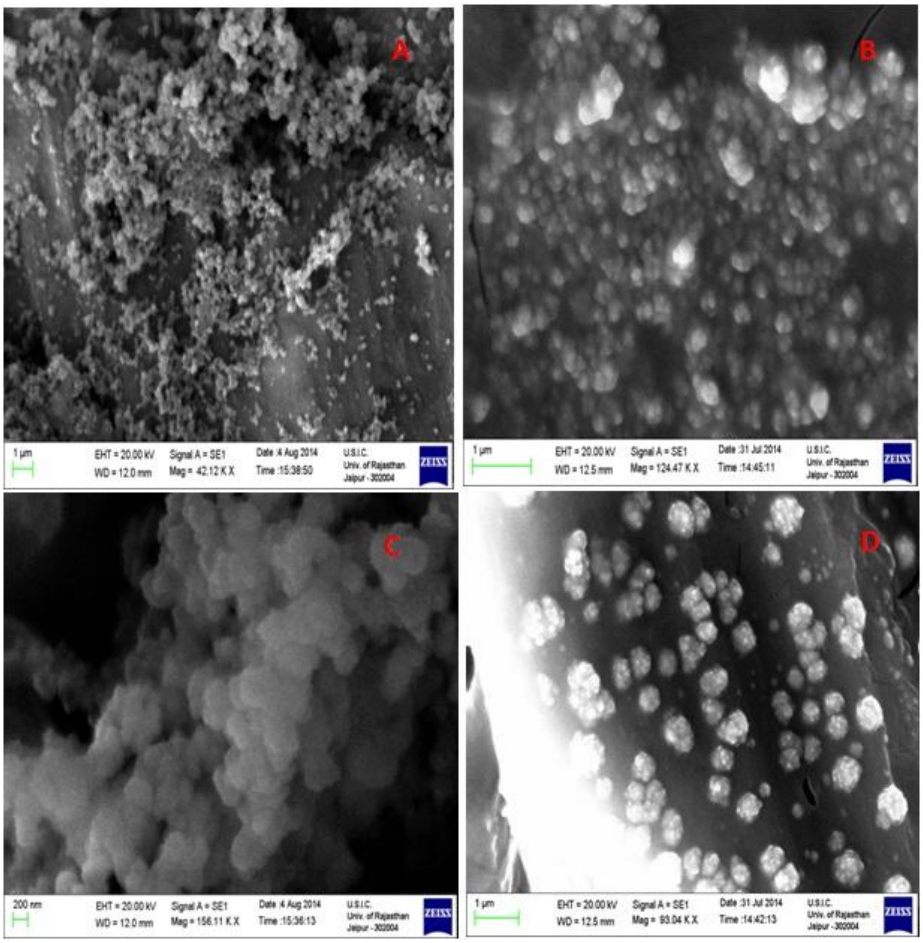

Figure 2. SEM images of the synthesized copper nanoparticles with various concentration of the precursor salt ($CuCl_2.2H_20$) (A) 0.01 mol L^{-1}, (B) 0.015 mol L^{-1}, (C) 0.02 mol L^{-1}, (D) 0.03 mol L^{-1}

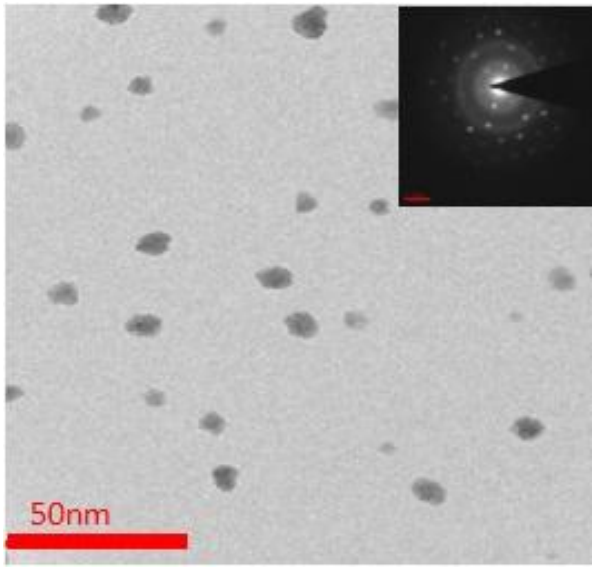

Figure 3. TEM image of synthesized copper nanoparticles At the optimal experimental conditions

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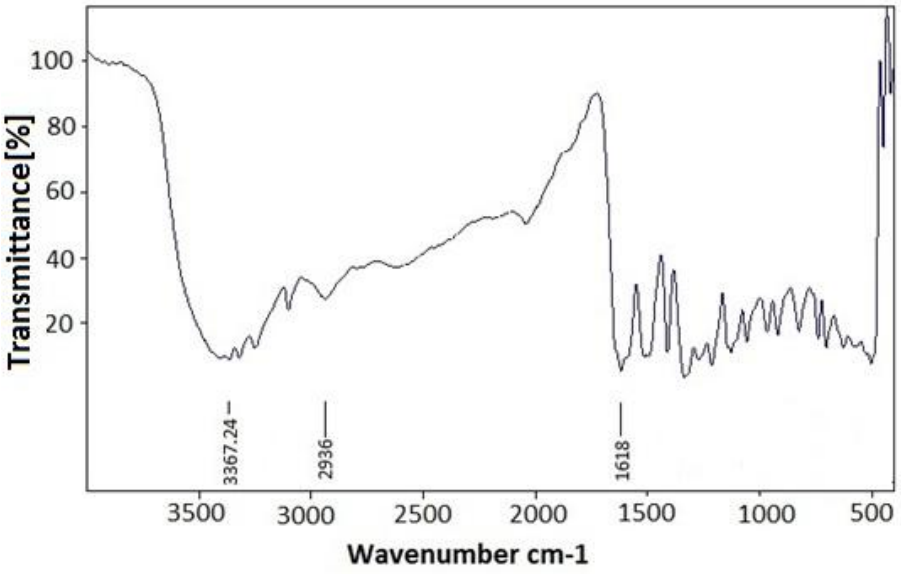

Figure 4. The FTIR Spectra of the oxidation product of serine oxidation

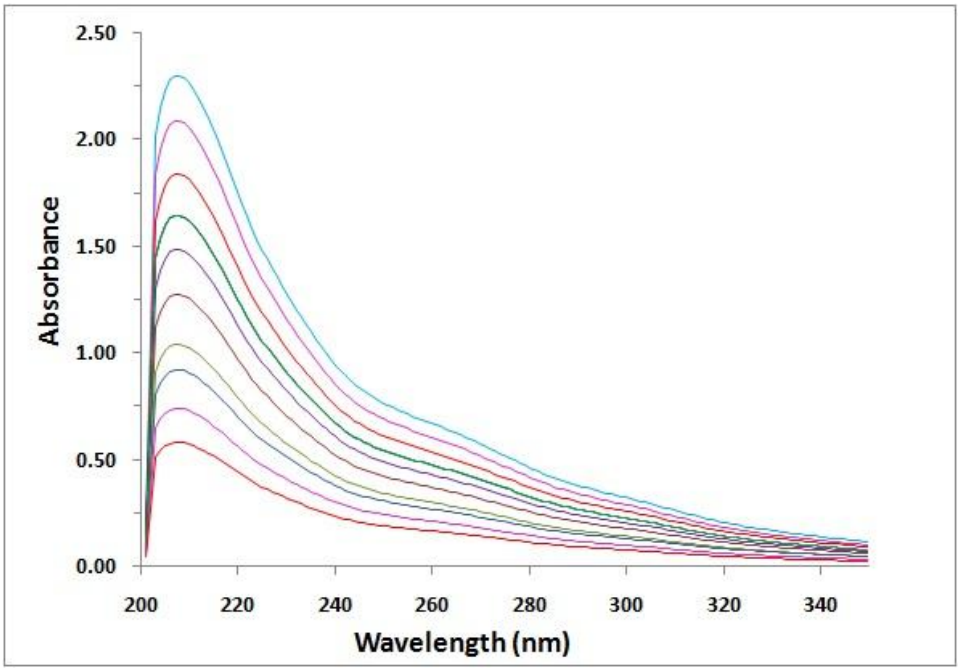

Figure 5. UV absorption spectra for the deamination of L-serine in the presence of the copper nanoparticles

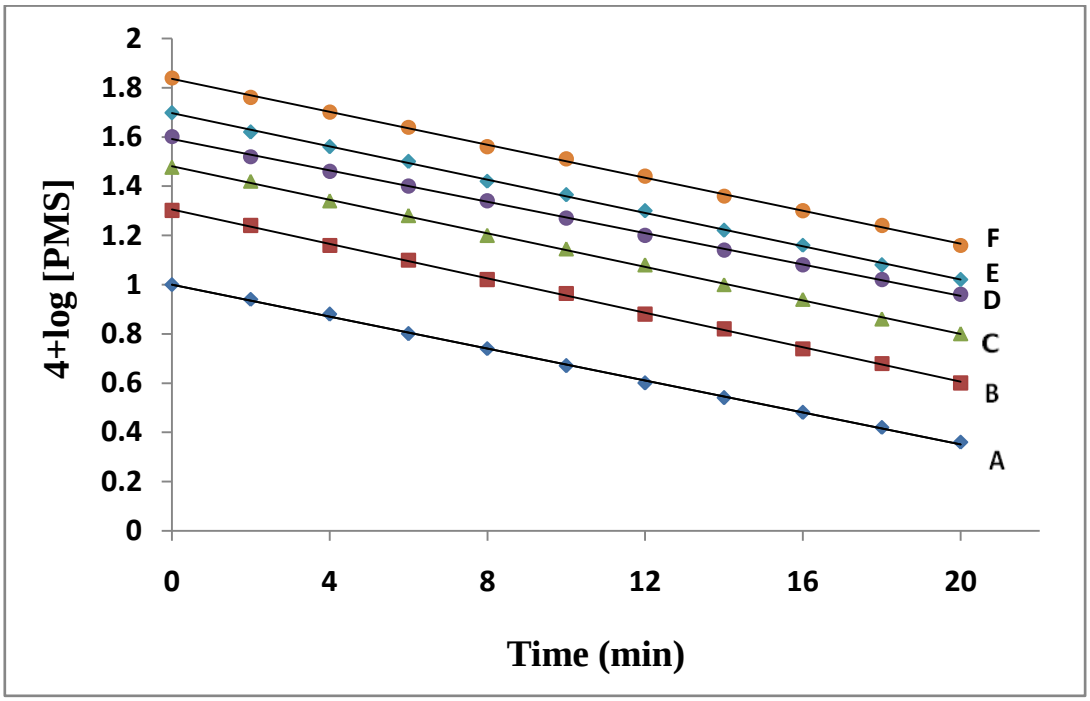

Figure 6. First order plots of the variation of Peroxomonosulphate concentration at 308 K [Serine]= 5.0×10^{-2} mol L^{-1}, [Cunps] = 5.0×10^{-6} mol L^{-1}, $[H^+]$ = 0.01 mol L^{-1}, I = 0.02 mol L^{-1}. [PMS]$\times10^{-3}$ mol L^{-1} = (A) 1.0, (B) 2.0, (C) 3.0, (D) 4.0, (E) 5.0, (F) 7.0

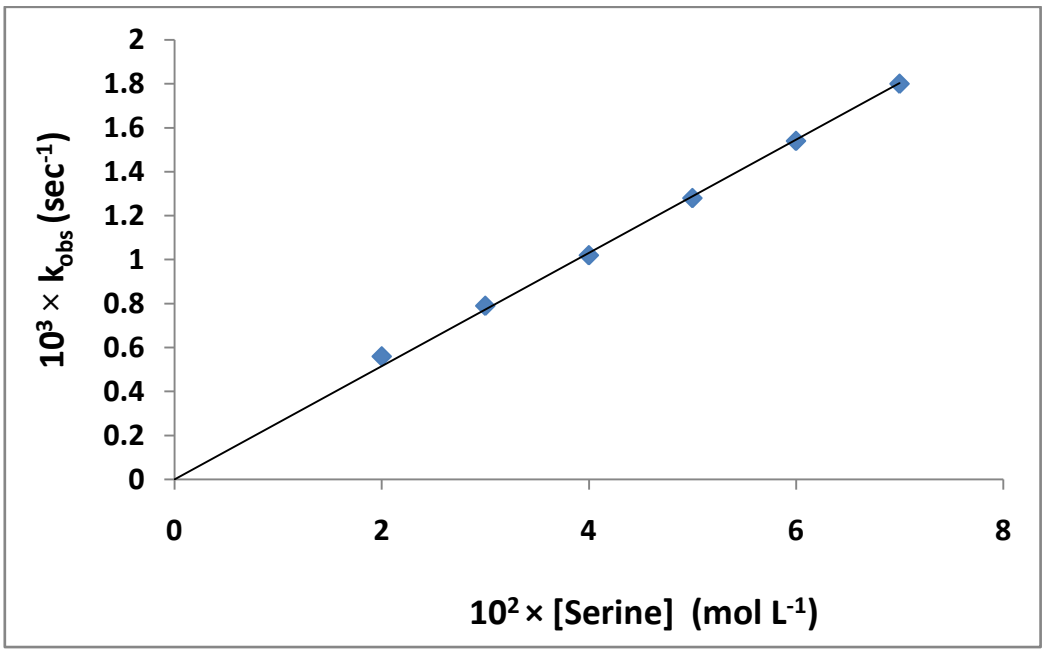

Figure 7. The variation of Serine concentration [PMS] = 5.0×10^{-3} mol L^{-1}, [Cunps] = 5.0×10^{-6} mol L^{-1}, $[H^+]$ = 0.01 mol L^{-1} and I = 0.02 mol L^{-1} at temperature 308K

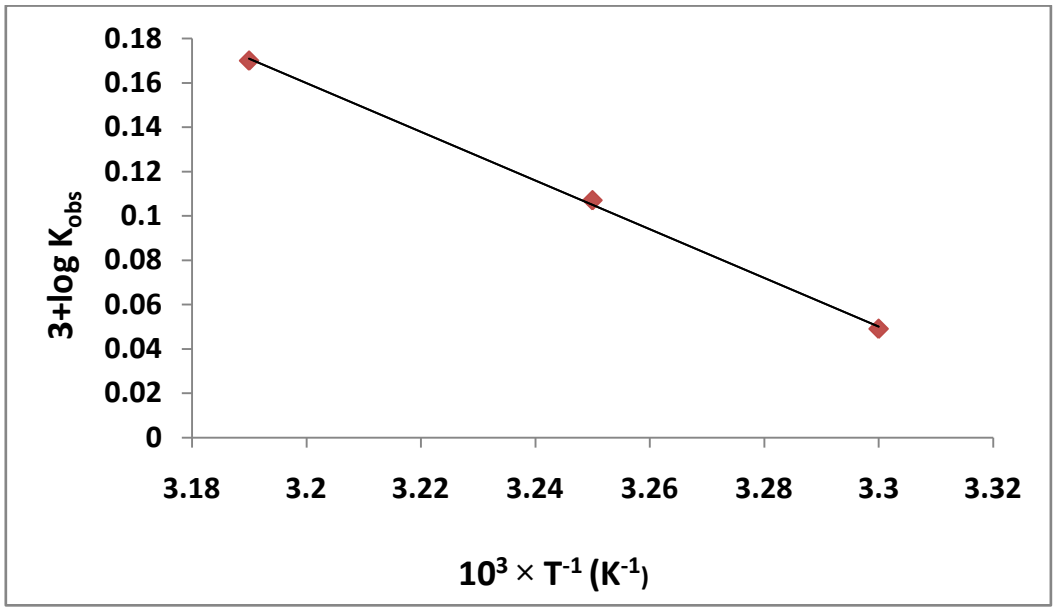

Figure 8. Plot of Temperature dependence

[PMS] = 5.0×10^{-3} mol L^{-1}, [Serine] = 5.0×10^{-2} mol L^{-1}, [Cunps] = 5.0×10^{-6} mol L^{-1}, $[H^+]$ = 0.01 mol L^{-1} and I = 0.02 mol L^{-1}

TABLE

Table 1: Effects of variation of [PMS], [Serine], [Cunps], $[H^+]$ on the oxidation of Serine by Peroxomonosulphate at fixed Ionic Strength (I) = 0.02 and Temperature 308 K.

S. No.	10^3 [PMS] (mol L^{-1})	10^2 [Serine] (mol L^{-1})	10^6 [Cunps] (mol L^{-1})	10^2 $[H^+]$ (mol L^{-1})	10^3 k_{obs} (s^{-1})
1.	1.0	5.0	5.0	1.0	1.26
2.	2.0	5.0	5.0	1.0	1.28
3.	3.0	5.0	5.0	1.0	1.27
4.	4.0	5.0	5.0	1.0	1.27
5.	5.0	5.0	5.0	1.0	1.28
6.	7.0	5.0	5.0	1.0	1.26
7.	5.0	2.0	5.0	1.0	0.56
8.	5.0	3.0	5.0	1.0	0.79
9.	5.0	4.0	5.0	1.0	1.02
10.	5.0	5.0	5.0	1.0	1.28
11.	5.0	6.0	5.0	1.0	1.54
12.	5.0	7.0	5.0	1.0	1.80
13.	5.0	5.0	1.0	1.0	0.40
14.	5.0	5.0	2.0	1.0	0.64
15.	5.0	5.0	3.0	1.0	0.84
16.	5.0	5.0	4.0	1.0	1.06
17.	5.0	5.0	5.0	1.0	1.28

18.	5.0	5.0	6.0	1.0	1.57
19.	5.0	5.0	7.5	1.0	1.83
20.	5.0	5.0	10.0	1.0	2.30
21.	5.0	5.0	5.0	1.0	1.52
22.	5.0	5.0	5.0	2.0	1.47
23.	5.0	5.0	5.0	4.0	1.38
24.	5.0	5.0	5.0	5.0	1.28
25.	5.0	5.0	5.0	7.0	1.22
26.	5.0	5.0	5.0	10.0	1.12

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