6.1 Introduction

Oxidation reactions of α-amino acids (AA) are one of the most relevant biochemical reactions because, such reactions serve as models for protein oxidations[180,261]. Also, uncharacterized oxidation reactions of α-amino acids involving a wide range of oxidants are of particular concern in biotechnology and medicine. Simple amino acids present in municipal waste waters cause serious eutrophication in water bodies. Pharma industries dealing with biochemcials and tanneries are some of the major sources of waste waters containing amino acids[262]. It is essential to remove or oxidatively degrade the dissolved amino acids from waste waters. Non enzymatic model oxidation reactions involving α – amino acids and a wide variety of oxidants are reported plenty in literature [263-265]. Some selective oxidation reactions are reported involving metal catalysts. Transition metal ions of Ag, V, Fe, Ru, Mn etc. are reported to act as catalyst for some of the α – amino acid oxidations[266-268].

With the emergence of metal oxide nanoparticles possessing appreciable stability and high surface area per particle, their potential use as catalyst for organic biochemical relevant reactions stands well documented in recent years[139-160 ]. The bio polymers stabilized metal oxide nanoparticles of cheap, cost effective and
abundant transition metals like Cu, Ni, Fe etc. when used as catalysts are expected to produce ecofriendly process enroutes[147,157-159]. Since two decades of time oxidations of abundant transition metals like Cu, Ni, Fe etc. have been extensively used in many chemical areas including catalysis, synthetic organic chemistry, paints, electronic semiconductors etc. The nanoparticles of oxides of transition metals are considered as new materials with potentials in electronics, chemicals and in optics[261]. Among the metal nanoparticles is a well known p-type semiconductor and gained increasing attention in research due to natural abundance, low production cost, high stability and good electrical properties that make it suitable for application as sensors, photocatalysts and electrochemical sensor, etc. In addition, there are many reports where nanoCuO has been used as catalyst for carbanoscientous reactions. In the present work the bio polymers such as poly ethylene glycol(PEG) and carboxy methyl cellulose(CMC) are used in the preparation of Copper oxide nanoparticles(CuOnps) and the subsequent catalytic activities are compared with the similarly synthesized CuOnps having poly N-vinyl pyrrolidone (PVP) which is a synthetic polymer, as the stabilizer. PVP is a widely used metal nanoparticle stabilizer in numerous mono and bi metal nanoparticle preparations. α-aminoacids such as glycine(gly), phenyl alanine(phe), leucine(leu), valine(val) and serine(ser) are chosen for the oxidation with sodium peroxomonosulphate, an hydrophilic oxidant. The follow up of AA oxidations in the presence of catalysts which are ecofriendly are widely used in the areas of environment, biotechnology, food industry, chemical laboratory and leather industries. In the breakdown of proteins which is a major process in the leather industry oxidation of AAs are involved. Such studies are helpful to design and develop electrochemical sensors that are made with
inert and conducting metal plates serving as electrodes coated with nanoCuO particles using nafion as the binder. Such coated electrodes after characterization can be used as electrochemical sensor of the analytes containing α-AA precursors either in the pure or mixture form. Sodium peroxomonosulphate (PMS) is a biogenic oxidant which after oxidation gets converted to sodiumbisulphate. Nano CuO, nanoNiO and nano Fe₂O₃ are interactive towards HSO₅⁻ ion through hydrogen bonding interactions. Hence in the present work, the role of nanoCuO, nanoNiO and nano Fe₂O₃ serving as catalysts for the oxidation of α-AAs under ambient conditions using PMS as the oxidant has been undertaken. Pseudo first order rate coefficient values are used to investigate the catalytic activity of CuOnps, having three different stabilizers.

6.2 Sizes of nanoCuO, nanoNiO, nano Fe₂O₃ particles

The details of the α-AAs and the preparations of nanoCuO, nanoNiO and nano Fe₂O₃ particles are presented in the experimental section. The particle size characterizations are carried out using UV spectra, FESEM, HRTEM and PXRD measurements.

The UV spectra of the three types of Cu nps having PEG, CMC and PVP stabilisers are presented in Fig.6.1. The UV peaks at 303nm, 307nm and 309nm correspond to the CuOnps having PEG, CMC and PVP as stabilizers[270]. The larger wavelength peak samples show higher nanosize range. The nanoparticles are analyzed by powder XRD using Bruker Advance D8 model diffractometer. Fig.6.2 presents the PXRD profiles of CuO, NiO and Fe₂O₃ nps. The HRTEM and FESEM
photographs are shown in Fig 6.3 & 6.4. The morphology and the size of the nano crystallites are measured from HR-TEM images. The values coincided with those calculated from Scherrer formula using XRD data. 9.0nm, 13.0nm and 16nm ±1.0nm sizes are found for PEG, CMC and PVP stabilized CuOnps respectively.

6.2.1 Morphology and Nanoparticle size Analysis

The CuOnps formation pathway in the presence of NaOH can be considered as follows:

\[
\text{Cu}^{2+} + 2\text{Cl}^- + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2\text{NaCl}
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO} \text{ (nano)} + \text{H}_2\text{O}
\]

Table 6.1 Sizes of nano metal oxides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nanoparticles</th>
<th>PEG</th>
<th>CMC</th>
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<td>Fe$_2$O$_3$</td>
<td>13</td>
<td>16</td>
<td>19</td>
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</tbody>
</table>

The peak patterns in the PXRD patterns of the CuOnps shown in Fig. 6.2 are assigned according to JCPDS data file[271-273]. Applying the Scherrer formula on the peak with highest intensity, the sizes are found to be 8.5nm, 13nm and 16nm corresponding to PEG, CMC and PVP stabilized CuOnps respectively. In Fig. 6.4 FESEM photographs are given and the nano particles are found to be spherical and
nearly monodisperse in nature. From the HRTEM photographs shown in Fig.6.3, the average particle size was determined by counting 300 particles and found to be 9nm, 13nm and 16.5nm with ±1nm precision corresponding to the CuOnps of PEG, CMC and PVP stabilizers. These values agree with the PXRD results. The polydispersity of the sample was found to be narrow and within 8% of the particles with differed sizes. In Table 6.1 size of nano metal oxides are given. The trend in the sizes of CuOnps increases as PEG<CMC<PVP. That is, the biostabilisers produce smaller nanoparticles than the synthetic polymer PVP, under similar conditions.

6.3 Catalytic Oxidation

In a typical experiment, double walled three necked 100ml glass round bottomed flask was used into which 50ml of fresh aqueous solution of 10mM sodium peroxomonosulphate was added drop wise.10ml solution of the 1mM α-amino acid and 1mg of CuOnpsand diluted to 30ml aqueous solution are added drop wise from the each neck of the flask simultaneously with continuous stirring. The temperature was maintained at 30ºC by circulating thermo stated water.

The absorbance spectra of the solution are recorded at regular time intervals immediately after the addition of the catalyst. In the absence of CuOnps, it took more than 8 hours to initiate the oxidation of amino acids and proceeded very slowly for several hours under the same conditions. In the presence of CuOnps, the reaction completed within 2-3 hours time. The product was recovered by EtOH solvent extraction. The completion of the reaction was ensured by UV-VIS spectra where the absorbance decreased to baseline. The time of completion of the reaction
was noted during this process. If any unreacted reactant remained, from the absorbance values the concentrations are noted and the % substrate reacted within the time of reaction was calculated. From the absorbance variation with time intervals, the progress of the reaction was monitored. Pseudo first order conditions were maintained by adding excess of oxidant with respect to the reductants. Kinetic plots constituting logOD₀/ODₜ versus time are plotted and the slope values when multiplied by 2.303 produced the rate coefficient (k) values. OD₀ and ODₜ are the values of absorbances at time equal to zero and at any time ‘t’ respectively.

6.3.1 Catalytic oxidation of α – amino acids

A combination of CuOnps and the oxidant PMS are found essential to bring out the oxidation reaction of α – amino acid at 30°C. All the oxidations are carried out with excess of the oxidant for pseudo kinetic conditions. The products are isolated from solvent extraction technology after the completion of the reaction. Using TLC method, the oxidized products are sorted out and by doing so, only single spots are obtained. In scheme 1, the overall oxidation reaction studied in the present work has been put forth. PMS acts as an oxidant through its oxygen atom transfer. Hence the reaction under mild thermal effects, involves amine group transformation to N-hydroxyl amino group. This forms the initial stage of oxidation of amino acids and may be so in case of proteins comprising these α – amino acids. Presence of N-hydroxyl amino groups are ascertained using FT-IR.
Scheme 1 The overall oxidation of $\alpha$-amino acid by an oxygen atom transfer from peroxomonosulphate in aqueous medium

In Fig. 6.5, the typical UV–VIS spectra of the $\alpha$–amino acids and their time variance spectra under various catalyst conditions are presented. The absorbance – time variance spectra for the six $\alpha$–amino acids in presence of the three types of CuOnps are presented in Fig 6.6. The corresponding kinetic plots for the rate coefficient values determination by plotting $\log \text{OD}_0/\text{OD}_t$ versus time, are presented in Fig 6.7. When the slope values of the linear plots are multiplied by 2.303, the rate coefficient(k) values are obtained. In Table 6.2 & 6.3, the reaction parameters such as reacted, time of reaction and the pseudo first order rate coefficient values for the three types of CuOnps, NiOnps and Fe$_2$O$_3$Onps employed as catalyst are given.

In Table 6.2 based on the k values, it may be seen that CuOnps stabilized with PEG catalyse better than the CuOnps containing CMC and PVP. The catalytic activity of the CuOnps seems different when the organic stabilizer nature was changed such as PEG, CMC and PVP. Although there are no particular chemical interaction between the organic stabilizer and the respective amino acids, the difference in catalytic activity can be attributed to the size variations in the resulting CuOnps. Interestingly it was found that keeping other conditions constant, the
catalytic activity depends on the sizes of nanoparticles. The trend in the size of the nanoparticles being \textbf{PVP}\textgreater\textbf{CMC}\textgreater\textbf{PEG}. The trend in the rate coefficient values being \textbf{PEG}\textgreater\textbf{CMC}\textgreater\textbf{PVP}. This effect can be attributed to the nanosizes of the particles, that as size decreases surface area increases and the active centers proportionately increase too. Upon comparing the nanoparticle sizes, PEG – CuOnps are smaller than CMC – CuOnps which in turn is smaller than PVP – CuOnps. Because of the larger surface area to volume ratio value per particle, and for the PEG and CMC polymers having more oxy (-O-) and hydroxyl (-OH) functional groups that efficiently help in the binding of the oxygen from the peroxomonosulphate ion through H-bonding, the above trend seem to be followed. PEG and CMC possibly show greater extents of H-bonding forces in addition to the capping and stabilizing effects of CuOnps than the PVP stabilized CuOnps. Keeping the PEG-CuOnps in constant amounts, the reactivity trend set among the six $\alpha$ – amino acids investigated here has been found to be \textbf{ala}\textgreater\textbf{gly}\textgreater\textbf{leu}\textgreater\textbf{val}\textgreater\textbf{phe}\textgreater\textbf{ser}. Also, the overall trend determined correlates to the structural effects of the $\alpha$ – amino acids. The rate coefficient values observed are comparable with the reported values of analogous oxidation reactions of $\alpha$ – amino acids reported[29]. Hence CuO being a cheap and abundant metal oxide when converted as nanoparticles using polymeric stabilizers, it has been found to act as a good catalytic agent. It is also encouraging to note that CuOnps having greener stabilizers like PEG and CMC prove to be effective catalysts than those with synthetic polymer(PVP) as stabilizer.
6.4 FT – IR spectral studies

After completion of the reaction when the contents are analyzed through TLC, single and bigger spots are extracted out using organic solvents like EtOH. The end products are recovered from the extractions and subjected to FT – IR analysis. In Fig.6.8, the FT – IR of N-hydroxylated α-amino acid products are presented. The highest frequency peaks are observed around 3650cm\(^{-1}\) in the products from all the amino acids which are identified with the O-H stretchings. Identification of strong peaks around 3300cm\(^{-1}\) can be assigned for N-H stretchings. Around 895cm\(^{-1}\) region strong peak is observed which is attributed for N-O stretching. The IR peaks at 1625cm\(^{-1}\), 1357cm\(^{-1}\) and 1115cm\(^{-1}\) are attributed to ONH, NOH and HNO bending and asymmetric modes respectively. The skeletal vibrations and the overall finger print region all remain same with the parent compounds which indicates that the amino group is selectively hydroxylated.

6.5 Cyclic Voltammetric studies

A fully computerized electrochemical system (CHI 660B) was used along with the three electrode system cell under nitrogen purging. Glassy carbon electrode (purchased from Sinsil International) as the working electrode, Ag/AgCl as the reference electrode and platinum wire as the counter electrode are used. 1M KNO\(_3\) aqueous solution served as the supporting electrolyte. Milli-Q deionised water was used throughout.

The glassy carbon electrode(GCE) was polished with fine alumina powder (lower than 0.3micron grain size) on a wet polishing cloth and washed
repeatedly with Milli-Q water. This procedure was repeated until GCE surface was a shiny black mirror. The cell was filled with the desired volume (20ml) of the analyte solution and nitrogen purged. nitrogen (analar grade) gas was used for purging.

CuOnps possess p-type semiconductor properties. Using chemical kinetics the catalytic properties of nanoCuO for the AA oxidations having PMS oxidant has been found successful based on the reports in the earlier sections in this chapter. In recent years, compared to many methods that have been developed for the determination of organics that are essential, the electro chemical detection and oxidation-reduction method has attracted much attention. Using the nps many kinds of electrochemical sensors and electrode surface coatings with unique and special properties are constructed. Among these catalysts such as CuOnps have gained increasing attention for its applications such as gas sensors, photocatalysts and electrochemical sensors. Previous investigations on nano Fe$_2$O$_3$ modified electrodes and certain nanoCuO structures coated on electrodes have been used for detection, estimation and to follow the redox processes of organic substrates. Due to the large specific surface area, low detection limits, fast response time and simplicity of operations, CuO coated modified electrodes are expected to exhibit improved performances.

In the present work, electrochemical studies involving CuOnps coated glassy carbon electrode (GCE) has been fabricated to follow up the oxidation of simple $\alpha$-AAs using PMS as the oxidant.
The GCE with diameter 3mm was polished with 1700micron diamond salt paper and washed successfully with double distilled water and EtOH in an ultrasonic bath. 25 cyclic scans were carried out in the potential +2.0V to -2.0V (Vs SCE) in the solution of 1M H$_2$SO$_4$ analyte. Exactly weighed 5mg nanoCuO powder was dispersed in 3ml EtOH solution. 20µl of nanoCuO solution was cast on the cleaned surface of GCE and dried using N$_2$ gas. The nanoCuO modified GCE was used for various electrochemical studies. In Fig.6.9, the cyclic voltammograms of GCE in the absence and presence of nano-CuO at pH=7.0 in 0.1M PBS analyte recorded are given. No redox peak was observed when bare GCE was used. However nanoCuO/GCE was used as the working electrode a pair of well-defined redox peaks was obtained with an average formal potential of -0.1895V. The cathodic peak and the anodic peak are found at -0.282V and -0.097V when a scan rate of 50mV/s was used. The redox peaks are attributed to the electrochemical reduction of CuO. Based on the literature reports the cathodic peak corresponds to the reduction of CuO to Cu$_2$O and the anodic peak is due to Cu$_2$O conversion to CuO. When bare GCE was used to run the cyclic voltammogram in the same analyte containing the α-AAAs, there was feeble response regarding the current and the peak potentials. However when the cyclic voltammograms of PEG-CuOnps coated GCE having α-AA and PMS in the analyte are run, redox peaks found are analysed as follows: In Fig.6.9A, the cyclic voltammograms are recorded in sequence as a, b, c etc. In a, PEG-CuO/GCE electrode in the absence of PMS and AA is recorded. When PMS was added, instantly the anodic peak occurring at -0.097V intensity shoots up significantly. This is because the anodic peak corresponding to Cu$_2$O to CuO oxidation is favoured by PMS shown in 6.9Ab. Thus, oxidant PMS,
significantly increases this process and the peak current is increased enormously. The cathodic peak at -0.282V corresponding to CuO to Cu$_2$O remains unchanged. To the analyte containing PMS when the AA α-leu added, the nanoCuO/GCE responded with major alterations in the cyclic voltammograms. There was no change in the cathodic peak at -0.282V corresponding to CuO to Cu$_2$O (Cu(II)→Cu(I) takes place) and an additional cathodic peak at -0.42V with significant peak current was observed. This occurs due to Cu(I)-leu complex formation. In the anodic region an anodic peak at -0.36V appears which is due to leu-Cu(I) to Cu(II) while the original anodic peak at -0.097V disappeared completely. This observation indicates that presence of AA enhances the oxidation of Cu$_2$O to CuO through complexation.

In order to bring out the catalytic activity of nanoCuO in the AA oxidation using PMS, cyclic voltammograms are recorded separately by changing the sequence of addition in the analyte. In Fig.6.9BnanoCuO/GCE in the bare form produced the same cyclic voltammogram recorded in the earlier case. As soon as α-AA leu was added and without PMS, the cyclic voltammogram showed two cathodic peaks and two anodic peaks. The cathodic peak 1 occurred at -0.282V corresponding to CuO→Cu$_2$O and the second cathodic peak occurred at -0.42V due to Cu(I)-leu complex and anodic peak at -0.36V occurred due to Cu(I)-leu to Cu(II) and the anodic peak at -0.097 due to Cu$_2$O to CuO conversion. To this analyte mixture when PMS was added the cyclic voltammogram retained cathodic peak at -0.282V and the second cathodic peak at -0.42V. In the anodic region, the anodic peak at -0.36V corresponding to leu-Cu(I) to Cu(II) exhibited very high peak current because PMS aids Cu(I) to Cu(II) oxidation and the original anodic peak at -0.097V
vanished completely. This cyclic voltammogram resembles almost to the cyclic voltammogram of nanoCuO/GCE+PMS+leu. These visible changes recorded in cyclic voltammograms clearly indicate that PMS interacts well with the CuOnanocatalyst and further oxidises the AA.

All the AAs chosen in the present work are not found electroactive themselves, but the electrochemical response is through the changes in the nanoCuO/GCE peak potentials. The plausible mechanism in support of the observed kinetics and electrochemical observation is given as follows:

\[
\begin{align*}
\text{HSO}_5^- + 2\text{Cu}^{II}\text{O} & \quad \rightarrow \quad \text{Cu}_2\text{O} + \text{HSO}_4^- + 2\text{(O)} \\
2\text{(O)} + \text{Cu}_2\text{O} + \text{AA-} \text{NH}_2 & \quad \rightarrow \quad 2\text{CuO} + \text{AA-NHOH} + \text{HSO}_4^- \\
\text{HSO}_5^- + 2\text{Cu}^{II}\text{O} + \text{AA-} \text{NH}_2 & \quad \rightarrow \quad 2\text{CuO} + \text{AA-NHOH} + \text{HSO}_4^- 
\end{align*}
\]

**Scheme 2 The plausible enroute of CuOnps catalyzed oxidation of α-amino acids.**

In the electrochemical studies nanoNiO particles and nano Fe$_2$O$_3$ particles were not tried. However since the GCE electrode was coated with transition metal oxide nanoparticles, the redox peaks will be varying depending on the various redox states of Ni and Fe. The interaction between the metal oxide np and AA with PMS may remain the same. Since AA is not a powerful oxidant it is the interaction of PMS with the metal oxide nps that control the catalytic process.
6.6 Conclusions

In this study a range of six α-AAs are oxidized to the respective AA derivatives using CuOnps, NiOnps and Fe$_2$O$_3$tnps as catalysts and PMS as the oxidant. Upon varying the capping agents from biostabilizers PEG, CMC and the synthetic stabilizer PVP, PEG produced smaller nps than the CMC compared to PVP. PVP stabilized larger nps of metal oxides. Within the range of AAs investigated, based on the pseudo first order rate coefficient values the trend in the reactivity observed was $\text{ala > gly > leu > val > phe > Ser}$. The catalytic activity of the nano particles among the capping agents show the trend as $\text{PEG > CMC > PVP}$. Keeping all conditions constant, the trend in the catalytic activity among the metal oxides is $\text{CuO > NiO > Fe}_2\text{O}_3\text{tnps}$.
Fig 6.1 Typical UV spectra of CuO-nps in EtOH medium at 25°C
Fig 6.2 XRD patterns of (i) CuOnps (ii) NiOnps (iii) Fe$_2$O$_3$npss having a) PEG, b) CMC and c) PVP as stabilizers
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Fig 6.4 FESEM images of metal oxide nanoparticles

a. CuO-PEG b. CuO-CMC
c. CuO-PVP d. NiO-PEG e. NiO-CMC f. NiO-PVP g. Fe$_2$O$_3$-PEG h. Fe$_2$O$_3$-CMC i. Fe$_2$O$_3$-PVP nps
Fig 6.5 UV – VIS spectra of (A) the six \( \alpha \)-amino acids and the time variance spectra of (B) Alanine in the presence of CuO-PEG nps and (C) Glycine in the presence of CuO-CMC nps.
Fig 6.5 UV – VIS time variance spectra of (D) phenyl alanine in the presence of NiO-PVP nps (E) Valine in the presence of NiO-CMC nps (F) Serine in the presence of Fe₂O₃-CMC and (G) Leucine in the presence of Fe₂O₃-PVP nps
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Fig 6.6 Absorbance – time dependence plots for the oxidation of α-amino acids by sodium peroxomonosulphate in the presence of metal oxide nanoparticles

a)ala  b)gly  c)leu

- CuO-PEG  - NiO-PEG  - Fe₃O₄-PEG
- CuO-CMC  - NiO-CMC  - Fe₂O₃-CMC
- CuO-PVP  - NiO-PVP  - Fe₃O₄-PVP
Fig 6.6 Absorbance – time dependence plots for the oxidation of α-amino acids by sodium peroxomonosulphate in the presence of metal oxide nanoparticles.

d) val e) phe f) ser

- CuO-PEG
- NiO-PEG
- Fe$_2$O$_3$-PEG
- CuO-CMC
- NiO-CMC
- Fe$_3$O$_4$-CMC
- CuO-PVP
- NiO-PVP
- Fe$_3$O$_4$-PVP
Chapter VI

Fig. 6.7 Kinetic plots for the rate coefficient determination of the oxidation of α-amino acids with sodium peroxomonosulphate catalysed by metal oxide nanoparticles a) ala b) gly c) leu

- CuO-PEG
- NiO-PEG
- Fe$_3$O$_4$-PEG
- CuO-CMC
- NiO-CMC
- Fe$_3$O$_4$-CMC
- CuO-PVP
- NiO-PVP
- Fe$_3$O$_4$-PVP
Fig. 6.7 Kinetic plots for the rate coefficient determination of the oxidation of α-amino acids with sodium peroxomonosulphate catalysed by metal oxide nanoparticles:

d) vale  e) phe
f) leu

- CuO-PEG
- NiO-PEG
- Fe$_3$O$_4$-PEG
- CuO-CMC
- NiO-CMC
- Fe$_3$O$_4$-CMC
- CuO-PVP
- NiO-PVP
- Fe$_3$O$_4$-PVP
Chapter VI

Fig. 6.8FT-IR spectra in KBR pellets at 25°C of the N-hydroxylated products from the oxidation reactions of aminoacids a) glycine; b) leucine
Fig. 6.8 FT-IR spectra in KBR pellets at 25°C of the N-hydroxylated products from the oxidation reactions of amino acids: c) valine; d) phenyl alanine.
Fig. 6.9 Cyclic voltammograms of the α-Leucine, PMS and PEG-CuOnps with two different sequential additions.

A) a- PEG-CuO/GCE  b- PEG-CuO/GCE+PMS  c- PEG-CuO/GCE+PMS+α-Leucine

B) a- PEG-CuO/GCE  b- PEG-CuO/GCE+α-Leucine  c- PEG-CuO/GCE+α-Leucine+PMS
Table 6.2 Rate coefficient $k \times 10^{-4} \text{ s}^{-1}$ values under pseudo first order conditions and times of 80% reaction for the oxidation reactions of $\alpha$- amino acids with peroxomonosulphate and CuO, NiO and Fe$_2$O$_3$ nps with PEG, CMC and PVP stabilizing agents, as catalysts, at 30°C.

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<td></td>
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<td>Fe$_2$O$_3$ $k$</td>
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<td>Serine</td>
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<td>5.89</td>
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Table 6.3 Times of 80% reaction for the oxidation reactions of α- amino acids with peroxomonosulphate and metal oxide nps with PEG, CMC and PVP stabilizing agents, as catalysts, at 30°C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amino acids</th>
<th>PEG</th>
<th>CMC</th>
<th>PVP</th>
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<tr>
<td></td>
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<td>CuO</td>
<td>NiO</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_{80%}$</td>
<td>$t_{80%}$</td>
<td>$t_{80%}$</td>
</tr>
<tr>
<td>1</td>
<td>Alanine</td>
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<td>31</td>
</tr>
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<td>2</td>
<td>Glycine</td>
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