Chapter 5

Photocatalytic Degradation of the Dyes using Visible Light

5.1 OVERVIEW

This chapter deals with the photocatalytic degradation of the methylene blue dye in aqueous suspension using prepared CuS photocatalysts under visible light irradiation in a homemade photoreactor. An attempt has been made to optimize the process parameters viz., dye initial concentration, pH of the solution and catalyst loading for the degradation of the dye using CuS catalyst. The photocatalytic mechanism is also studied in detail. The efficiency with which the catalyst can be recycled was determined.

5.2 DEGRADATION OF THE DYE USING PHOTOCATALYSTS

The photocatalytic performance of the as-prepared CuS catalyst was evaluated by photocatalytic degradation of methylene blue (MB) under visible light in room temperature. About 30 mg of the as-prepared CuS catalyst was added to 40 ml MB aqueous solution (20 mg/l). The mixed suspensions were magnetically stirred in visible light. During stirring, the samples were collected at given intervals to measure the dye degradation concentration; about 2 ml of the solution was extracted, diluted and separated by centrifugation to remove the photocatalyst. The degradation process was monitored by measuring the absorption of MB in the filtrate at 663 nm using UV–vis absorption spectrometer.

According to Beer-Lambert’s law, the concentration of MB is linearly proportional to the intensity of the absorption peak at 663 nm, and thus the decomposition efficiency of MB can be calculated using the following Eq. (5.1).

\[
\text{Degradation Rate} \ (\%) = \left(1 - \frac{A_t}{A_o}\right) \times 100
\]  

(5.1)

where \(A_t\) and \(A_o\) are the absorbance at time \(t\) and at initial time.
5.3 CATALYTIC ACTIVITY OF CuS NANOSTRUCTURES FOR MB dye DEGRADATION

Methylene Blue (MB) dye is most commonly used dye, which was chosen to evaluate the visible light catalytic performance of as-prepared CuS nanostructures of various morphologies. The catalytic activity was monitored by the MB characteristic peak of 663 nm. Initially, CuS nanostructures were prepared with different experimental parameters like, effect of Cu, S sources, reaction temperature, time, effect of solvents and surfactants. In the former cases, the corresponding photocatalytic activity was investigated and the same has been tabulated in table 5.1. We have tested the photocatalytic properties of all the prepared CuS catalyst. Table 5.1 shows the photodegradation efficiency of CuS photocatalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNO₃ + TU</td>
<td>99.6</td>
</tr>
<tr>
<td>CuNO₃ + STS</td>
<td>75.2</td>
</tr>
<tr>
<td>CuNO₃ + TU</td>
<td>78.5</td>
</tr>
<tr>
<td>CuCl₂ + STS</td>
<td>68.1</td>
</tr>
</tbody>
</table>

Table 5.1 Photodegradation efficiency of CuS photocatalyst on the effect of copper and sulfur sources used

As observed from the table 5.1, it is clearly seen that the higher photodegradation efficiency is achieved for the CuNO₃ copper source and TU sulfur source in 60 mins time duration at 150°C for 24 hrs. Further we also tested the photocatalytic property for effect of solvents and surfactants. After these testing, a detailed photocatalytic degradation study was carried out using CuS nanostructures prepared using different solvents and surfactants. The above study was given a
slightly more emphasis as solvent and surfactant played a major role deciding the morphology and surface area of the products.

5.4 EFFECT OF SOLVENTS BASED CuS CATALYST

The photocatalytic properties of the prepared CuS based on effect of solvents was tested for the methylene blue dye in 60 mins time duration. Various parameters like effect of CuS catalyst loading, effect of MB dye initial concentration and effect of pH variation was also studied in detail to know the better degradation efficiency of CuS catalyst.

5.4.1 EFFECT OF CuS CATALYST LOADING

To avoid the excessive usage of CuS photocatalyst, the degradation experiment was carried out by varying the amount of CuS catalyst on MB degradation. Figure 5.1 shows the effect of CuS catalyst at different loading. From the figure, it clearly tells that the degradation rate increases for the loading of 30 mg catalyst. This might be due to the increase in the active sites on CuS surface. The addition of excess amount of catalyst turns the solution more turbid and decelerates the light penetration into the solution. The increase in catalyst dosage will increase the active surface on the catalyst surface; the active becomes constant and loss of surface area by particle-particles interactions (agglomeration). The degradation rate always depends on the catalyst dosage.

Figure 5.1 MB degradation rate of different CuS catalyst loadings at different time durations
a) 20 mg and b) 40 mg catalyst
5.4.2 EFFECT OF MB DYE INITIAL CONCENTRATION

The initial concentration of MB dye plays a significant role on the dye degradation. By varying the dye concentration 10 mg L\(^{-1}\), 20 mg L\(^{-1}\) and 30 mg L\(^{-1}\), the photocatalytic activity of CuS catalyst was measured. Figure 5.2 shows the effect of dye concentration on CuS catalyst. From the graph the C/Co values for 20 mg L\(^{-1}\) concentration shows a drastic decrement. The figure clearly depicts that the decolourization rate increases with increasing initial concentration up to 20 mg L\(^{-1}\) and it decreases for 30 mg L\(^{-1}\) concentration. The high concentration of dye results in decreasing the number of active sites, which is due to absorption of more dye molecules on the catalyst surface.

![Figure 5.2 MB degradation rate of different MB dye concentration at different time durations](image)

5.4.3 EFFECT OF pH VARIATION

The pH is also an important parameter, which influences the photocatalytic reactions. Figure 5.3 depicts the effect of pH on the photodecolorization at three different pH values (5, 6.5 & 8). The decolorization C/Co rate of MB dye was decreased with increasing the pH values. This is due to electrostatic interactions between negative surface and cationic dye loading to the strong adsorption on the metal sulfide support. According to the results, pH 6.5 i.e., the original solution pH of the solution was selected as optimum value, which shows that the degradation efficiency is about 100%.
Figure 5.3 MB degradation rate on CuS catalyst on various pH at different time durations

a) 5 pH and b) 8 pH

With an investigation on the effect of catalyst loading, MB concentration and effect of pH variation, we have chosen the optimum values for dye degradation. The CuS catalyst exhibited better degradation efficiency at 30 mg catalyst loading, 20 mg L\(^{-1}\) of dye and 6.5 pH. So for all the degradation experiments, the same has been taken.

Figure 5.4 shows the UV-Vis absorption spectra of MB solution at different time durations of CuS samples prepared in different solvents viz. CuS/W, CuS/EG and CuS/G samples and CuS/E when exposed to normal light. As the irradiation time continued, the intensity of MB absorption peak started decreasing rapidly and completely vanished in 60 mins time interval for CuS/W sample. The inset figure of 5.4 (d) shows the decolorization of P25-TiO\(_2\) sample. CuS/W sample shows high percentage degradation of 99.6% in 60 mins and completely got decolorized (inset of figure 5.4 (a)) when compared with other samples. The degradation % rate of CuS/W is much higher than that of commercially available P25-TiO\(_2\) sample. Figure 5.5 shows the MB degradation rate of CuS products.
Figure 5.4 UV-Vis absorption spectra of MB solution at different time durations of CuS samples prepared in different solvents: (a) water (inset photograph shows decolorization of MB solution i) 0 mins, ii) 30 mins and iii) 60 mins), (b) ethylene glycol, (c) ethanol and (d) glycerol (inset fig. shows photodegradation using degussa P25- TiO$_2$ decolourization)

Difference in the degradation rate percentage is CuS/W (99.6%), CuS/EG (80.9%), CuS/E (82.5%) and CuS/G (76.2%) and such difference in the degradation rate is due to the changes in the CuS morphology. Almost complete (99.6%) MB photodegradation was achieved with the CuS/W photocatalyst in 60 mins duration under visible light exposure. The photodegradation efficiency of all the photocatalyst is given in the table 5.2. Hierarchical self-assembled tubular morphology of CuS/W sample showed highest catalytic activity which allows multiple reflections of light. It can be seen that the CuS/EG (hexagonal nano plates), CuS/G (flower-like) and CuS/E (nanoparticles) showed lower degradation rate due to poor light reflection. The higher catalytic activity of CuS/W sample is due the increased photogenerated holes and electrons of CuS/W samples and enhancement of material transfer. The above result suggests that the unique morphology of CuS product is responsible for enhanced
catalytic activity. Figure 5.6 shows the kinetic fit plot of \( \ln \left( \frac{C}{C_0} \right) \) vs. time for different photocatalyst.

![Kinetic fit plot](image)

Figure 5.5 MB degradation rate of CuS samples prepared in different solvents and degussa P25-TiO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Irradiation time (mins)</th>
<th>Photodegradation efficiency, ( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS/W</td>
<td>60</td>
<td>99.6</td>
</tr>
<tr>
<td>CuS/EG</td>
<td>60</td>
<td>80.9</td>
</tr>
<tr>
<td>CuS/E</td>
<td>60</td>
<td>82.5</td>
</tr>
<tr>
<td>CuS/G</td>
<td>60</td>
<td>76.2</td>
</tr>
<tr>
<td>P25-TiO$_2$</td>
<td>60</td>
<td>38.1</td>
</tr>
<tr>
<td>Only MB</td>
<td>60</td>
<td>17.12</td>
</tr>
</tbody>
</table>

Table 5.2 Photodegradation efficiency of CuS photocatalysts for effect of solvent
5.4.4 KINETICS STUDY

Many reports are available for the photocatalytic kinetic behavior, which can be obtained from Langmuir-Henshelwood model and the kinetics of catalytic decomposition was studied by using two kinetic models viz. pseudo first and second order (Zhou, Gao, Hu, Chen, & Hu, 2013). The amount of MB adsorbed at equilibrium was calculated by using the following equation (5.2).
where $C_o$ and $C_t$ are the initial and final concentration of MB in the solution (mg/L) respectively, $q_t$ (mg/g) is the amount of MB dye absorbed, $V$ is the volume of MB dye in ml and $m$ is the initial mass of CuS catalyst used (mg).

The pseudo-first-order kinetics equation is given as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

(5.3)

where, $q_e$ and $q_t$ (mg/g) are the adsorption capacity at equilibrium and time $t$ respectively, $k_1$ is the rate constant of pseudo-first-order model. The first order kinetic graph was plotted between log ($q_e$-$q_t$) vs. time as shown in figure 5.7 (a). The obtained correlation coefficient ($R^2$) is 0.9428 and results show the first-order model is not a good fit. The kinetics was further investigated by pseudo-second-order model. The pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \left(\frac{t}{k_2 q_e^2}\right) + \frac{t}{q_e}$$

(5.4)

where $q_t$ (mg/g) is the amount of dye absorbed mg/g at time $t$ (min), $k_2$ is the second order rate constant. By plotting the graph between $t/q_t$ vs. time, a linear plot was obtained with a high correlation coefficient. The correlation coefficient obtained was high viz. $R^2$ is 0.9941 i.e., close to 1 as shown in figure 5.7 (b). Thus bleaching of CuS follows the pseudo-second-order kinetics for the catalytic process. In general, the adsorption and desorption of molecule is responsible for the catalytic process on the surface of the catalyst.

### 5.4.5 RECYCLABILITY PROPERTY OF CuS/W CATALYST

Stability and reusability are further vital considerations for the assessment of the catalyst because photoanodic corrosion limits their stability. To further know the stability and recyclability property of CuS catalyst, it has been tested by repeating the degradation process of CuS photocatalyst. Figure 5.8 shows the degradation plot vs number of cycles. After each cycle, the CuS
catalyst can be easily separated by precipitation and centrifuge method and reused for its catalytic property.

From figure 5.8, up to 99.59% (almost 100%) of MB is degraded after 60 min in the first cycle of degradation and from the second to fifth cycle, 96.3%, 95.32%, 95.22%, and 90.87% of MB degradation could be observed. Thus the efficiencies with respect to the photodegradation of MB dye of the CuS catalyst and the photocatalyst reused in five cycles are nearly the same. After five cycles, there was no significant loss of photocatalytic activity, which indicates that CuS catalyst were not deactivated and having excellent stability and recyclability properties.

Figure 5.8 Repeated degradation cycle of CuS/W catalyst in MB solution under visible light irradiation

5.5 EFFECT OF SURFACTANTS BASED CuS CATALYST

To further know the effect of surfactant on CuS catalyst, the photocatalytic properties of the prepared CuS catalyst based on effect of surfactants by using water as a solvent was tested for the methylene blue dye in 60 mins time duration.
Figure 5.9 shows the UV-Vis absorption spectra of MB solution at different time durations of CuS samples viz. CuS/CTAB, CuS/PVA, CuS/PEG and CuS/PVP samples exposed to visible light.

The characteristic absorption peak at 663 nm is used to monitor the photocatalytic dye degradation reaction. As the irradiation time continued, the intensity of MB absorption peak started decreasing rapidly and completely vanished in 60 mins time interval for CuS/CTAB sample. CuS/CTAB sample shows a high percentage degradation of 99.9% in 60 mins duration almost 100% completely decolorized. The degradation % rate of CuS/CTAB is much higher than that of commercially available P25-TiO$_2$ sample. The difference in the degradation rate was due to the changes in the CuS morphology. The photodegradation efficiency of all the photocatalyst is given in table 5.3. Figure 5.10 shows the MB degradation rate of CuS products and figure 5.11 shows the kinetic fit plot of ln (C/Co) vs. time.
Figure 5.10 MB degradation rate of CuS samples prepared by using different surfactants and degussa P25-TiO$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Irradiation time (mins)</th>
<th>Photodegradation efficiency, $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS/CTAB</td>
<td>60</td>
<td>99.9</td>
</tr>
<tr>
<td>CuS/PVA</td>
<td>60</td>
<td>97.7</td>
</tr>
<tr>
<td>CuS/PEG</td>
<td>60</td>
<td>96.3</td>
</tr>
<tr>
<td>CuS/PVP</td>
<td>60</td>
<td>94.8</td>
</tr>
<tr>
<td>P25-TiO$_2$</td>
<td>60</td>
<td>38.1</td>
</tr>
<tr>
<td>Only MB</td>
<td>60</td>
<td>17.12</td>
</tr>
</tbody>
</table>

Table 5.3 Photodegradation efficiency of CuS photocatalysts for effect of surfactant
5.5.1 KINETICS STUDY

The CuS catalyst follows the pseudo-second-order kinetics for the catalytic process. The obtained correlation coefficient ($R^2$) is 0.9428 and results show that the first-order model did not fit. The kinetics was further investigated by pseudo-second-order model. The correlation coefficient obtained was high viz. $R^2$ is 0.99566 i.e., close to 1 as shown in figure 5.12 (b) and hence concluded that the adsorption process
followed pseudo second order model. In general, the adsorption and desorption of a molecule is responsible for the catalytic process on the surface of the catalyst.

5.5.2 RECYCLABILITY PROPERTY OF CuS/CTAB CATALYST

To further know the stability and recyclability property of CuS catalyst, it has been tested by repeating the degradation process of CuS photocatalyst.

![Figure 5.13 Repeated degradation cycle of CuS/CTAB catalyst in MB solution under visible light irradiation](image)

Figure 5.13 shows that up to 99.9% (almost 100%) of MB is degraded after 60 min in the first cycle of degradation and from the second to fifth cycle, 98.2%, 97.8%, 95.3%, and 93.2% of MB degradation could be observed. Thus the efficiencies with respect to the photodegradation of MB dye of the pristine catalyst and the photocatalyst reused in five cycles are nearly the same. After five cycles, there was no significant loss of photocatalytic activity, which indicates that CuS catalyst were not deactivated and having excellent stability and recyclability properties.
5.6 SCHEMATIC MECHANISMS OF CuS CATALYST ON MB DYE DEGRADATION

Scheme 5.1 shows the schematic diagram of MB photodegradation over CuS/W catalyst under visible light irradiation. As a narrow band gap semiconductor, CuS absorbs more number of photons resulting in higher catalytic activity under visible light irradiation.

The proposed degradation mechanism for the CuS catalytic activity was suggested as follows (Aarthi, Narahari, & Madras, 2007),

\[ CuS + h\nu \rightarrow h^+ (VB) + e^- (CB) \] \hspace{1cm} (5.5)

\[ OH^- + h^+ \rightarrow OH^* \] \hspace{1cm} (5.6)

\[ H_2O + h^+ \rightarrow OH^* + H^+ \] \hspace{1cm} (5.7)

\[ O_2 + e^- \rightarrow O_2^{*-} \] \hspace{1cm} (5.8)

\[ O_2^{*-} + e^- + 2H^+ \rightarrow H_2O_2 \] \hspace{1cm} (5.9)

\[ 2O_2^{*-} + 2H^+ \rightarrow O_2 + H_2O_2 \] \hspace{1cm} (5.10)

\[ H_2O_2 + e^- \rightarrow OH^- + OH^* \] \hspace{1cm} (5.11)

\[ Dye + h^+ \rightarrow Dye \rightarrow \text{deg radation products} \] \hspace{1cm} (5.12)
Under visible light irradiation, $e^-/h^+$ pairs will be created and the excitation of valence band electron takes place. The excited electron will further transfer the electron to the conduction band, which results in the formation of $e^-/h^+$ pairs. The valence band holes from CuS react with surface hydroxyl groups to produce highly reactive hydroxyl radicals (•OH) by breaking up the water molecules. The conduction band electron reacts with oxygen molecules adsorbed on CuS to form super oxide anion ($\bullet O_2^-$) radicals. The highly reactive (•OH) hydroxyl radicals and superoxide anion radicals ($\bullet O_2^-$) react with MB dye adsorbed on the CuS catalytic surface. The CuS catalyst reduces the recombination of photogenerated $e^-/h^+$ pairs and generates large number of $\bullet O_2^-$ and $\bullet OH$ radicals which results in enhanced catalytic activity. The highly reactive hydroxyl radicals that oxidize MB into smaller molecules as intermediates such as CO$_2$, H$_2$O, etc., The release of degraded intermediates (CO$_2$, H$_2$O, NH$_4$, SO$_4$) from the catalyst surface can poison the catalyst surface by the produced intermediates. For the repeated degradation (see figure 5.8) of MB aqueous solution using CuS/W catalyst, there is no significant loss of catalytic activity, which remains still active for the five cycles. This result proves that CuS/W catalyst has a promising catalytic activity towards dye degradation and excellent recyclable photocatalyst.

5.7 DEGRADATION OF ORGANIC CONTAMINANTS

The organic pollutant causes a major threat to living systems. Nitro based organic compounds are the major by-products in various industrial sectors like leather, pharmaceutical products, agrochemical industries, printing and painting industries as colouring agent. Particularly phenol and its derivatives have become common organic pollutant in industrial and agricultural effluents, which is toxic to the environmental ecosystem. CuS nanostructures were studied for the organic contaminant degradation. Due to the interesting morphologies, the prepared CuS was tested for their photocatalytic properties towards the degradation of organic compounds. In this regard, nitrobenzene and 4-nitrophenol were chosen as organic contaminants and the experiment was carried out under visible light irradiation.
5.7.1 DEGRADATION OF 4-NITROPHENOL (4-NP) CONTAMINANTS

An aqueous solution of pollutant and catalyst mixture was stirred in dark to obtain equilibrium on the catalyst surface. After that, the aqueous solution was exposed to visible light. The samples were taken out at different time durations, centrifuged to separate the CuS catalyst and their concentration was monitored by UV–vis spectrometer. Figure 5.14 and 5.15 shows the UV–vis absorbance spectra of CuS/W and CuS/CTAB catalyst at different time intervals. As the irradiation time prolonged, the 4-nitrophenol absorbance peak at 325 nm started decreasing as the irradiation time continues. The photocatalytic activity increases with increasing the reaction time. Absorption peak of 4-NP completely disappeared after 60 min for
CuS/CTAB catalyst. When compared to the CuS/W sample (η = 84.5 %), the CuS/CTAB sample showed a higher degradation rate of η = 95.6 % in 60 mins duration. It is clearly seen from the graph that there is only negligible decrease for the absorbance peak without catalyst. Figure 5.14 and 5.15 (a) depicts the degradation activity of CuS catalysts and its corresponding C/Co ratios vs time is shown in figure 5.14 and 5.15 (b). As observed from the graph, in the absence of catalyst, there was only a negligible degradation. Without catalyst, there was not much decrease in the 4-NP concentration.

5.7.2 DEGRADATION NITROBENZENE (NB) CONTAMINANTS

Figure 5.16 (a) Photodegradation of nitrobenzene (b) C/Co plot vs. irradiation time for CuS/W catalyst

Figure 5.16 and 5.17 shows the UV–vis absorbance spectra of CuS/W and CuS/CTAB catalyst at different time intervals. As the irradiation time prolonged, the nitrobenzene absorbance peak at 263 nm started decreasing as the irradiation time continues. The photocatalytic activity increases with increasing the reaction time. Absorption peak of NB completely disappeared after 60 min for CuS/CTAB catalyst. When compared to the CuS/W sample (η = 85.14 %), the CuS/CTAB sample showed a higher degradation rate of η = 89.41 % in 60 mins duration. It is clearly seen from the graph that there is only negligible decrease for the absorbance peak without catalyst. Figure 5.16 and 5.17 (a) depicts the degradation activity of CuS catalysts and its corresponding C/Co ratios vs. time. As observed from the graph, in the absence of
catalyst, there was only a negligible degradation. Without catalyst, there was not much decrease in the NB concentration.

Figure 5.17 (a) Photodegradation of nitrobenzene (b) C/Co plot vs. irradiation time for CuS-CTAB catalyst

5.8 DEGRADATION OF TEXTILE EFFLUENTS

The CuS catalyst was further tested towards the degradation of textile effluents collected from two different industrial sites situated in the Thirupur textile industries, Tamil Nadu, India.

Figure 5.18 (a) Photodegradation of industrial effluent from site A (b) C/Co plot vs. irradiation time for CuS/W catalyst
For the industrial effluent from site A, the photodegradation studies were carried out and the degradation results shows higher degradation of $\eta = 97.4\%$ for CuS-CTAB catalyst and lower degradation of $\eta = 91.9\%$ for CuS/W catalyst in 60 mins time duration. Figure 5.18 and 5.19 (a) depicts the degradation activity of CuS catalysts and its corresponding C/Co ratios vs. time. As observed from the graph, in the absence of catalyst, there was only a negligible degradation.

Figure 5.19 (a) Photodegradation of industrial effluent from site A (b) C/Co plot vs. irradiation time for CuS/CTAB catalyst

Figure 5.20 (a) Photodegradation of industrial effluent from site B (b) C/Co plot vs. irradiation time for CuS/W catalyst
Figure 5.21 (a) Photodegradation of industrial effluent from site B (b) C/Co plot vs. irradiation time for CuS/CTAB catalyst

For the industrial effluent from site B, the photodegradation studies were carried out and the degradation results shows higher degradation of $\eta = 98.4\%$ for CuS-CTAB catalyst and lower degradation of $\eta = 99.7\%$ for CuS/W catalyst in 60 mins time duration. Figure 5.20 and 5.21(a) depicts the degradation activity of CuS catalysts and its corresponding C/Co ratios vs. time. As observed from the graph, in the absence of catalyst, there was only a negligible degradation.

5.9 CONCLUSIONS

From the above results, CuS/CTAB photocatalyst showed good recyclability property and better photocatalytic activity for methylene blue dye and other organic contaminants like 4-nitrophenol, nitrobenzene and textile effluents. This is due to the unique and interesting morphology of CuS catalyst using CTAB surfactant. Experiment results showed that CTAB played a key role in the formation of hexagonal nanoplates. The CuS catalyst acted as an efficient photocatalyst for dye degradation under visible light. This work emphasizes that the highly efficient CuS nanocatalyst will be useful for the treatment of dye pollutant towards eliminating pollution and environmental protection.