Photocatalytic bleaching of amaranth dye over ZnO powder

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The photocatalytic bleaching of amaranth over zinc oxide powder was observed spectrophotometrically. The effects of the concentration of amaranth, pH, amount of semiconductor, light intensity on the rate of the photocatalytic bleaching were also studied. A tentative mechanism for the photocatalytic bleaching of amaranth is proposed.

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Keywords: Amaranth dye, photocatalytic bleaching, ZnO powder, mechanism

The evolution of the chemistry of dyes began in 1856 with the discovery and industrial production of Mauvein by W.H. Perkin. Today, nearly 540,000 tons of dyes are produced every year. After using dyes, many industries like textile, pulp, paper, leather, wool, silk, etc. discharge effluents into sewers, drains, etc. and create various environmental problems.

Dyes cause various biochemical and morphological effects on plants and animals. There are several techniques like coagulation, floatation, ion-exchange, adsorption, reverse-osmosis, biological oxidation, etc., which are used for the removal/destruction of dyes in polluted water.

One very specific and promising technology for the degradation of dyes is heterogeneous photocatalysis which has attracted a great deal of attention over the last two decades because of its wide use in xerography, photography, chemical synthesis, conversion and storage of solar energy.

Photocatalytic reactions in presence of ZnO suspension have been studied by Morrison and Freund\textsuperscript{1}. Mansoori \textit{et al.}\textsuperscript{2} used ZnO as a photocatalyst for photocatalytic degradation of Rh-6G. The photocatalysis of methylene blue sensitized by TiO\textsubscript{2} was studied in the presence and absence of oxygen by Mills and Wang\textsuperscript{3}. Ma and Yao\textsuperscript{4} prepared a thin film of TiO\textsubscript{2} and used it to study photodegradation of Rh-B. Ciping \textit{et al.}\textsuperscript{5} observed the formation of free radical intermediates in photoreaction with ZnO dispersion. Richard \textit{et al.}\textsuperscript{6} reported that oxidizing species involved in photocatalytic transformation on ZnO is either hydroxy radicals or holes. Effect of addition of sodium bicarbonate/carbonate on the rate of photocatalytic bleaching of methylene blue over CdS powder was studied by Chhabra \textit{et al.}\textsuperscript{7} whereas Chen and Chou\textsuperscript{8} reported the photobleaching of methyl orange in aqueous solution with suspended TiO\textsubscript{2}. Sharma \textit{et al.}\textsuperscript{9} investigated the photocatalytic bleaching of rose bengal in aqueous ZnO solution.

An exhaustive literature survey revealed that no work has been reported on the photocatalytic bleaching of amaranth using zinc oxide as photocatalyst; however this dye is extensively used in textile industries. This was the motivation behind the present work.

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**Experimental Procedure**

Amaranth and zinc oxide were obtained from C.D.H. and Merck respectively. The stock solution of amaranth (1.0 \times 10^{-3} \text{M}) was prepared in doubly distilled water (0.6040 \text{ g L}^{-1}). Some controlled experiments were carried out to confirm that reaction follows photocatalytic pathway. 0.60 g of zinc oxide was added to 50.0 mL of 4.4 \times 10^{-5} \text{ M amaranth solution. The desired pH of the solution was adjusted by addition of previously standardized H}_2\text{SO}_4/\text{NaOH solutions. The pH of the solution was measured by a Systronics digital 335 pH meter. A Mysore 200W tungsten lamp was used as irradiation source. The intensity of light was measured by a Surya Mapi (CEL-SM-201) solarimeter. A water filter was used to cut-off thermal radiations. The progress of the reaction was measured using a Systronics Model 166 digital spectrophotometer by recording the absorbance of the dye solution at different time intervals. For absorbance measurements, the solution was made free from ZnO particles and other impurities by centrifugation (Remi Model 1258).

**Results and Discussion**

The photocatalytic bleaching of amaranth was observed at \( \lambda_{\text{max}} = 515 \text{ nm} \). The optimum condition was obtained at [amaranth] = 4.4 \times 10^{-5} \text{ M}, light intensity =29.0 \text{ mW cm}^{-2}, \text{pH}=8.50, \text{ZnO} = 0.60 \text{ g} \text{ and temperature} = 308 \text{ K}.

\[ \text{Rate} = K \times \text{[Amaranth]} \]

\[ k = 2.303 \times \text{slope} \quad \text{...(i)} \]

The plot of \( 2 + \log \text{O.D.} \) versus exposure time is a straight line, which indicates that the photocatalytic bleaching of KB-R follows pseudo first order kinetics. The rate constant (k) for the reaction was determined using the expression (i). The data for a typical run is presented in Table 1.

**Effect of variation of pH**

The effect of variation of pH on the rate of photocatalytic bleaching of amaranth was investigated. The data are reported Table 2. ZnO dissolves in the presence of highly acidic media and, therefore, photocatalytic bleaching could not be investigated in the lower pH range.

The rate of photocatalytic bleaching of amaranth was found to increase with increase in pH upto 8.5, then it decreased again. This behaviour may be explained on the basis, that, the increase in the rate of photocatalytic bleaching may be due to greater availability of OH at higher pH values. By combining with holes, OH ions will generate more hydroxyl radicals (OH\(^{•}\)), which are considered to be responsible for the photocatalytic bleaching.

At pH > 8.5, the OH\(^{•}\) ions will make the surface of the semiconductor negatively charged and as a consequence of repulsive force between two negatively charged species (OH\(^{•}\) ion and dye anion) the approach of amaranth anion to the semiconductor surface will be retarded. This will result in a decrease in the rate of photocatalytic bleaching of amaranth dye.

**Effect of variation of dye concentration**

The effect of variation of dye concentration on the rate of the reaction was also studied by using different concentrations of the amaranth solution. The results are given in Table 2.

With the increase in the concentration of amaranth, the rate of photocatalytic bleaching was found to increase, reaching a maximum value at [amaranth] = 4.4 \times 10^{-5} \text{ M}. Further increase in amaranth concentration resulted in a decrease in the rate of photocatalytic bleaching. It may be due to the fact, that, as the concentration of the dye increased, more dye molecules were available for excitation and for energy transfer but at concentrations above 4.4 \times 10^{-5} \text{ M}, the dye started acting as a filter for the incident light.

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**Table 1**

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<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (O.D.)</th>
<th>2+log O.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.916</td>
<td>1.9618</td>
</tr>
<tr>
<td>40.0</td>
<td>0.668</td>
<td>1.8247</td>
</tr>
<tr>
<td>80.0</td>
<td>0.459</td>
<td>1.6618</td>
</tr>
<tr>
<td>120.0</td>
<td>0.316</td>
<td>1.4996</td>
</tr>
<tr>
<td>160.0</td>
<td>0.224</td>
<td>1.3502</td>
</tr>
<tr>
<td>200.0</td>
<td>0.113</td>
<td>1.1251</td>
</tr>
<tr>
<td>240.0</td>
<td>0.118</td>
<td>1.0718</td>
</tr>
<tr>
<td>280.0</td>
<td>0.079</td>
<td>0.8976</td>
</tr>
<tr>
<td>300.0</td>
<td>0.068</td>
<td>0.8325</td>
</tr>
</tbody>
</table>

\[ k = 4.71 \times 10^{-5} \text{ sec}^{-1} \]
light causing decrease in the rate of photocatalytic bleaching of amaranth.

**Effect of variation of amount of ZnO**

The effect of variation in the amount of ZnO was also observed on the rate of the photocatalytic bleaching of the amaranth. The results are reported in Table 2. It is observed that the rate of reaction increases with increase in the amount of ZnO up to 0.60 g in 50 mL solution and beyond this, the rate of reaction becomes almost constant. This may be due to the fact, that, in the initial stage, as the amount of semiconductor increases, the exposed surface area of the semiconductor also increases, but after this limiting value (0.60 g), any further increase in the amount of semiconductor does not increase the exposed surface area and only increases the thickness of the semiconductor layer. This was confirmed by using reaction vessels of different dimensions.

**Effect of variation of light intensity**

The effect of variation of light intensity on the rate of photocatalytic bleaching of amaranth was observed. The results are reported in Table 2. It is seen, that, an increase in light intensity increases the rate of photocatalytic bleaching. It may be due to the fact that as the intensity of light increases, the number of photons striking per unit area of the semiconductor (ZnO) also increases. A linear behaviour between light intensity and the rate of reaction is thus, observed. Since an increase in the light intensity increases the temperature of dye solution also and a thermal reaction may occur, much higher intensities were avoided.

**Mechanism of photocatalytic bleaching**

On the basis of the observed data, the following tentative mechanism may be proposed for photocatalytic bleaching of amaranth.

\[
\begin{align*}
\text{amaranth}_0 & \overset{\text{hv}}{\longrightarrow} \text{amaranth}_1 \\
\text{amaranth}_1 & \overset{\text{ISC}}{\longrightarrow} \text{amaranth}_1 \\
\text{amaranth}_1 + \text{ZnO} & \longrightarrow \text{amaranth}^+ + \text{ZnO}(e^-) \\
\text{ZnO} (e^-) + \text{O}_2 & \longrightarrow \text{ZnO} + \text{O}_2^- \\
\text{amaranth}^+ + \text{OH}^- & \longrightarrow \text{amaranth} + \text{OH}^* \\
\text{amaranth} + \text{OH}^* & \longrightarrow \text{Product}
\end{align*}
\]

<table>
<thead>
<tr>
<th>pH</th>
<th>$k \times 10^5$ s$^{-1}$</th>
<th>[amaranth] $\times 10^{-5}$ M</th>
<th>$k \times 10^5$ s$^{-1}$</th>
<th>Mass of ZnO g</th>
<th>$k \times 10^5$ s$^{-1}$</th>
<th>$I \times $ mWcm$^{-2}$</th>
<th>$k \times 10^5$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>3.60</td>
<td>2.0</td>
<td>3.50</td>
<td>0.10</td>
<td>3.50</td>
<td>11.0</td>
<td>3.44</td>
</tr>
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<td>5.5</td>
<td>3.72</td>
<td>2.5</td>
<td>3.84</td>
<td>0.20</td>
<td>3.86</td>
<td>14.6</td>
<td>3.72</td>
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<tr>
<td>6.0</td>
<td>3.86</td>
<td>3.0</td>
<td>4.00</td>
<td>0.30</td>
<td>4.34</td>
<td>18.4</td>
<td>3.98</td>
</tr>
<tr>
<td>6.5</td>
<td>4.06</td>
<td>3.5</td>
<td>4.22</td>
<td>0.40</td>
<td>4.58</td>
<td>20.8</td>
<td>4.16</td>
</tr>
<tr>
<td>7.0</td>
<td>4.28</td>
<td>4.0</td>
<td>4.45</td>
<td>0.50</td>
<td>4.68</td>
<td>26.4</td>
<td>4.54</td>
</tr>
<tr>
<td>7.5</td>
<td>4.46</td>
<td>4.4</td>
<td>4.71</td>
<td>0.60</td>
<td>4.71</td>
<td>29.0</td>
<td>4.71</td>
</tr>
<tr>
<td>8.0</td>
<td>4.56</td>
<td>5.0</td>
<td>4.58</td>
<td>0.70</td>
<td>4.71</td>
<td>33.8</td>
<td>5.08</td>
</tr>
<tr>
<td>8.5</td>
<td>4.71</td>
<td>5.7</td>
<td>4.30</td>
<td>0.80</td>
<td>4.71</td>
<td>40.8</td>
<td>5.42</td>
</tr>
</tbody>
</table>
| 9.0 | 4.54 | 6.0 | 4.06 |  &  
| 9.5 | 4.34 | 6.5 | 3.80 |  &  
| 10.0 | 4.00 |  &  

*a [amaranth] = 4.4 \times 10^{-5} M, ZnO = 0.60 g, light intensity = 29.0 mWcm$^{-2}$

*b ZnO = 0.60 g, pH = 8.50, light intensity = 29.0 mWcm$^{-2}$

*c [amaranth] = 4.4 \times 10^{-5} M, pH = 8.5, light intensity = 29.0 mWcm$^{-2}$

*d [amaranth] = 4.4 \times 10^{-5} M, pH = 8.5, ZnO = 0.60 g,
When the dye solution is exposed to light, in the presence of zinc oxide, initially the \textsuperscript{1}amaranth\textsubscript{0} molecules are excited to first excited singlet state (\textsuperscript{1}amaranth\textsubscript{1}). Then these excited molecules are transferred to the triplet state through inter system crossing (ISC). The triplet dye (\textsuperscript{3}amaranth\textsubscript{1}) may donate its electron to the semiconductor and become positively charged. The dissolved oxygen of the solution will pull an electron from the conduction band of the semiconductor, thus, regenerating the semiconductor. The positively charged molecules of the dye (amaranth\textsuperscript{+}) will immediately react with OH\textsuperscript{-} ions to form OH\textsuperscript{•} radicals, which will convert the dye molecules into products (colourless). The participation of OH\textsuperscript{•} as an active oxidizing species was confirmed by carrying out same reaction in the presence of some hydroxyl radical scavengers like 2-propanol, where the rate of bleaching was drastically reduced.

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**References**