Photocatalytic bleaching of Evans blue over zinc oxide particulate system

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Evans blue, an azo dye, and its mixture with amaranth are degraded photocatalytically in presence of zinc oxide. The optimum conditions for photobleaching of these dyes, like concentration of dye, pH, amount of semiconductor, light intensity, etc., have been studied. During the photocatalytic degradation, the semiconductor (ZnO) remains unaffected as evident from its FT-IR. The studied dyes are commonly used in dyeing, printing and textile industries and hence, the present work will be helpful in the treatment of coloured effluents from these industries.

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Various technologies and methodologies ranging from physical methods to biodegradable processes are available for removing colour from water. However, these methods are not cost-effective. The effluents from dyeing and printing industries when discharged into the river, ponds not only disturb the ecosystem but are also a serious health hazard for the human beings. With the increase in the environmental awareness all over the world, search for new cost effective and green routes to treat water contaminated with dye effluents has increased in recent years. The heterogeneous photocatalytic processes give an excellent pathway to treat the coloured water to make it colourless, which may then be used for cleaning, cooling and irrigation purposes.

Sakthivel et al.2,3 reported that the photocatalytic efficiency of ZnO in the photodegradation of dyes is slightly higher than that of TiO2. Sharma et al.4 have investigated the photocatalytic bleaching of Orange-G in aqueous ZnO solutions. Ameta et al.5 used ZnO as a photocatalyst for the photocatalytic bleaching of basic blue-24. Effect of TiO2 acidic pre-treatment on its photocatalytic properties for phenol degradation has been reported by Colon et al.6 while Wang et al.7 have reported the photocatalytic degradation of biphenyl–A on TiO2 enhanced by β-cyclodextrin.

Matsuo and Udea8 have used SrTiO3-TiO2 composite powder for the photocatalytic bleaching of methylene blue. Preparation and characterization of ZnO/TiO2, photocatalyst and their photocatalytic activity were reported by Liao et al.9

Sekli et al.10,11 have investigated the photocatalytic transformation of chloroaromatic derivatives such as chlorophenol and dichlorobenzenes on ZnO involving the formation of an adduct between OH radicals and aromatic compound. Driessen et al.12 have studied surface band(CB) and gas phase products and intermediates with FT-IR spectroscopy during photocatalytic oxidation of trichloroethylene on ZnO. Synthesis and photocatalytic activity of ZnO/ZrO2 composite have been reported by Hsu and Wu.13 Raj et al.14 used ZnO as a photocatalyst for the photocatalytic bleaching of rhodamine-6G. Photocatalytic bleaching of Evans blue (EB) has not been reported in literature although it is extensively used in dyeing, printing and textile industries. It was thus, thought worthwhile to study the present reaction.

Experimental

Evans blue (EB, I), amaranth and zinc oxide were analytical grade chemicals. The stock solution (1.00 × 10^{-3} M) of EB was prepared in doubly distilled water (0.0960 g/100 mL). Some controlled experiments were carried out to confirm that this reaction follows the photocatalytic pathway. Zinc oxide (0.60 g) was added to 50.0 mL of 1.50 × 10^{-5} M EB solution. The pH of the solution was adjusted to the desired value by addition of previously standardized H2SO4/NaOH solutions. The pH of the solution was measured by a digital pH meter (Systronics, model 335).

6, 6′-{[(3, 3′-Dimethyl [1, 1′-biphenyl]-4, 4′-diyl bis (azo)] bis [4-amino-5-hydroxy-1, 3-naphthalene-disulphonic acid] tetrasodium salt (Evans blue) (I)
A 500 W tungsten lamp (Mysore) was used for irradiation. 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 spectrophotometer (Systronics, model 116). The solution was made free from ZnO particles and other impurities by centrifuging before absorbance measurements.

**Results and discussion**

The photocatalytic bleaching of EB was followed at $\lambda_{\text{max}} = 611$ nm. UV-visible spectrum of the reaction mixture at different time intervals i.e. before exposure, during exposure and after complete experiment were recorded. It is clear from the spectral data that absorption at 611 nm (for EB) decreases during the course of the reaction and ultimately there is negligible absorption. There was no absorption band above 400 nm, which indicates that no colour compounds (dye or its coloured components) are formed. The optimum condition was obtained at [Evans blue] = $1.50 \times 10^{-5}$ M, light intensity = 50.0 mW cm$^{-2}$, pH = 8.0, ZnO = 0.60 g and temperature = 308 K.

The plot of $2 + \log \text{O.D.}$ versus exposure time was linear, which indicates that the photocatalytic bleaching of Evans blue follows first order kinetics. The rate constant ($k$) for the reaction was determined using the expression (2).

**Effect of pH**

The effect of pH on the rate of photocatalytic bleaching of EB was investigated. ZnO dissolves in highly acidic medium, and therefore, photocatalytic bleaching of EB could not be investigated in lower pH range.

The rate of photocatalytic bleaching of EB increases with increase in pH up to pH 8.0 and with further increase, it decreases. This behaviour may be explained on the basis that an increase in the rate of photocatalytic bleaching may be due to the increased availability of OH ions at higher pH values. The OH ions will generate more hydroxyl radicals (\^•OH) by combining with holes, which are considered responsible for the photocatalytic bleaching.

Above pH value 8.0, more OH ions will compete with the electron rich dye for adsorption on semiconductor surface. Also, the OH ions will make the surface of the semiconductor negatively charged and as a consequence, the approach of Evans blue molecules to the semiconductor surface will be retarded due to repulsive force between two negatively charged species (OH ions and the electron rich dye). This will result in a corresponding decrease in the rate of photocatalytic bleaching of Evans blue at higher pH value i.e., pH $> 8.0$.

**Effect of dye concentration**

The effect of dye concentration on the rate of the reaction was studied by using different concentrations of EB solution. It was observed that as the concentration of EB was increased; the rate of photocatalytic bleaching also increases, reaching a maximum at $1.50 \times 10^{-5}$ M. Further increase in concentration of dye resulted in a decrease in the rate of photocatalytic bleaching. This may be due to the fact that as the concentration of the dye increased, more dye molecules were available for excitation and consecutive energy transfer.

But if the concentration of EB was increased above $1.50 \times 10^{-5}$ M, the dye starts acting as a filter for the incident light and prohibits the desired light intensity to reach the dye molecules near the semiconductor particles. Thus, a decrease in the rate of photocatalytic bleaching was observed.

**Effect of amount of ZnO**

The effect of amount of ZnO powder on the rate of photocatalytic bleaching of the EB was also studied. It was observed that the rate of reaction increases with increase in the amount of ZnO up to 0.60 g. Beyond 0.60 g, the rate of reaction becomes virtually constant. This may be due to the fact that as the amount of semiconductor was increased in the initial stage, the exposed surface area of the semiconductor also increases. However, after this limiting value (0.60 g), increase in the amount of semiconductor increases only the thickness of the semiconductor layer and not the exposed surface area. This was also confirmed by using reaction vessels of different dimensions.

To know the state of ZnO, the FT-IR spectrum of ZnO were recorded in dry and wet state as well as at the end of the experiment (Fig. 1). It is clear from the FT-IR spectral data that there is no reasonable change, in the nature of ZnO during this photocatalytic process indicating that ZnO remains intact or is regenerated back.

**Effect of light intensity**

The effect of light intensity on the rate of photocatalytic bleaching of EB was studied. The
results show that an increase in light intensity results in a corresponding increase in the rate of photocatalytic bleaching. As the intensity of light was increased, the number of photons striking per unit area of the semiconductor (ZnO) also increases. An almost linear behaviour between light intensity and the rate of reaction was observed. Since an increase in the light intensity also increases the temperature of dye solution leading to a thermal reaction, higher intensities were avoided.

**Effect of mixing Amaranth**

To investigate the effect of one photocatalytic dye on another photocatalytic dye or a simple dye under photocatalytic conditions, the photocatalytic bleaching of mixture of dyes (both anionic azo dyes, EB and Amaranth) was also investigated.

The effect of various parameters like pH, EB concentration, Amaranth concentration, amount of semiconductor, intensity, etc., are reported in Table 1.

![FT-IR spectrum of Evans blue.](image)

**Mechanism**

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

\[
\begin{align*}
1\text{EB}_0^- & \xrightleftharpoons[\text{h}^{-}\nu]{\text{hv}} 1\text{EB}_1^- \\
1\text{EB}_1^- & \xrightarrow{\text{ISC}} 3\text{EB}_1^- \\
\text{ZnO} & \xrightarrow{\text{hv}} \text{ZnO} (h^+) + \text{ZnO} (e^-) \\
3\text{EB}_1^- + \text{ZnO} & \rightarrow \text{EB} + \text{ZnO} (e^-) \\
\text{ZnO} (e^-) + \text{O}_2 & \rightarrow \text{ZnO} + \text{O}_2^* \\
\text{OH} + \text{ZnO} (h^+) & \rightarrow {^\bullet}\text{OH} + \text{ZnO} \\
3\text{EB}^- + {^\bullet}\text{OH} & \rightarrow \text{Products}
\end{align*}
\]

When the solution of the dye was exposed to light in presence of zinc oxide, the \(^1\text{EB}_0^-\) molecules are excited to first excited singlet state \(^1\text{EB}_1^-\). Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). The triplet dye \(^3\text{EB}_1^-\) may donate its electron to the semiconductor making the dye neutral. The dissolved oxygen of the solution will pull an electron from the

<table>
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<tr>
<th>pH (^a)</th>
<th>(k_E \times 10^5) (s(^{-1}))</th>
<th>(k_A \times 10^5) (s(^{-1}))</th>
<th>([\text{EB}]b \times 10^5) (M)</th>
<th>(k_E \times 10^5) (s(^{-1}))</th>
<th>(k_A \times 10^5) (s(^{-1}))</th>
<th>(\text{ZnO}c) (g)</th>
<th>(k_E \times 10^5) (s(^{-1}))</th>
<th>(k_A \times 10^5) (s(^{-1}))</th>
<th>(I_d) (mWcm(^{-2}))</th>
<th>(k_E \times 10^5) (s(^{-1}))</th>
<th>(k_A \times 10^5) (s(^{-1}))</th>
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<td>3.83</td>
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\(^a\) [EB] = 1.50 \times 10^{-5}M; [Amaranth] = 3.00 \times 10^{-5}; ZnO = 0.60 g; light intensity = 50.0 mWcm\(^{-2}\).

\(^b\) pH = 7.00; [Amaranth] = 3.00 \times 10^{-5}; ZnO = 0.60 g; light intensity = 50.0 mWcm\(^{-2}\).

\(^c\) [EB] = 1.50 \times 10^{-5}M; [Amaranth] = 3.00 \times 10^{-5}; pH = 7.00; light intensity = 50.0 mWcm\(^{-2}\).

\(^d\) [EB] = 1.50 \times 10^{-5}M; [Amaranth] = 3.00 \times 10^{-5}; ZnO = 0.60 g; pH = 7.00.
conduction band of the semiconductor, thus, regenerating the semiconductor.

The OH reacts with hole of the semiconductor to generate \(^{1}\)OH radicals and these radicals convert the dye molecules into products, which are colourless. The participation of \(^{1}\)OH radicals as an active oxidizing species was confirmed by carrying out the same reaction in presence of some hydroxyl radical scavengers like 2-propanol, where the rate of bleaching was drastically reduced.

The study shows that EB and its mixture with amaranth in dye effluents can be efficiently photodegraded by ZnO photocatalyst in a short duration. The total (EB + amaranth) rate of photocatalytic bleaching increases. The photodegradation efficiency depends upon the initial concentration of EB, pH, amount of semiconductor, light intensity, etc.

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**References**