Use of semiconducting iron(III) oxide in photocatalytic bleaching of some dyes

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The biggest consumers of water are textiles, tannery, electroplating and pulp and paper industries and these are also the most serious polluters of environment. Photocatalytic degradation has been considered to be an efficient process for degradation of organic pollutants, which are present in the effluents released by these industries. The photocatalytic bleaching was carried out on cationic dyes (methylene blue, crystal violet, malachite green) in the presence of semiconducting iron(III) oxide and was observed spectrophotometrically. The effect of various operating variables like pH, concentration of dyes, amount of semiconductor, light intensity, particle size, stirring, etc. was also observed on the efficiency of the reaction. A tentative mechanism has also been proposed for this photocatalytic bleaching.

Keywords: Photodegradation, Photocatalytic bleaching, Iron(III) oxide, Methylene blue, Crystal violet, Malachite green
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Water is one of the fundamental requirements of life and any undesired addition of chemical substances leads to its contamination and makes it unfit for human utility. Generally, various dyes found in industrial effluents, ultimately, enter the aquatic ecosystem and can create various environmental hazards. These have very adverse and sometimes irreversible effects on other animals and plants as well. The main purpose of wastewater treatment is the removal of these toxic substances and colour and try to make the water usable for industrial or domestic use.

There are various methods like adsorption, osmosis, flocculation, etc. which have been used traditionally to remove these dyes from the water bodies, but these methods suffer from some drawbacks. Environmental photochemistry using semiconductor nanoclusters in combating against environmental pollution, forms a part of group of waste treatment methods called AOPs (Advance Oxidative Procedures) such as photo-fenton, photocatalysis, sonolysis, etc. which are being investigated to tackle these environmental problems.

Exhaustive researches in the field of photocatalysis have shown various fascinating applications of photocatalytic reactions based on the use of semiconductors. The photocatalytic bleaching was found to be the most promising and efficient process in dealing with environmental pollution, wastewater treatment, etc., in which the semiconductor particles act as photocatalysts or short-circuited micro-electrodes on excitation. This method involves the generation of hydroxyl radicals and use of these radicals as the primary oxidant for degrading organic pollutants.

Iron(III) oxide is n-type semiconductor with a band gap of 2.2 eV. Though it has been extensively investigated for its possible use in photoelectrolysis cells\textsuperscript{1,2}, little is known about its use as a photocatalyst. Cunningham et al.\textsuperscript{3} obtained evidences for the photocatalytic formation of hydroxyl radicals in illuminated suspensions of $\alpha$-FeOOH. The visible light induced photodegradation of organic pollutants on dye adsorbed TiO$_2$ surface has been reported by Chatterjee and Mahata\textsuperscript{4}. Sharma et al.\textsuperscript{5,6} reported the use of zinc oxide particulate system as a photocatalyst in the photobleaching of Brilliant Green and Rose Bengal. Mrowetz and Selli\textsuperscript{7} have reported the effect of iron species in photocatalytic degradation of an azo dye in TiO$_2$ aqueous suspension. Swarnkar et al.\textsuperscript{8} performed photocatalytic bleaching of gentian violet on cadmium sulphide powder. TiO$_2$ assisted photooxidation of a squarylium cyanine dye in aqueous dispersions under visible light radiations was observed by Wu et al.\textsuperscript{9}. The photocatalytic degradation of textile azo dye Sirius Gelb GC on TiO$_2$ or Ag-TiO$_2$ particles in the absence and presence of UV-irradiation effect has been reported by Ozkan et al.\textsuperscript{10} Ameta et al.\textsuperscript{11} reported photobleaching of basic blue 24 using photocatalyst and also studied the role of
surfactant in this photobleaching reaction. Mu Y et al.\textsuperscript{12} performed the photocatalytic degradation of orange II in presence of Mn\textsuperscript{2+}. Daneshwar et al.\textsuperscript{13} conducted the photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO\textsubscript{2}. Maruthamuthu et al.\textsuperscript{14} assessed the photocatalytic activity of Bi\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} selecting photodecomposition of peroxomonosulphate in visible radiations as the model. Ranjit et al.\textsuperscript{15} used Fe\textsubscript{2}O\textsubscript{3} and ZrO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} coupled photocatalyst for photocatalytic reduction of nitrite and nitrate ions to ammonia. Baxi\textsuperscript{16} has reported the photocatalytic oxidation of oxalic, malonic, succinic, glutaric and adipic acids over semiconducting iron(III) oxide powder. The present work describes the use of iron(III) oxide as photocatalyst in degradation of some dyes.

**Experimental Procedure**

Cationic dyes (methylene blue, crystal violet and malachite green) and iron(III) oxide were used in the present investigations. All the solutions were prepared in doubly distilled water. The photocatalytic bleaching of the dyes was observed by taking dye solution and iron(III) oxide was added to it. Irradiation was carried out keeping the whole assembly exposed to a 200W Tungsten lamp (Philips; light intensity = 60.0 mWcm\textsuperscript{-2}). The intensity of light at various distances from the lamp was measured with the help of a solarimeter (SM CEL 201). A water filter was used to cut out thermal radiations. The digital pH meter (Systronic Model 335) was used to measure the pH of the solution. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. The necessary condition for correct measurement of the optical activity is that the solution must be free from semiconductor particles and impurity; a centrifuge (Remi–1258) was used to remove these species. The progress of the photocatalytic reaction was observed by taking absorbance at regular time intervals using ultraviolet-visible spectrophotometer (JASCO 7800).

**Results and Discussion**

The photocatalytic degradation of the dyes were observed at $\lambda_{\text{max}} = 660, 590$ and 650 nm respectively for methylene blue, crystal violet and malachite green. The results of the typical run are graphically represented in Fig. 1.

It was observed that the absorbance of the dye solutions in presence of semiconductor was much low as compared to sample without semiconductor at the same time intervals. It means that the rate of this photocatalytic degradation is favourably affected by ferric oxide in the case of these dyes. A plot of log (absorbance) versus time was linear and hence, this reaction follows pseudo-first order kinetics. The rate constants of this reaction were determined by the expression.

$$k = 2.303 \times \text{slope}$$

**Effect of pH**

The pH of the solution is likely to affect the bleaching of the dyes and hence, the effect of pH on the rate of bleaching of dye solutions was investigated in the pH range, 6.0–10.5. The results are graphically presented in Fig. 2. It has been observed that the rate of photocatalytic bleaching of these dyes increase on increasing the pH in the alkaline range. This can be explained on the basis that as the pH of the medium is increased, there is a corresponding increase in the concentration of OH\textsuperscript{-} ions. These OH\textsuperscript{-} ions will
adsorb on the surface of the semiconducting ferric oxide, making it negatively charged. Thus, there will be a coulombic attraction between semiconductor surface and cationic dyes. This results in an increase of rate of photobleaching of all the three dyes on increasing pH.

**Effect of dye concentration**

The effect of dye concentration was also observed by taking different concentrations of the dyes. The results are represented in Fig. 3. The rate of photocatalytic bleaching of dyes was found to increase on increasing the concentration up to [methylene blue] = 1.60 × 10⁻⁵ M, [crystal violet] = 4.00 × 10⁻⁵ M and [malachite green] = 2.00 × 10⁻⁵ M. It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for excitation and consecutive energy transfer. As a result, increase in the rate of bleaching was observed. The rate of photocatalytic bleaching was found to decrease with further increase in the concentration of the dyes, i.e. above their corresponding limits. This decrease may be attributed to the fact that the dye itself will start acting as a filter for the incident light. It will not permit the desired intensity of light to reach the semiconducting ferric oxide particles; thus, decreasing the rate of photocatalytic bleaching of the dyes.

**Effect of amount of semiconductor**

The amount of semiconductor may also affect the process of dye bleaching and hence, different amounts of photocatalysts were used. It was observed that initially, the rate of photobleaching of the dyes increases with an increase in the amount of semiconductor but it becomes virtually constant after a certain amount of ferric oxide. This may be attributed to the fact that as the amount of semiconductor is increased, the exposed surface area of
semiconductor also increases. After a certain limit, there was no increase in the exposed surface area of the photocatalyst, even if the amount of semiconductor was further increased. A plateau is then obtained, which may be considered like a saturation point; above which, any increase in the amount of semiconductor has no or negligible effect on the rate of photocatalytic bleaching of the dyes, because any further increase in the amount of semiconductor after this point will only increase the thickness of the layer at the bottom of the vessel and not the exposed surface area. It is also confirmed by taking reaction vessels of different dimensions. It was observed that the point of saturation shifted to a higher value for vessels of larger capacities while it shifted to lower side for vessels of smaller capacities.

**Effect of light intensity**

To observe the effect of light intensity on the photocatalytic bleaching of the dyes, either light sources of different wattages were used or the distance between the light source and the exposed surface area was varied. It was observed that bleaching of the dyes was enhanced on increasing the intensity of light. This may be due to an increase in the number of photons striking per unit area of ferric oxide powder on increasing the intensity of light. A linear behaviour between light intensity and rate of reaction was observed.

**Effect of particle size**

The effect of particle size on the rate of photocatalytic bleaching of dye was investigated by varying the size of semiconductor particles (0.8–4.0 μm). The results are summarized in Table 1. The rate of photobleaching of dyes increases with decreasing particle size. This enhancement in the rate may be explained on the basis of the increased surface area of the photocatalyst as the particle size was reduced. The expected increase in the surface area of the semiconductor is four times on reducing the particle size to its half. This should increase the rate of reaction four times, but it has never been achieved. This irregularity may be due to the fact that the surface area exposed to light may not increase to the extent as expected theoretically.

**Effect of stirring**

The effect of stirring on the rate of photocatalytic bleaching of the dyes was also determined and results are reported in Table 2. It has been determined that the rate of degradation of the dyes was higher in the stirred solution as compared to unstirred one. The saturation point is shifted to a higher value of Fe₂O₃ depending upon the number of revolutions per minute. It may be explained on the basis that as the solution was stirred; the particles are better exposed to the light in all directions, while it is not possible in case of unstirred solution as only the upper hemispheres and that too of the particles on the surface are exposed.

**Mechanism**

On the basis of these observations, a tentative mechanism for photocatalytic bleaching of dyes may be proposed as –

Dye absorbs radiations of suitable wavelength and is excited to its higher energy state. The semiconducting solution as compared to unstirred one. The saturation point is shifted to a higher value of Fe₂O₃ depending upon the number of revolutions per minute. It may be explained on the basis that as the solution was stirred; the particles are better exposed to the light in all directions, while it is not possible in case of unstirred solution as only the upper hemispheres and that too of the particles on the surface are exposed.

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\[
\text{hv} \rightarrow \text{Dye} \rightarrow \text{Dye}^* \\
\text{hv} \rightarrow \text{SC} \rightarrow e^- (\text{CB}) + h^+ (\text{VB}) \text{ or SC}^+ \\
h^+ + \text{OH}^− \rightarrow \text{OH}^* \\
\text{Dye}^* + \cdot\text{OH} \rightarrow \text{Leuco [Dye]} \\
\text{Leuco [Dye]} \rightarrow \text{Products}
\]

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<th>pH</th>
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<th>Crystal violet</th>
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<td>4.00 × 10⁻⁵ M</td>
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<td>9.0</td>
<td>0.10 g</td>
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<td>-</td>
<td>k × 10⁻⁵ (s⁻¹)</td>
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ferric oxide utilizes the incident light energy to excite its electron from valence band to the conduction band, thus leaving behind a hole. This hole can abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of •OH radical as an active oxidizing species was confirmed by using hydroxyl radical scavengers, where the rate of bleaching was drastically reduced.

**Conclusion**

Photoinduced electron transfer reactions have attracted the attention of photochemists all over the world because these reactions are capable of converting toxic compounds into non-toxic or less toxic materials. The photocatalytic bleaching of dyes using low cost semiconducting powder like ferric oxide may open new avenues for the treatment of waste water from dyeing, printing and textile industries. Not only this, the treated wastewater may be used for cooling, cleaning, waste land irrigation, etc., which is not possible otherwise with coloured water. Time is not far-off, when photocatalytic route will be firm footed as a promising technology in wastewater treatment.

**References**