Artificial light assisted photocatalytic degradation of lissamine fast yellow dye in ZnO suspension in a slurry batch reactor

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The photocatalytic degradation of lissamine fast yellow has been carried out in the aqueous suspension of ZnO under artificial light. The effects of process parameters such as catalyst loading, \( \text{H}_2\text{O}_2 \), \( \text{FeCl}_3 \), etc., on the extent of degradation have been studied. The influence of pH, bubbling of \( \text{N}_2 \) and \( \text{O}_2 \) and temperature on degradation of the dye has also been studied. ZnO degrades the dye effectively in the presence of both artificial and solar light. The pH has a significant effect on reaction rate. \( \text{H}_2\text{O}_2 \), \( \text{O}_2 \), and \( \text{FeCl}_3 \) have a synergetic effect on degradation of the dye. The rate constant has an optimal value at 35°C. \( \text{N}_2 \) has a detrimental effect on dye degradation. Both \( \text{Fe}^{3+}/\text{ZnO}/\text{AR} \) and \( \text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{ZnO}/\text{AR} \) processes have been found to be effective for the decolorisation of dye. However, the \( \text{H}_2\text{O}_2/\text{Fe}^{3+}/\text{ZnO}/\text{AR} \) process is more efficient for the decolorisation of the selected dye. Increased COD-removal percentage, significant release of \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) ions and UV-vis spectral analysis confirm mineralization of the selected dye in aqueous phase. Power law has been applied to find the net rate of degradation.

Keywords: Photocatalysis, Degradation, Dyes, Azo dyes, Zinc oxide

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Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent increasing environmental danger. Recent studies indicate that during manufacturing and processing operations, substantial amounts of dyestuff are lost and the resultant color enters the environment through effluents from industrial wastewater treatment plants. Lissamine fast yellow (LFY) dye, an azo dye, is used as colorant in food, textile and leather industries. Due to its stability and carcinogenic nature, this dye forms toxic amines and poses a serious threat to the environment. It causes an allergic reaction to asthmatic patients. Recently, advanced oxidation processes (AOPs) have been proposed for the wastewater treatment since AOPs are able to oxidize a wide range of compounds that are otherwise difficult to degrade by traditional physico-chemical and biological methods. Dye-sensitized semiconductor photocatalytic degradation involving ZnO (Band gap energy = 3.2 eV) and visible light is a promising technology for the removal of toxic organic and inorganic contaminants from wastewater. Upon irradiation with near UV light, electron-holes are formed on the surface of ZnO. Holes can oxidize adsorbed water molecules or hydroxide radicals to produce hydroxyl radicals, a very strong oxidizing agent. Many studies reveal that OH• is the main oxidising species responsible for the mineralization of organic pollutant in aqueous system (Scheme 1). Other workers have reported that dye molecules act as a sensitizer by the absorption of visible light. The transfer of photogenerated electrons from the dye molecule to the conduction band of the semiconductor has been reported to be very effective (Scheme 1).

Amongst the AOPs, catalytic oxidation using Fenton and Fenton-like reagent, is an attractive treatment for the effective decolourisation and degradation of dyes because of its low cost and lack of toxicity of the reagents (\( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \) or \( \text{Fe}^{3+} \)). In recent years, many research workers have reported the degradation of dyes using Fenton and visible/solar light system. Excited dye molecule reduces ferric ion into the ferrous ion and the reduced ferrous ion reacts with hydrogen peroxide to generate hydroxyl...
radicals\textsuperscript{17,18}. The main objective of this work is to study the mineralization of LFY dye by using ZnO in the presence of artificial radiations (AR). The study also testifies the efficiency of H$_2$O$_2$/ZnO/AR, Fe$^{3+}$/ZnO/AR and H$_2$O$_2$/Fe$^{3+}$/ZnO/AR systems for the degradation of LFY dye. The complete mineralization of LFY dye with ZnO/AR system has been confirmed by COD removal and UV spectral analysis.

**Materials and Methods**

Lissamine fast yellow (mol. wt. = 551 mg mol$^{-1}$) dye (I) was purchased from Sigma-Aldrich Company (India) and was used as received. All chemicals used were of AR grade. The photocatalyst, ZnO, was obtained from Merck (about 99% pure). FeCl$_3$, H$_2$O$_2$ and Na$_2$CO$_3$ were of analytical grade and used without further purification. All the solutions were prepared by dissolving the calculated amounts of appropriate chemicals in doubly distilled water.

![Scheme 1](image)

**Photoreactor and radiation source**

The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor having double walled pyrex vessel of dimension of 7.5 cm$\times$6 cm (height $\times$ dia.) (Fig. 1). The pyrex vessel was surrounded by a thermostatic water circulation arrangement to keep the temperature in the range of 30±0.3°C. The irradiation was carried out by using 500 W halogen lamp (Philips, India) which emitted irradiation comparable to sunlight. The lamp was surrounded with aluminum reflectors in order to avoid loss of irradiation. The doubled wall pyrex vessel was placed on a magnetic stirrer. Thermometer, conductivity meter and $p$H-meter were also incorporated in the photoreactor.

![Fig. 1—Schematic representation of the photoreactor](image)
Procedure
During the photocatalytic experiment, after stirring for ten minutes, the slurry composed of dye solution and catalyst was placed in dark for half an hour in order to establish equilibrium between adsorption and desorption. Then, the slurry containing the dye and semiconductor catalyst was placed inside the reactor and stirred magnetically for agitation with simultaneous exposure to visible light. At specific time intervals, an aliquot (3 mL) of the mixture was withdrawn and centrifuged for 2 minutes at the rate of 3500 rpm to remove the ZnO particles in order to assess the extent of decolorization photometrically. The detection was observed at 405 nm. The intensity was estimated by titrating with ferrous ammonium sulphate using ferroin indicator. NO$_3^-$ and SO$_4^{2-}$ ions were detected by UV spectroscopic screening method and turbidimetric methods respectively. The efficiency of photocatalytic process was calculated as: efficiency % = $C_0 - C/C_0 \times 100$, where $C_0$ is the initial COD/absorbance and $C$ is the COD/absorbance at different time intervals of photocatalytic process.

Results and Discussion
Effect of initial dye concentration
The initial concentration of dye was varied from 2.0x10$^{-3}$ mol dm$^{-3}$ to 8.0x10$^{-3}$ mol dm$^{-3}$. It was observed that the rate constant increases from 1.8x10$^{-4}$ s$^{-1}$ to 3.37x10$^{-4}$ s$^{-1}$ with increase in dye concentration from 2.0x10$^{-5}$ mol dm$^{-3}$ to 5.0x10$^{-5}$ mol dm$^{-3}$. Thereafter, the rate constant decreases to 2.15x10$^{-4}$ s$^{-1}$ with increased dye concentration (8.0x10$^{-5}$ mol dm$^{-3}$). Maximum rate constant at 5.0x10$^{-5}$ mol dm$^{-3}$ of dye concentration is due to fact that more dye molecules are available in the photoactive volume for the photodegradation process. Rate constant decreases with further increase in concentration of dye above the optimal value. The decrease is attributed to fact that the dye itself will start acting as a filter for the incident irradiation, reducing the photoactive volume. At low concentration, the reverse effect was observed. This decreasing phenomenon can further be explained in terms of the increase in requirement of catalyst surface for the increased concentration of the dye. However, the irradiation time and amount of catalyst have been kept constant. Hence, the relative number of O$_2^*$ and OH$^-$ radicals formed on the surface of ZnO are also constant. Excessive adsorption of dye molecule on the catalyst surface hinders the competitive adsorption of OH$^-$ ions and lowers the formation rate of hydroxyl radicals. Consequently, above the optimal concentration with increase in dye concentration, the rate of degradation decreases.

Effect of pH
An important parameter in the photocatalytic reaction taking place on the particulate surface is the pH of the solution. Therefore, the photodegradation of LFY dye was studied at different pH values (in the range 3-10). The rate constant was maximal at pH 5.2. Further increase in pH caused a reduction in the rate of decolorization. At lower pH (~ 4), positively charged active sites on the surface of catalyst result in high concentration of negatively charged dye molecule on the surface of catalyst. Hence, at lower pH values, adsorption of anionic dye on the surface of ZnO increases. ZnO is amphoteric in nature, and is dissolved at lower pH to form salts. At higher pH, it forms zincates such as [Zn(OH)$_4$]$^{2-}$. Above pH 5.2, OH$^-$ concentration is very high. Due to this, the concentration of anionic dye is very low at the catalyst surface. All these factors are responsible for optimum value of photodegradation of neutral red at pH 5.2.

ZnO/AR system
In order to avoid excess of catalyst and to ensure total absorption of light, the effect of catalyst loading was studied. With increase in catalyst loading from 100 mg/100 mL to 300 mg/100 mL, the rate constant increased from 2.14x10$^{-4}$ to 3.87x10$^{-4}$ s$^{-1}$. These observations can be explained in terms of availability of active sites on the catalyst surface and the penetration of visible radiation into the suspension. The total active surface area increases with increasing catalyst dosage. However, further increase in catalyst loading (300 mg/100 mL to 700 mg/100 mL) caused a reduction in rate of decolorization. At higher loading level, there is decrease in the visible light penetration due to increased scattering of light. This light scattering attenuates light absorption inside reaction medium. Due to all these factors, the most effective decomposition of LFY was at 300 mg/100 mL of catalyst loading.
**H₂O₂/AR/ZnO system**

The rate of photocatalytic degradation of organic pollutants is significantly improved either in the presence of oxygen or by the addition of hydrogen peroxide. The rate constant has maximal value at optimal concentration. Further addition of H₂O₂ had a retarding effect on the degradation efficiency. This dual effect of H₂O₂ can be explained by the radical reaction mechanism. The added hydrogen peroxide inhibits the electron-hole recombination by accepting photogenerated electron from the conduction band of semiconductor and promotes charge separation and also forms OH⁻ radicals. Excess H₂O₂ acts as hydroxyl radical or hole scavenger to form the perhydroxyl radical (HO₂⁻), which is a much weaker oxidant than hydroxyl radicals.

**Effect of process parameters**

The influence of temperature was studied in the range 30-55°C. Rate constant was found to increase (3.07×10⁻⁴ s⁻¹ to 3.7 to 10⁻⁴ s⁻¹) with increase in temperature from 30-35°C. However, further increase in temperature reduced the rate constant. Increased temperature tends to reduce electron-hole recombination; however, an increase in temperature also decreases the solubility of oxygen in water. The two above mentioned conflicting factors have been equipoised at 45°C. Significant amount of solution also evaporated at higher temperature.

**Remarks**

Use of solar light instead of artificial irradiation is preferred from the industrial point of view. Aqueous solution of LFY and ZnO was exposed to sunlight (Table 1). It was found that the degradation of selected dye proceeds much more rapidly in the presence of solar light (intensity = 185×10²±5 lux). Blank experiments were carried out under sunlight in absence of ZnO where no observable loss of dye was observed.

Dissolved gases in a aqueous sample play an important role in the degradation of dissolved organic pollutants. The degradation of LFY was severely retarded by bubbling of pure N₂ but increases rapidly on bubbling oxygen through the dye solution (Fig. 2). Dissolved oxygen traps the conduction band electron by forming superoxide ions (O₂⁻) and thus preventing the electron-hole recombination while at the same time H₂O₂ is formed from O₂⁻ (Refs 25 & 26).

In the ZnO/FeCl₃/AR system addition of FeCl₃ caused an increase in rate constant (5.7×10⁻⁴ s⁻¹) up to concentration of 9×10⁻⁵ mol dm⁻³. Photoactivation of surface adsorbed complex ion (Fe³⁺OH⁻) results in the formation of Fe⁵⁺OH⁴⁻ species which injects electrons into the conduction band of ZnO. The increase in rate of decolorization in the case of FeCl₃ is due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals.

Above the optimal concentration, the rate constant decreased from 5.7×10⁻⁴ s⁻¹ to 4.5×10⁻⁴ s⁻¹ on addition of solar light (Fig. 2). The absorbed light increases from 2.1 to 3.7 to 10⁻⁴ s⁻¹ with increase in temperature from 30°C to 35°C. Aqueous solution of LFY and ZnO was exposed to sunlight.

**Table 1—Effect of various photocatalytic systems on the photocatalytic degradation of dye. ([LFY] = 5.0×10⁻⁵ mol dm⁻³; ZnO = 30 mg/100 mL; pH = 8.1; H₂O₂ = 9×10⁻⁵ mol dm⁻³; FeCl₃ = 9×10⁻⁵ mol dm⁻³; [Fe³⁺: H₂O₂] = 1:1.14; irradiation intensity = 134×10² lux; sunlight = 185×10² lux; temp. = 30 ± 0.3°C; irradiation time = 30 min; rate of bubbling of N₂/O₂ = 100 lb/in²)***

<table>
<thead>
<tr>
<th>Photocatalytic system</th>
<th>Degradation (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/AR</td>
<td>67</td>
<td>ZnO/AR system degrades dye effectively</td>
</tr>
<tr>
<td>H₂O₂/ZnO/AR</td>
<td>84</td>
<td>H₂O₂ has synergetic effect on dye degradation</td>
</tr>
<tr>
<td>FeCl₃/ZnO/AR</td>
<td>81</td>
<td>Fe³⁺ has synergetic effect on dye degradation</td>
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<tr>
<td>Fe³⁺/H₂O₂/ZnO/AR</td>
<td>95</td>
<td>Fe³⁺/H₂O₂ is most efficient for dye degradation</td>
</tr>
<tr>
<td>ZnO/sunlight</td>
<td>75</td>
<td>ZnO/sunlight system is effective for dye degradation</td>
</tr>
<tr>
<td>ZnO/AR/O₂</td>
<td>74</td>
<td>Addition of O₂ increases the rate of degradation</td>
</tr>
<tr>
<td>ZnO/AR/N₂</td>
<td>62</td>
<td>Addition of N₂ reduces the rate of degradation</td>
</tr>
</tbody>
</table>

**Fig. 2**—Effect of solar light on the degradation of dye. ([LFY] = 5.0×10⁻⁵ mol dm⁻³; ZnO = 300 mg/100 mL; pH = 8.1; irradiation intensity = 134×10² lux; temp. = 30±0.3°C. 1, Only sunlight ( ); 2, ZnO+AR+N₂ ( ▲ ); 3, ZnO+AR ( □ ); 4, ZnO+AR+O₂ ( ■ ); 5, ZnO+sunlight ( △ ).}
Fe⁺³/H₂O₂/ZnO/AR process

Efficiency of Fe⁺³/H₂O₂/ZnO system was studied for decolorization of LFY in the presence of artificial light (Table 1). The rate constant had a value of 4.07×10⁻⁴ s⁻¹ on addition of [Fe⁺³; H₂O₂] in the molar ratio 3:1. In the presence of [Fe⁺³; H₂O₂] in the molar ratio 1:1.4, decolorization rate was found to be four times greater than the ZnO/AR process. Upon irradiation of the Fe⁺³/H₂O₂/ZnO/LFY system with artificial radiations, production of OH⁻ radicals increased involving a very complex mechanism. The dye absorbs visible irradiation and is excited to high energy state. This excited dye molecule reduces the ferric ion complex to ferrous ion complex. The ferrous ions react with hydrogen peroxide to decompose and produce hydroxyl radical. The OH⁻ radicals also decomposed H₂O₂ to HO₂⁻. Our results are in agreement with

Spectral changes and COD measurements during mineralization

LFY is an azo dye in which the chromophore part of the molecular structure contains azo linkage and shows strong absorbance in visible region. The height of the peaks due to different molecular parts of the dye decreased with the passage of time. The decrease in absorption peaks at λmax 405 nm, indicates the removal of the -N=N- chromophoric group from the azo dye. The almost total disappearance of peaks in UV and visible region reveals that LFY dye is eliminated in the presence of ZnO after 8 h of irradiation. COD values have been related to the total concentration of organics in the solution. The percentage of COD removal during mineralization is in agreement with the spectral trend. Nearly 98% COD removal was achieved in 8 h of irradiation time (Fig. 2). Significant amounts of NO₃⁻ and SO₄²⁻ ions respectively were formed during the mineralization of LFY (Fig. 3). Maximum of 30×10⁻³ mg/L and 29 mg/L of NO₃⁻ and SO₄²⁻ were formed during 8 h of irradiation time. Slight decrease in pH and increase in conductivity also confirms the mineralization of organic dye into CO₂ and inorganic ions.

Photocatalytic degradation is of very complex nature. Under the chosen experimental conditions, photolysis had no effect on the degradation process. The simple power law model was examined to find rate of the photocatalytic degradation. The order of reaction for photocatalysis (2.16) indicates intricacy of degradation process. The rate constant for degradation of LFY was found to be 12.2×10⁻² (mol dm⁻³)²².²² s⁻¹. Our results are in agreement with

of FeCl₃ (9×10⁻³ mol dm⁻³ to 13×10⁻⁶ mol dm⁻³). In the presence higher concentration of FeCl₃, there is excessive surface adsorption of anionic dye on the surface of catalyst. This reduces the total photoactive area of catalyst and lowers the reaction rate. In the AR/FeCl₃ system, no significant changes were recorded in the absorption spectra of LFY dye for 2 h. Addition of FeCl₃ was governed by two opposing factors: (i) enhancement in production of OH⁻ radicals, and, (ii) adsorption of cationic dye molecule on the surface of ZnO. Below the optimal concentration, the former dominates while above the optimal concentration, the latter plays an important role in the retardation of degradation of dye. Therefore, higher concentration of FeCl₃ inhibits the reaction rate of decolorization by competing with production of hydroxyl radicals.
other studies reported in literature\textsuperscript{11,24,34}. Under chosen experimental conditions, the net rate of degradation of LFY can be written as \(1.2 \times 10^{-2} [\text{LFY}]^{2.16} \text{mol dm}^{-3} \text{s}^{-1}\).

**Conclusions**

The results of our study show that Fe\(^{3+}/\text{H}_2\text{O}_2/\text{ZnO}/\text{AR}, \text{H}_2\text{O}_2/\text{ZnO}/\text{AR}, \text{Fe}^{3+}/\text{ZnO}/\text{AR} \) and \(\text{ZnO}/\text{AR} \) processes can be efficiently used for the degradation of selected dye. The optimal pH for the dye degradation is 5.2. Rate of reaction is maximal at 300 mg/100 mL of catalyst loading and \(5.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ dye concentration. Rate constant has maximal value at optimal concentration of \(\text{H}_2\text{O}_2 \) (9×10\(^{-5} \text{ mol dm}^{-3}\)) \) and \(\text{FeCl}_3 \) (9×10\(^{-5} \text{ mol dm}^{-3}\)). At optimal molar ratio of \(\text{FeCl}_3/\text{H}_2\text{O}_2 \) (1:1.4), the rate constant has a value of \(1.5 \times 10^{-4} \text{ s}^{-1}\). Solar light is efficient for the decolourisation of selected dye. At the optimal concentrations of the reagents for all the studied processes, the following sequence of rate constant for different photocatalytic systems has been obtained for the decolourisation of lissamine fast yellow dye: \(1.1 \times 10^{-4} \text{ s}^{-1} \) (\(\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{ZnO}/\text{AR} \)) > \(7.5 \times 10^{-4} \text{ s}^{-1} \) (\(\text{H}_2\text{O}_2/\text{ZnO}/\text{AR} \)) > \(5.7 \times 10^{-4} \text{ s}^{-1} \) (\(\text{Fe}^{3+}/\text{ZnO}/\text{AR} \)) > \(3.87 \times 10^{-4} \text{ s}^{-1} \) (\(\text{ZnO}/\text{AR} \)). The \(\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{ZnO}/\text{AR} \) process has been found to be most efficient. The estimated COD-removal percentage and studies with varying pH, conductivity, and \(\text{NO}_3^- \) and \(\text{SO}_4^{2-} \) ions, indicates that the \(\text{ZnO}/\text{AR} \) system mineralizes LFY dye completely in 8 h of irradiation time. These studies show that \(\text{ZnO} \) and visible light process can be employed as a powerful tool for the decolorization and reduction of LFY dye from wastewater. The use of low cost and biologically inactive catalyst and possibility of activating it with solar light offer an economical and feasible solution for the processing of liquid waste, especially in regions of abundant sunlight.

**References**