Photocatalytic destruction of an organic dye, Acid Red 73 in aqueous ZnO suspension using UV light energy

A Nilamadanthai, N Sobana, B Subash, M Swaminathan & M Shanthi*

Department of Chemistry, Annamalai University, Annamalainagar 608 002, Tamil Nadu, India

Email: shanthismn@gmail.com

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Photocatalytic degradation of the azo dye Acid Red 73 (AR 73) in aqueous solution with zinc oxide as photocatalyst in slurry form has been investigated using UV light. There is a significant difference in adsorption of dye on ZnO surface with the change in solution pH. The effects of various parameters such as catalyst loading, pH and initial concentration of the dye on degradation have been determined. The degradation is strongly enhanced in the presence of electron acceptors such as H$_2$O$_2$, (NH$_4$)$_2$S$_2$O$_8$ and KBrO$_3$. Addition of dye-assisting chemicals such as Na$_2$CO$_3$ and NaCl inhibits the removal rate. The photodegradation analysis has been carried out using Langmuir-Hinshelwood kinetic model.

Keywords: Photocatalytic degradation, Degradation, UV light, Acid Red 73, Dye degradation, Zinc oxide, Oxides

Colour is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Most of the industries in India, viz., textile, paper, printing, leather, food, cosmetics, etc., use dyes to colour their final product. Discharge of such coloured effluents imparts colour to the receiving water bodies (rivers and lakes) and interferes with its intended beneficial use. Colour impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which produce micro-toxicity to fish and other organisms. It should be noted that the contamination of drinking water by dyes at even a concentration of 1.0 mg/L could impart significant colour making it unfit for human consumption. Most of the dyes are resistant to aerobic biodegradation. Although anaerobic treatment can remove the colours of azo dyes by transforming the azo bond to aromatic amines, amines are carcinogenic and more dangerous than dyes. The current dye house wastewater treatment methods are ineffective to completely remove the dye from the environment. Conventional treatment methods like adsorption and membrane separation, etc. do not mineralize the pollutants to harmless products.

In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. AOP generates powerful oxidizing agent (hydroxyl radicals) which completely destroy the pollutants in wastewater. Heterogeneous photocatalysis through illumination of UV (or) solar light on a semiconductor surface is an attractive advanced oxidation process. The photocatalyst, titanium dioxide (TiO$_2$), is a wide band gap semiconductor (3.2 eV) and is successfully used as a photocatalyst for the treatment of organic and dye pollutants. ZnO is found to be a suitable alternative to TiO$_2$ and has proved to be more efficient than TiO$_2$ in several applications. For the practical application of ZnO-UV light process for dye wastewater, there is a need to determine the optimal conditions of experimental parameters. In our earlier work, we have reported the degradation of some organic pollutants by advanced oxidation process using UV and solar light. In the present investigation we have undertaken a reactive class bis-azo dye Acid Red 73 (AR 73) and examined the various parameters to find out the optimum conditions for degradation of dye. The study would provide an insight into their efficiencies in the detoxification of industrial dye waste water. Dye industries can utilize these results for designing efficient treatment plants.

Experimental

The commercial diazo dye, Acid Red 73 (AR 73; 3×10$^{-4}$ M; pH = 6.8) obtained from Colour Chem, Pondicherry, India, was used as such. The photocatalyst, zinc oxide, was purchased from E Merck (99% purity). The ZnO had a particle size 0.1-4 μm and surface area 5 m$^2$ g$^{-1}$. The experiments were carried out in slurry form of the catalyst. AnalalR grade reagents H$_2$O$_2$, (NH$_4$)$_2$S$_2$O$_8$, KBrO$_3$ (E Merck), Na$_2$CO$_3$ and NaCl were used as received. Doubly distilled water was used to prepare experimental solutions. The pH of the solutions were adjusted using H$_2$SO$_4$ and NaOH and measured using a Hanna Phep (model H 198107) digital pH meter. UV absorbance
measurements were carried out using Hitachi U-2001 spectrophotometer.

The photocatalytic experiments were carried out in a Heber multilamp photoreactor model HML-MP88 comprising eight medium pressure mercury vapour lamps (8 W) set in parallel and emitting at wavelength 365 nm. After adsorption in the dark, the first sample was taken. At specific time intervals 2–3 mL of the sample was withdrawn and centrifuged to separate the catalyst. The centrifugate (1 mL) was diluted to 10 mL and its absorbance at 246 nm was measured. The absorbance at wavelength 246 nm is a characteristic absorption of the dye. The absorbance at 246 nm represents the aromatic content of AR 73 and the decrease of absorbance at 246 nm indicates the degradation of aromatic part of the dye. Similar results have been reported for AB 1 dye degradation by ZnO.

**Results and discussion**

The results of photodegradation with and without ZnO-UV light are shown Fig. 1. There is no dye degradation in the absence of the photocatalyst on irradiation with the UV light up to 2 hours. In presence of zinc oxide and in the absence of UV light there is a small decrease in dye concentration initially, after which the dye solution is stable till the end of the experiment. The initial decrease is due to the adsorption of the dye on zinc oxide. The dye undergoes 70% degradation in 120 min on irradiation with light wavelength 365 nm in presence of zinc oxide. The degradation of the aromatic part of the dye molecule takes a longer time for its removal. Initially the degradation is fast while at the end of the photocatalytic process the removal rate is slow. This is due to the formation of intermediate compounds in the dye degradation. The competition of the intermediate compounds with the parent molecules in the photocatalytic degradation process slows down the rate. This shows that the dye undergoes degradation only in the presence of light and catalyst, i.e. the dye is degradable photocatalytically.

The amount of catalyst is one of the main parameters for degradation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process. The effect of catalyst weight on the photocatalytic degradation of the dye has been carried out in the range 50-200 mg of the catalyst for 50 mL of dye solution (Fig. 2). The results clearly show that the increase of catalyst weight from 50 mg to 100 mg increases the dye degradation from 55.55% to 70.57% at 120 min. The enhancement of removal rate is due to the increase in the density of catalyst particles in the area of illumination. Increase of the catalyst loading beyond 100 mg may cause screening effect which may reduce the activity of the catalyst. At high concentrations of the catalyst, particle

![Fig. 1 - Photodegradability of Acid Red 73. ([AR 73] = 3 × 10^{-4} M; pH = 7.0 ± 0.1; catalyst suspended = ZnO (100 mg/50 mL); incident wavelength = 365 nm; absorbance measured at 246 nm. 1, dye solution irradiated with UV light in the presence of ZnO; 2, dye solution treated with ZnO in the dark; 3, dye solution irradiated with UV light in the absence of ZnO).](image1)

![Fig. 2 - Effect of catalyst weight on the photodegradation of dye using UV light. ([AR 73] = 3×10^{-7} M; pH = 7.0±0.1; temp = 30±0.1 °C; incident wavelength = 365 nm; absorbance measured at 246 nm. Amt. of catalyst (mg): 1, 50; 2, 75; 3, 100; 4, 150; 5, 200).](image2)
aggregation may also reduce the catalytic activity. The optimum amount of catalyst loading is found to be 100 mg for the degradation of AR 73. Hence 100 mg/50 mL was used as the catalyst dosage for the photocatalytic reactions.

The effect of solution pH was investigated on the photocatalytic degradation (Fig. 3). Increase of pH of the dye solution from 3 to 11 increases the degradation from 57.82 to 99.91% at 90 min. The photocatalytic degradation was observed to be faster in alkaline pH than in acidic pH. Similar observations have been reported earlier.24,25 In the acidic pH range, the removal efficiency is minimum. This is due to two reason (i) at low pH value ZnO may undergo dissolution which decreases its activity. The increased efficiency in the alkaline pH range is due to the increase in the formation of OH radicals from hydroxide ions (OH$^- + h^+ \rightarrow \cdot OH$).

The photocatalytic degradation of AR 73 is mainly due to the hydroxyl radical attack on dye molecule. The production of hydroxyl radical in the acidic medium is different from the basic medium. The change of pH after irradiation was not significant.

The pollutant concentration is an important parameter in wastewater treatment. The photocatalytic degradation of dye has been carried out at different initial concentrations of the dye in the range 1×10$^{-4}$ to 7×10$^{-4}$ M (Fig. 4). Increase in the concentration of dye from 1×10$^{-4}$ to 7×10$^{-4}$ M decreases the degradation rate constant from 0.0178 to 0.0082 min$^{-1}$. Similar results have been reported for the photocatalytic oxidation of other dyes.20,26 When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of ZnO. The increase in dye concentration also decreases the path length of the photon entering into the dye solution. At high dye concentration, a significant amount of UV light may be absorbed by the dye molecules rather than by the catalyst and this reduces the catalytic efficiency.27

The photocatalytic degradation of AR 73 dye containing ZnO obeys pseudo-first order kinetics.28 At low initial dye concentration the rate expression is given by $-d[C]/dt = k'[C]$, where $k'$ is the pseudo-first order rate constant. The dye is adsorbed onto the ZnO surface and the adsorption-desorption equilibrium is reached. After adsorption, the equilibrium concentration of dye solution was determined and taken as the initial dye concentration for kinetic analysis. A plot of ln $C_0/C$ versus $t$ for photodegradation shows a linear relationship between dye concentration and irradiation time (Fig. 5). The regression co-efficients for the different concentrations studied are in the range of 0.979-0.999. Many workers29-31 have used the Langmuir-Hinshelwood (L-H) kinetic expression to analyse the heterogeneous photocatalytic reaction successfully. Experimental data has been rationalised in terms of the modified form of L-H kinetic model to describe the solid-liquid reaction successfully.32 The rate of oxidation of AR 73 dye at the surface reaction is proportional to the surface coverage of dye on the ZnO assuming that the dye is more strongly adsorbed.

Fig. 3 – Effect of pH on the photocatalytic degradation of dye using UV light. {[AR 73] = 3×10$^{-4}$ M; pH = 7.0±0.1; catalyst suspended = ZnO (100 mg/50 mL); incident wavelength = 365 nm; absorbance measured at 246 nm. 1, pH = 3; 2, pH = 5; 3, pH = 7; 4, pH = 11}.

Fig. 4 – Effect of various initial dye concentrations on the degradation of Acid Red 73 by UV/ZnO. [Catalyst suspended = ZnO (100 mg/50 mL); pH = 7.0±0.1; incident wavelength 365 nm; absorbance measured at 246 nm. Conc. of dye: 1, 7×10$^{-4}$ M; 2, 5×10$^{-4}$ M; 3, 3×10$^{-4}$ M; 4, 1×10$^{-4}$ M].
electron-hole recombination and generate the hydroxyl radicals and other oxidizing species.

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \cdot\text{OH} + \text{OH}^- \]

\[ \text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\cdot\text{OH} \]

\[ \text{SO}_4^{2-} + \text{e}^-_{\text{(CB)}} \rightarrow \text{SO}_4^{-} + \text{SO}_4^{2-} \]

\[ \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{SO}_4^{2-} + \text{H}^+ \]

\[ \text{BrO}_3^- + 6 \text{e}^-_{\text{(CB)}} + 6\text{H}^+ \rightarrow \text{Br}^- + 3\text{H}_2\text{O} \]

**Scheme 1**

The other chemicals used in the dye industry play a vital role in the dyeing process. Na\textsubscript{2}CO\textsubscript{3} is added to adjust the pH of the dye bath which is important in fixing the dye on the fabrics. Sodium chloride is mainly used in the dyeing process for the transfer of dye stuff to fabric.\textsuperscript{34} Therefore, the dye industry wastewater contains a considerable amount of carbonate and chloride ions. Hence, it is important to study the influence of CO\textsubscript{3}\textsuperscript{2-} and Cl\textsuperscript{-} ions in the photocatalytic degradation. Addition of Na\textsubscript{2}CO\textsubscript{3} and NaCl decreases the degradation efficiency of ZnO by 66 and 65% respectively, which is due to the hydroxyl radical and hole scavenging effects of Na\textsubscript{2}CO\textsubscript{3} and NaCl respectively (Eqs 1-3). Addition of H\textsubscript{2}O\textsubscript{2}, (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} and KBrO\textsubscript{3} increases the degradation by 95, 76 and 85.2% respectively, which is due to the inhibition of electron-hole recombination and production of oxidising species. The inhibitory effect of chloride and phosphate ion on the photocatalytic degradation has been reported earlier.\textsuperscript{35}

\[ \text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{OH}^- + \text{CO}_3^{2-} \]  \( \ldots (1) \)

\[ \text{Cl}^- + \text{h}_{\text{VB}}^+ \rightarrow \text{Cl}^* \]  \( \ldots (2) \)

\[ \text{Cl}^* + \text{Cl}^- \rightarrow \text{Cl}_2^* \]  \( \ldots (3) \)

In the present study, AR 73 dye has been successfully degraded by ZnO assisted photocatalysis in aqueous dispersion under irradiation by UV light. The dye is resistant to direct photolysis. The optimum catalyst concentration for the degradation of 3×10\textsuperscript{4} M solution at room temperature is 100 mg/50 mL, while the optimum pH is 7. The photocatalytic degradation obeys pseudo-first order kinetics at low initial concentration. Addition of electron acceptors such as H\textsubscript{2}O\textsubscript{2}, (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} and KBrO\textsubscript{3} enhances the
degradation, while the presence of auxiliary chemicals such as Na$_2$CO$_3$ and NaCl decreases the photocatalytic degradation.

References