

Comparative Evaluation of UV / Solar Light Induced Photodegradation of Azo Dye in Aqueous Solutions

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In present study, photocatalytic degradation of Acid Orange 7 (AO7), an anionic dye has been investigated in a batch reactor using titania P-25 (surface area: 50 m²/g) as a photocatalyst under UV/Solar light in slurry mode. The variables studied include catalyst dose, solution pH and dye concentration. The degradation rate of AO7 was favorable at pH 2. Optimum value of catalyst dose was found to be 1g/l. The disappearance of AO7 obeyed first order kinetics and the value of the rate constant k was $1.1 \times 10^{-4} \text{ S}^{-1}$. COD analysis revealed the mineralization of AO7 on TiO₂ surface. The complete degradation of AO7 was achieved in 15 h under UV irradiation, whereas under solar light, AO7 was degraded completely in 55 minutes only.

Key Words: Azo dye; Acid orange 7; Titanium dioxide; Photodegradation; Photocatalytic

INTRODUCTION

Azo dyes, aromatic moieties linked together by one or more azo bonds (–N=N–), represent the largest class of synthetic colored organic compounds used in a variety of applications¹. The presence of colorants in the aquatic system, even in small concentrations, can color large water bodies, which not only affect aesthetic merit but will also reduce the light penetration and photosynthesis². Apart from the environmental pollution, such colored dye effluents pose a major threat to the surrounding ecosystems since, some of the dyes and their intermediates pose documented health hazards³. Environmental concerns and the need of meeting the stringent international standards for rejecting wastewaters have made the development of novel, efficient and low cost processes for the purification of textile aqueous effluents an issue of major technological importance. Among the various advanced oxidation processes that have been proposed for the degradation of recalcitrant azo-dyes, TiO₂-mediated photocatalysis under UV light has been shown to be potentially advantageous as it may lead to complete mineralization of pollutants to CO₂, water and mineral acids^{4,5}. As in tropical regions solar energy is abundant and 5% of total solar spectrum emits UV radiations. Therefore, the use of visible light of solar energy,

which is free and inexhaustible, has recently drawn considerable attention.

Acid orange 7 is an anionic azo dye, having versatile applications. It is used widely for dyeing wool, cotton fibers, silk, paper and leather. Aqueous solution of Acid orange 7 is reasonably photostable if subjected to sunlight. Therefore, the rate of degradation of Acid orange 7 using photocatalyst in presence of solar and UV light appears to be quite promising. The present study reports the degradation of Acid orange 7 using TiO₂ in presence of UV light and solar light. The effect of change of pH, amount of catalyst and concentration of dye has also been studied.

EXPERIMENTAL

Titania P-25 (surface area 50 m²/g) was obtained from Degussa and was used as received. Acid orange 7 was purchased from Merck and used without purification. pH of the solutions was adjusted with 1M HCl or 1M NaOH. Photochemical degradation is carried out in specially designed reaction vessels in the photoreactor equipped with 4 UV tubes each of 30W (Philips). For solar experiments, the borosilicate glass reactors of diameter 0.17m and 800 ml capacity were made with ports at the top for sampling, gas purge and gas outlet. The spectra were taken with UV-VIS Spectrophotometer (Systronics 119); pH meter (Thermo Orion 920A) was used to adjust the pH of the solution. COD analysis was carried with Thermo Orion Aqua Fast II AQ 2040 COD meter. For the degradation experiments, 1 gm of photocatalyst TiO₂ was added to 100 ml of dye solution and suspension was subjected to irradiation under UV light or solar light. The aqueous suspension was magnetically stirred and aerated throughout the experiment. At different time intervals aliquot was taken out with the help of syringe and then filtered through Millipore syringe filter of 0.45µm. The absorption spectra was recorded at $\lambda_{\text{max}} = 484 \text{ nm}$. The rate of degradation was studied in terms of changes in absorption spectra. Similar experiments were carried out by varying the pH of the solution, concentration of dye and dose of photocatalysts.

RESULTS AND DISCUSSION

Acid orange 7 shows characteristic absorption peaks at 484 nm, 430nm, 311nm, 256 nm and 230 nm. Fig. 1 shows a typical UV-VIS spectrum of acid orange 7 solution. The absorption peaks corresponding to dye diminished during photo degradation using TiO₂/UV photo catalytic system, which indicated that the dye has been degraded.

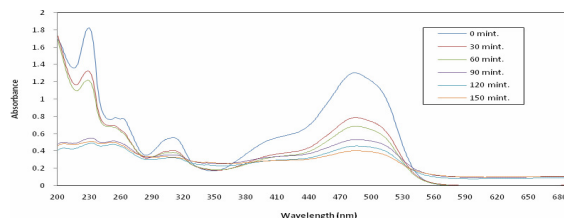


Fig. 1 Time dependent UV absorption spectra for degradation of Acid Orange 7(25 ppm; natural pH; TiO₂ 1g/l)

In order to optimize the dose of catalyst the experiments were performed by varying catalyst concentration from 0.25g/l to 2.0 g/l. The graph plotted (Fig. 2) between amount of catalyst used and percentage degradation reveals that with an increase in catalyst dose degradation efficiency (69.09%) increases upto 1g/l catalyst dose. Due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases⁶.

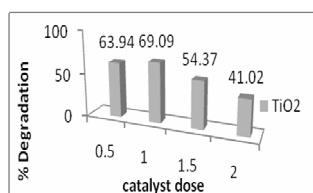


Fig. 2. Effect of catalyst dose on degradation of AO7 (25 ppm AO7; time 2.5 hrs)

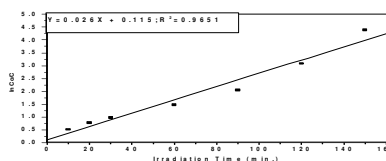


Fig.3. Kinetic analysis of AO 7 under optimized conditions

In the present study, the effect of pH of the solution on the percentage photodegradation was examined in the range 2-10. The results reveal that the lesser degradation of dye occurs in basic solution and higher in acidic region with TiO₂. Although the degradation occurs in basic medium (pH \geq 8) up to 38.68 % but it is maximum (79.58 %) at pH-2 with TiO₂. Findings of others^{7,8} also show that degradation of anionic dyes is more in acidic medium because at pH higher than pzc of titania, its surface becomes negatively charged so adsorption will be less.

After optimizing the experimental conditions, the photocatalytic discoloration of acid orange 7 was carried out by varying the initial concentrations of the dye from 5-100 ppm in order to assess the appropriate amount of catalyst dose. As the concentration of the dye is increased, the rate of photodegradation decreases indicating either to increase the catalyst dose or time span has to be increased for the complete removal.

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of an organic species, the percentage change in COD was studied for dye samples (initial concentration 25 mg/l) under optimized conditions (catalyst dose 1 g/l, pH natural, time 150 min.). The COD reduction is lesser (62.41%) in 2.5 h than percentage decolorization which may be due to the formation of smaller uncolored products. Therefore, it seems that to achieve complete mineralization of dyes, longer irradiation time is required.

Fig. 3 shows the kinetics of disappearance of AO7 for an initial concentration of 25 mg/l under optimized conditions with TiO₂. The results show that the photocatalytic decolorization of the dye can be described by the first order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t . The semilogarithmic plots of the concentration data gave a straight line. The correlation constant for the fitted line was calculated to be $R^2 = 0.9196$ for TiO₂. The rate constants were calculated $1.1 \times 10^{-4} \text{ s}^{-1}$.

The photoassisted decolorization of AO7 was also carried out using TiO₂ as photocatalyst and solar irradiation as light source. Fig 4(a) illustrate the results of photodecolorization of dye using optimized conditions as a function of irradiation time under solar light. The results indicate that decolorization of AO7 occur at a faster rate with solar light in comparison to UV light. 99.30% decolorization efficiency was observed in 55 min irradiation time under solar light, whereas in the presence of UV irradiation for the same duration, only 44.27% decolorization efficiency was recorded (Fig 4(b)). Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately for degradation of pollutants, it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries like India, intense sunlight is available throughout the year and, hence it could be effectively used for photocatalytic degradation of pollutants in wastewater. Moreover there is no material deterioration in case when sunlight is used as a radiation source⁹.

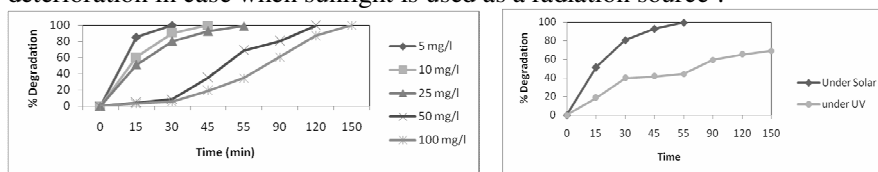


Fig. 4. (a) Effect of initial concentration of Acid Orange 7 on degradation under solar light (pH natural; 1 g/l catalyst dose) (b) Comparison of solar/UV irradiation on photocatalytic activity for AO 7

Conclusion

Photocatalytic activity of TiO₂ is greater in the presence of solar light as compared to UV light. Experimental results indicated that the decolorization of dyes is facilitated in the presence of catalyst and were favorable in acidic region. The optimum dose of the catalyst is required for the complete degradation of the known concentration of the dye solution because high as well as low catalyst dose reduce the percentage degradation of dye. As the initial concentration of dye was increased, the rate of decolorization decreased. The photocatalytic decolorization followed pseudo-first order kinetics. The COD analysis revealed that complete mineralization of dyes could be achieved in longer irradiation times.

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