

Photodegradation of Dye Acid Orange 67 by Titanium Dioxide in the Presence of Visible Light and UV Light

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Keywords: photocatalyst, AOP, UV irradiation, photodegradation,**ABSTRACT**

The photocatalytic degradation of azo dyes containing different functionalities has been reviewed using TiO₂ as photocatalyst in aqueous solution under solar and UV irradiation. The mechanism of the photodegradation depends on the radiation used. Kinetic analyses indicate that the photodegradation rates of azo dyes can usually be approximated as pseudo-first-order kinetics for both degradation mechanisms, according to the Langmuir-Hinshelwood model. The degradation of dyes depends on several parameters such as pH, catalyst concentration, and substrate concentration. The application of novel treatment methods encompasses investigations of advanced oxidation processes (AOP's), which are characterized by production of the hydroxyl radical (OH) as a primary oxidant. In this work, we investigated the photocatalytic oxidative degradation and discoloration of acid dye and dye intermediates using light (UV/visible)/semiconductor catalyst by optimizing the operational parameters to ensure the rapid and complete transformation of the toxic organic compounds to benign chemicals. The results showed that efficiency of dye degradation is much better when light source is UV in comparison to Visible.

INTRODUCTION

Today protection of environment has become a major and crucial factor. As we know that the increase in the number of industries and factories due to industrial revolution raises the issue of protection of the environment.

A lot of industries especially textile, dyeing and printing industries have generated environmental problems. Textile effluent are complex mixtures containing a wide variety of dyes, natural impurities extracted from fibers and other pollutants such as dispersants, levelling agents, herbicides, acids, alkalies, salts and sometimes heavy metals. These effluents are notoriously known to have a strong color, large amount of suspended and dissolved solids, broadly fluctuating pH, high chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and presence of metal ions [1].

The environmental concern of these potentially carcinogenic pollutants in contaminated water has drawn the attention of many research workers [2]. Wastewater originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature [3].

A large number of organic substances like dyes, phenols, pesticides, fertilizers, detergents and other chemical products are disposed of directly into the water system from various sources such as industrial effluent, agricultural runoff and chemical spills [4]. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [5].

It is therefore necessary to treat the contaminated water. Conventional oxidation treatments have found difficulty to oxidize these products and complex structure of organic compounds. AOPs are based on the generation of hydroxyl radical ([•]OH) which has high oxidation potential (2.8V) that completely convert organic contaminant into CO₂, H₂O and inorganic ions or biodegradable compounds [6]. Environmental pollution and destruction on a global scale have drawn attention to the vital need for totally new environmental friendly clean chemical technologies and processes.

Materials

For the present studies the commercial azo dye acid orange 67 was used. Photocatalyst TiO_2 (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used for photocatalytic degradation. For the photobleaching process, $1 \times 10^{-3}\text{M}$ stock solution of dye was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

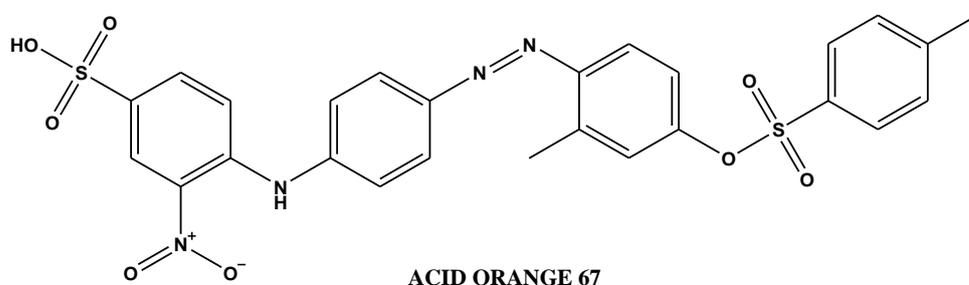


Fig. 1 Molecular formula- $\text{C}_{26}\text{H}_{21}\text{N}_4\text{NaO}_8\text{S}_2$ **Molecular weight -** 604.586

Procedure and Analysis

Under Visible light

Photocatalytic bleaching of Acid Orange 67 was studied by taking 100 ml of 3.5×10^{-5} dye solution in 250 ml round bottom flask and 0.35 g of solid TiO_2 catalyst powder was added to it. The pH of the reaction medium was alkaline (8.5) by adding 0.1 N NaOH and measured with pH meter (Systronic, 106). The mixture was then irradiated under light using $2 \times 200\text{W}$ Tungsten lamps (Sylvania Laxman) to provide energy to excite TiO_2 loading. A water filter was placed between light source and reaction vessel to avoid thermal effect. Air was continuously purged through reaction mixture with the help of an aerator for stirring purpose and availability of oxygen.

About 3ml of this dye solution was taken out after a specific time interval (30 min.) and its absorbance was measured using spectrophotometer at 485 nm after filtration through a G-3 sintered glass crucible. This process was repeated regular time intervals. The rate of decrease of colour with time was continuously monitored.

Under UV light

Photocatalytic bleaching of Acid Orange 67 was studied by taking 100 ml of $3.5 \times 10^{-5}\text{M}$ dye solution in 250 ml round bottom flask and 0.25 g of solid TiO_2 catalyst powder was added to it. The pH of the reaction medium was alkaline (7.5) by adding 0.1 N NaOH and measured with pH meter (Systronics, 106).

The reaction mixture was then irradiated under UV light. Photochemical degradation is carried out in specially designed reaction vessels in the photoreactor equipped with 4 UV tubes each of 30W (Philips). About 3ml of this dye solution was taken out after a specific time interval (30 min.) and its absorbance was measured using spectrophotometer at 485 nm after filtration through a G-3 sintered glass crucible.

RESULTS AND DISCUSSION

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst light to follow the photocatalytic path for the photobleaching of dye. The photo catalytic bleaching of Dye Acid Orange 67 using TiO_2 as photo catalyst and Solar/ UV irradiation as light source has been carried out and it could be say that complete degradation of dye requires more time in solar irradiation than UV. The energy of UV irradiation is large compared to band gap energy of catalysts. Hence the problem of electron - hole recombination is not fully but largely avoided with UV source. In sunlight only 5% of the total radiation possesses the optimum energy for photo catalytic excitation and ultimately degradation of textile dyes, it could be Safe and cost effective source.

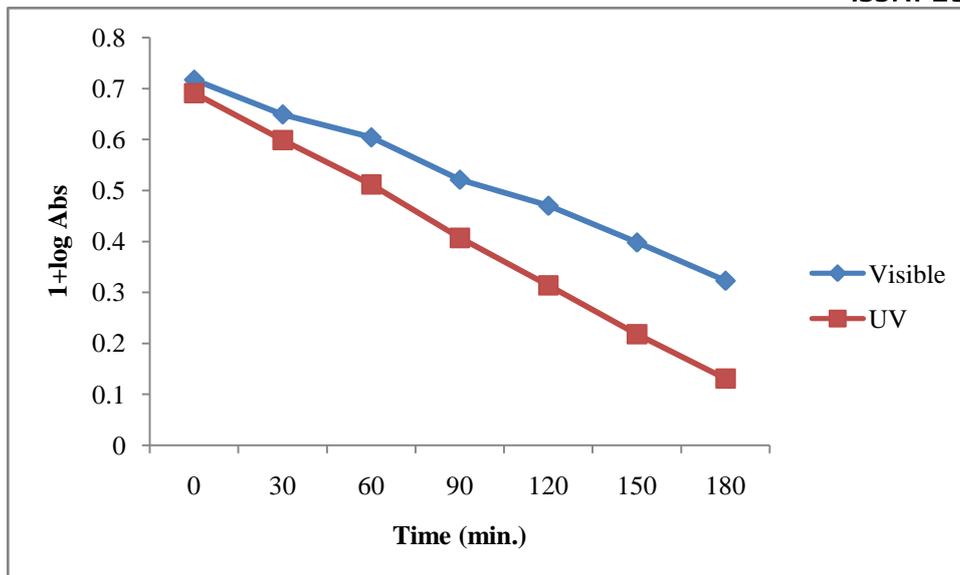


Figure 2: Effect of UV/Visible light on photo catalytic degradation of Acid Orange 67

In tropical countries intense sunlight is available throughout the years and hence, it could be efficiently used for photo catalytic degradation of pollutants in wastewater. No material deterioration in case the sunlight is used as radiation source, though the UV irradiation can efficiently degrade the dyes, visible irradiation is also very effective in the mineralisation of dye.

Effect of reaction parameters

- Effect of variation in pH
- Effect of amount of catalyst(TiO₂)
- Effect of concentration of dye

Effect of variation in pH

In the presence of visible light it was observed that the rate of photocatalytic bleaching increases with an increase in pH up to 8.5. This observation can be explained on the basis that as the pH of solution increases, more OH⁻ ions are available. These OH⁻ ions will generate more ·OH radicals by combining with the hole of the semiconductor. These hydroxyl radicals are responsible for photobleaching of dye. It was observed that the rate of photocatalytic bleaching increases with an increase in pH up to 9.0 in the presence of UV light.

After a certain pH value i.e. above pH 8.5 the rate of photobleaching decreases due to that more OH⁻ ions will make the surface of semiconductor negatively charged which repel the approach of anionic dye molecules toward the semiconductor surface. This results into a decrease in rate of photocatalytic bleaching of dyes. Same reason can be given for the dye when it was irradiated under UV light.

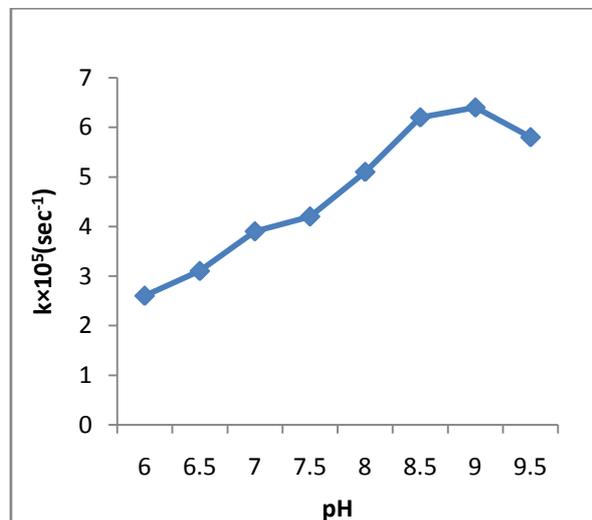
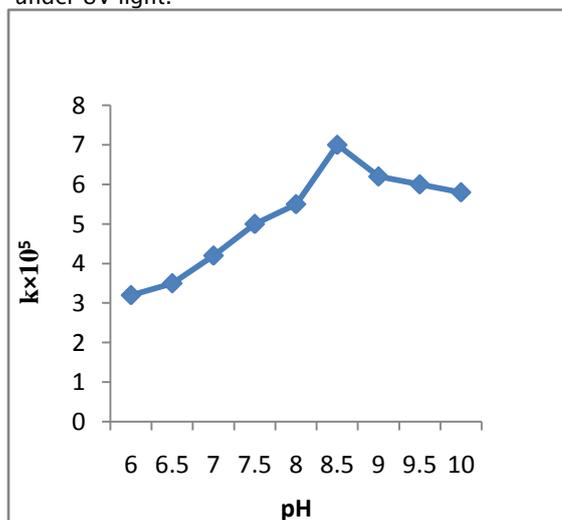


Figure 3 & 4: showing effect of variation in pH under UV/ Visible light

Effect of variation of amount of semiconductor [TiO₂]

As indicated in above data, the rate of photocatalytic bleaching of Acid Orange 67 increases with increase in amount of semiconductor catalysts but after a certain amount, the rate becomes almost constant. This may be due to the fact that, initially the increase in the amount of catalyst increases the number of TiO₂ active sites on the surface that in turn increases the number of ·OH and O₂⁻ radicals. After a certain level of catalyst concentration of dye, further dye molecules are not available for absorption. The additional catalyst particles therefore are not involved in the catalytic activity. Hence the degradation remains constant. But in the presence of UV light amount of semiconductor needed is less.

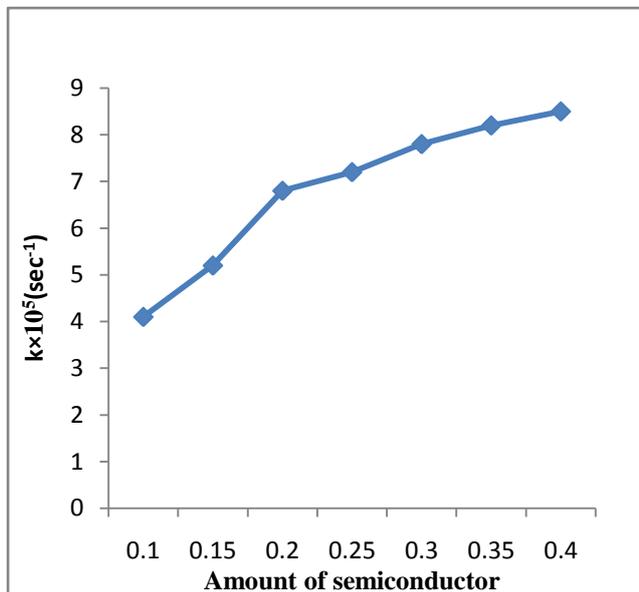
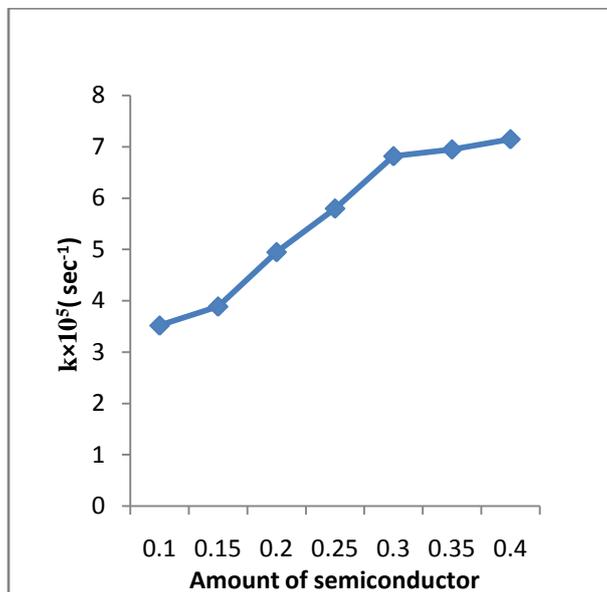


Figure 5 & 6: Showing effect of variation of amount of semiconductor [TiO₂] under UV/ Visible light

Effect of variation of Acid Orange 67 concentrations

It has been observed that the rate of photocatalytic degradation increases with increase in the concentration of Acid Orange 67 under UV and Visible light. The highest efficiency was observed at lower concentration. This can be explained on the basis that with the increase in initial concentration of the dye, while the irradiation period and amount of semiconductor are kept constant, more dye molecules are available for excitation and energy transfer and hence, an increase in the number of substrate ions accommodating in interlayer spacing inhibits the action of the catalyst, which thereby dye molecules and photodegradation efficiency.

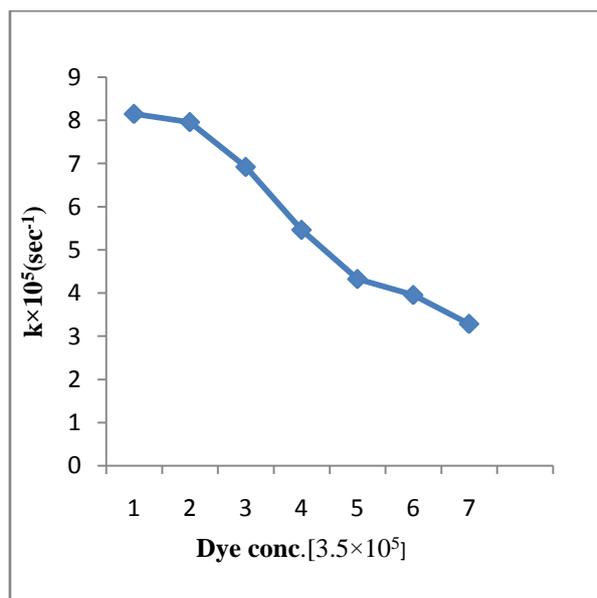
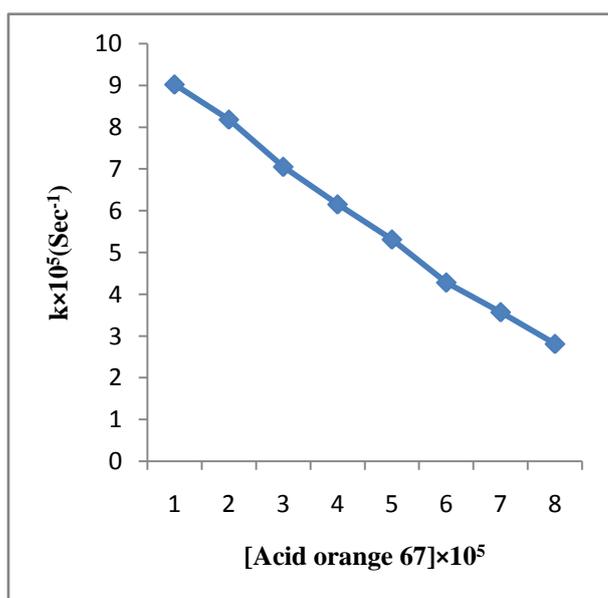


Figure 7 & 8: showing effect of variation of Acid Orange 67 concentrations under UV/ Visible light

CONCLUSION

Photo bleaching of dye Acid Orange 67 depends on the amount of dye, pH and light intensity. TiO_2 is an effective photo catalyst because of its large band gap and non corrosive nature. Though the UV irradiation can bring better efficiency in the degradation of dye, solar energy will emerge as an alternative and cost effective light source because of its abundance and non-hazardous nature. The photo catalytic decolourization followed first order kinetics.

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