



Photocatalytic Degradation of Hazardous Dye Acridine Orange Using Semiconductor Titanium Dioxide (TiO₂) Under Visible Light

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ABSTRACT

Inordinate population growth and advanced technological development, at one hand bettered the life of human and on the other hand it is greatly damaging the environment. In the present work the study of hazardous synthetic dyes, especially used in textile and leather industries, has been carried out. These dyes in wastewater are principal cause of pollution in water bodies of human use. The most effective decomposition of Acridine Orange dye was observed with catalyst amount 300 mg/100 mL with 3.8×10^{-5} mole dm⁻³ initial dye concentration at pH 9. The rate of reaction increases as the concentration of H₂O₂ increases and reaches the optimum at 9×10^{-6} mole dm⁻³. As the irradiation time increased, dye molecules got degraded and the estimated COD value decreases from 184 mg/L to 0 mg/L, and CO₂ value increases from 55 mg/L to 242 mg/L in 6 hours of illumination.

INTRODUCTION

Inordinate population growth and advanced technological development are greatly affecting the environment. Industrial wastewater containing synthetic dyes is a principal cause of pollution of water bodies used for drinking and domestic purposes. The treatment of coloured wastewater containing hazardous dyes is one of the growing needs of the present time. In recent years, advanced oxidation processes are found eco-friendly for destroying organic pollutants by using TiO₂ photocatalysis because of its low cost with high efficiency (Hoffmann et al. 1995). Photo-degradation process, in general, occurs with the attack of organic substances by the activated oxygen species, such as hydroxyl radical and super oxide radical, generated on TiO₂ particulate surface by the reduction of dissolved oxygen in solution and oxidation of surface hydroxyl by TiO₂. The photocatalysis process can breakdown a large variety of organic compounds to CO₂, water and mineral salts, as the degradation products (Subramani et al. 2007). Present study provides result describing the photo-catalytic decolorization and mineralization of Acridine orange dye over the semi-conducting powder TiO₂, under different experimental conditions. The structure of the dye is presented in Fig. 1.

MATERIALS AND METHODS

Materials: Titanium dioxide (Loba Chemie), Acridine orange dye (Loba Chemie) and all other reagents of analytical grade were used for experiments. Double distilled water was

used to prepare the solutions. The catalyst and dyes were used without further purification.

Apparatus: A 500W halogen lamp was used as the visible light source. The photocatalytic reaction was carried out in a batch reactor of a dimension of 7.5 × 6.0 cm (height × diameter) provided with an external water flow jacket connected to a thermostatic bath, able to maintain the temperature between 25-30°C.

Procedure: In the irradiation experiment 100 mL aqueous solution of the dye with desired concentration was taken in the photoreactor then this solution was stirred and bubbled with air for about 10 minutes in the dark to establish the adsorption equilibrium. Aliquots were taken after every 10 minutes time intervals and then centrifuged to separate the catalyst from the solution. The reaction mixture was analysed spectrophotometrically using a UV-Visible spectrophotometer (Systronic Model No. 118) for measuring the absorbance. The intensity of light was measured by digital lux meter (Lutron LX-101). The pH of the solution was measured by digital pH meter. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. To quantify the extent of mineralization of mixture, COD was measured at regular time intervals using closed reflux titrimetric method.

RESULTS AND DISCUSSION

Effect of TiO₂ loading: In order to determine the optimal

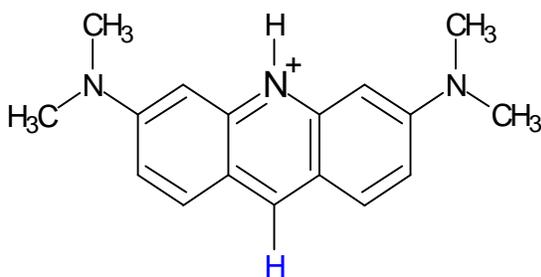
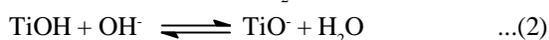


Fig. 1: Structure of acridine orange dye.

amount of photocatalyst few experiments were performed at pH 9.00 with different catalyst concentration. It was found that the degradation rate was increased rapidly with increasing catalyst concentration from 100 mg/100 mL to 300 mg/100 mL (Fig. 2), probably due to the increase of active sites with the suspensions of catalyst loading. The most effective decomposition of Acridine orange dye was observed at catalyst amount 300 mg/100 mL. Further increase of the TiO₂ concentration results in a decrease of rate of decolouration due to light scattering and reduction in light penetration through the solution. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates the reaction thus reducing the rate of reaction (Byrappa et al. 2006).

Initial dye concentration: The effect of initial dye concentration was investigated by varying the concentration from 1.8×10^{-5} mol dm⁻³ to 7.8×10^{-5} mol dm⁻³ at pH 9.00 with catalyst loading of 300 mg/100 mL. It was found that rate constant increases with increase in dye concentration from 1.8×10^{-5} mol dm⁻³ to 3.8×10^{-5} mol dm⁻³, and observed maximum at 3.8×10^{-5} mol dm⁻³ (Fig. 3). The dye concentration inversely affects adsorptive decolouration and reactive processes. Increasing initial dye concentration enhances the rate of the liquid phase reaction and surface reaction as well. The adsorption of dye molecules on the catalyst surface hinders competitive adsorption of OH⁻ ions, thus it lowers the formation rate of hydroxyl radicals and consequently, affects the rate of reaction (Ameta et al. 2007).

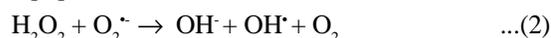
Effect of pH: The effect of pH on the rate of degradation was investigated in the pH range between 4.00 to 11.00. The change in the pH value, the surface hydroxyl group undergoes protonation and deprotonation according to the following reaction (Fox & Dulay 1993).



The point of zero charge of the TiO₂ is at pH 6.8, thus the TiO₂ surface is positively charged in acidic media, whereas negatively charged under alkaline conditions. Since, Acridine

orange dye is cationic dye, it has poor adsorption in the acidic medium, because the catalyst surface and dye both are positively charged. Thus, decrease in pH causes decrease in degradation rate. Higher pH favours electrostatic interactions between the negative TiO₂ surface and cationic dye, which lead to strong adsorption and enhance degradation rate. The results obtained in Fig. 4 indicate that, at pH 9.0, which is optimal, a strong adsorption of the Acridine orange dye on the TiO₂ particles was observed as a result of the electrostatic attraction of the negatively charged TiO₂ with the dye. The inhibitory effect seems to be more pronounced in the higher alkaline range (pH = 11.0). At high pH values the hydroxyl radicals are rapidly scavenged and they do not have the opportunity to react with dye (Epling & Lin 2002).

Effect of oxidants: The photocatalytic degradation was also been studied at different H₂O₂ concentrations. The addition of H₂O₂ enhances the degradation rate by several ways increasing the hydroxyl radical production, preventing the electron hole recombination by accepting the conduction band electron and it also forms OH⁻ radicals according to following equation.



The rate of reaction increases as the concentration of H₂O₂ increases and it reaches optimum at 9×10^{-6} mol dm⁻³ (Fig. 5); beyond it decreases as the concentration of the H₂O₂ increases, because excess H₂O₂ may act as a OH⁻ scavenger and formed peroxocompounds, which are detrimental to the photocatalytic action (Amisha et al. 2008).

Effect of inorganic salts: The decolorization of dye declined significantly with increasing concentration of sodium chloride and sodium carbonate like salts from 1×10^{-6} mol dm⁻³ to 13×10^{-6} mol dm⁻³ (Fig. 6). This is owing to that chloride and carbonate ions have scavenging effect on hydroxyl radical. Another possible explanation is that, additions of salts are believed to increase the degree of aggregation of ionic dyes in water, which is sometimes called the “common ion effect”. The dissolving situation of dye in water depends mainly on both their aggregation and ionization. It is believed that, aggregation enhanced by inorganic salts can limit significantly solubilization and ionization of dyes and lower capability of dye molecules to react with hydroxyl radicals. It is obvious that the “common ion effect” of salts mentioned above is able to inhibit the degradation of dyes (Yongchun et al. 2007).

Aggregation:



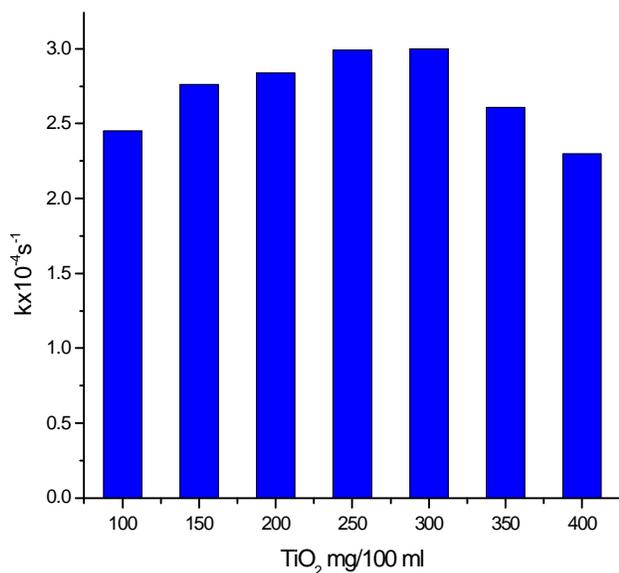


Fig. 2: Effect of TiO₂ loading: [AO] = 3.8 × 10⁻⁵ mol dm⁻³, Irradiation intensity = 15 × 10³ lux, pH = 9.0.

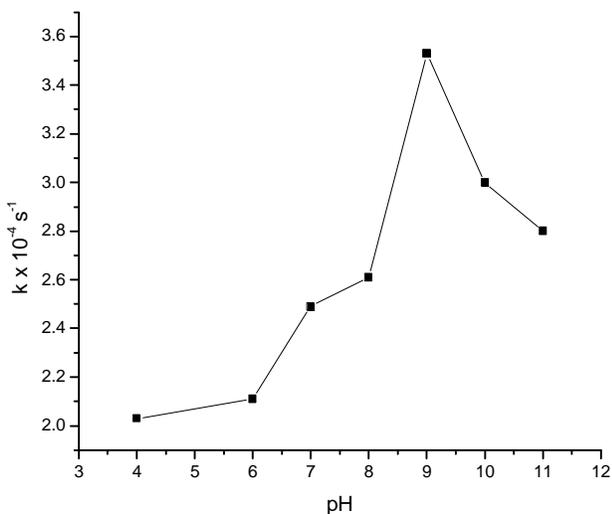


Fig. 4: Effect of pH: [AO] = 3.8 × 10⁻⁵ mol dm⁻³, TiO₂ = 300 mg/100 mL, Irradiation intensity = 15 × 10³ lux.

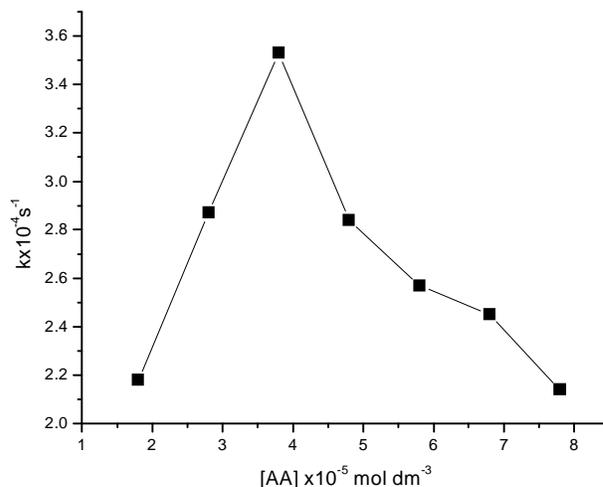


Fig. 3: Effect of initial dye concentration: TiO₂ = 300 mg/100 mL, Irradiation intensity = 15 × 10³ lux, pH = 9.0.

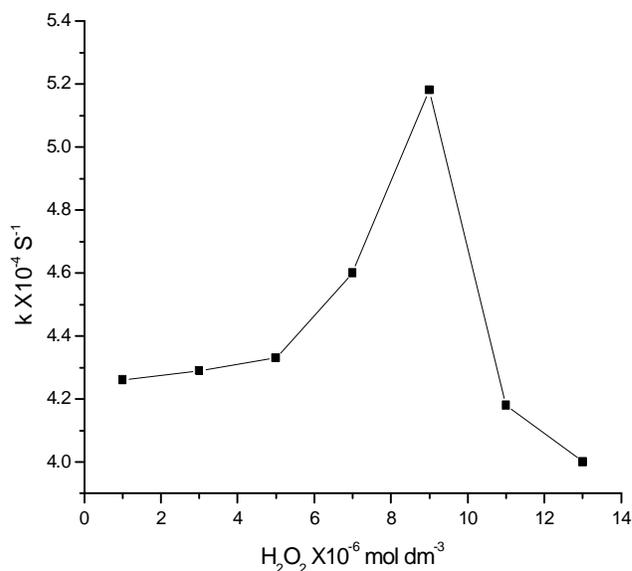
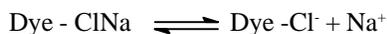


Fig. 5: Effect of hydrogen peroxide: [AO] = 3.8 × 10⁻⁵ mol dm⁻³, TiO₂ = 300 mg/100 mL, Irradiation intensity = 15 × 10³ lux, pH = 9.0.

Ionization:



UV-Vis spectra changes: The changes in the absorption spectra of Acridine orange solution during the photocatalytic degradation at different irradiation times are presented in Fig. 7, which shows a main band at 494 nm with maximum absorption. The decrease of absorption peak actually indicates a rapid degradation of Acridine orange dye. Complete discoloration was observed after 8 hours of irradiation.

Influence of potassium persulphate: The effect of persulphate ion on the photocatalytic degradation of the dye was also investigated. The concentration of K₂S₂O₈ was taken between 1 × 10⁻⁶ mol dm⁻³ and 13 × 10⁻⁶ mol dm⁻³. The data are presented in Fig. 8. The percentage degradation of the dye increased with increasing amount of persulphate ion concentration. It is also a beneficial oxidizing agent in photocatalytic detoxification because SO₄^{-•} is formed from the oxidant mentioned in reaction equation (1) and (2) with the semiconductor generated electrons (^e-_{cb})

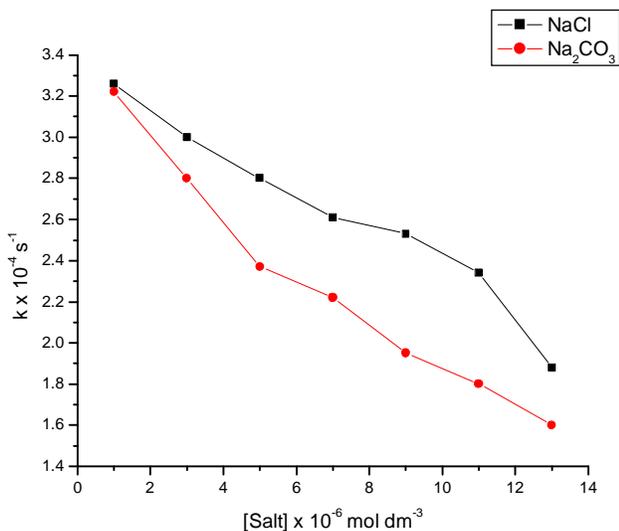


Fig. 6: Effect of Salt: [AO] = 3.8 × 10⁻⁵ mol dm⁻³, TiO₂ = 300 mg/100 mL, Irradiation intensity = 15 × 10³ lux, pH = 9.0.

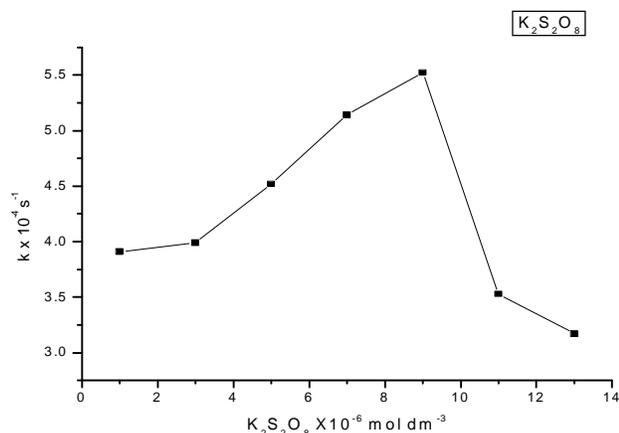
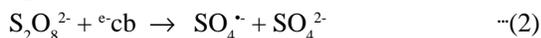
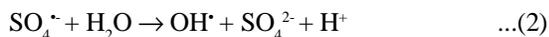


Fig. 8: Effect of K₂S₂O₈: [AO] = 3.8 × 10⁻⁵ mol dm⁻³, TiO₂ = 300 mg/100 ml, Irradiation intensity = 15 × 10³ lux, pH = 9.0.



The sulphate radical anion (SO₄^{•-}) is a strong oxidant (E° = 2.6 eV). It reacts with organic compounds in the following two possible modes of reactions. First abstracting a hydrogen atom from saturated carbon by adding it to an unsaturated or an aromatic carbon, and secondly, removing one electron from a carboxylate anion (Neppolian et al. 2002).



The formation of hydroxyl radical and sulphate radical anion which are powerful oxidants and can degrade the dye

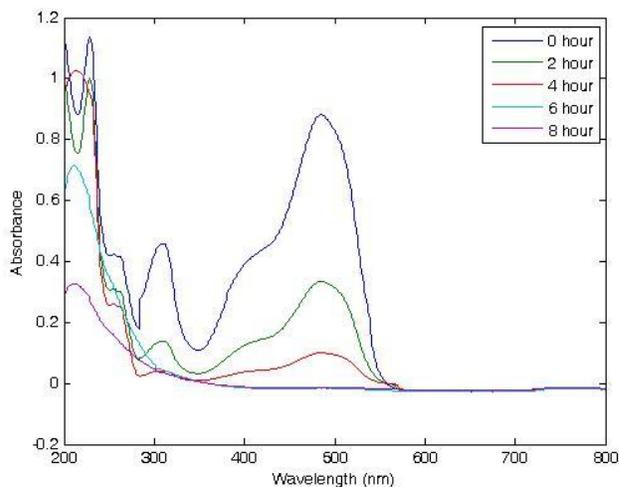


Fig. 7: Time dependent UV- visible absorption spectra depicting decolorization and complete degradation of Acridine orange using TiO₂.

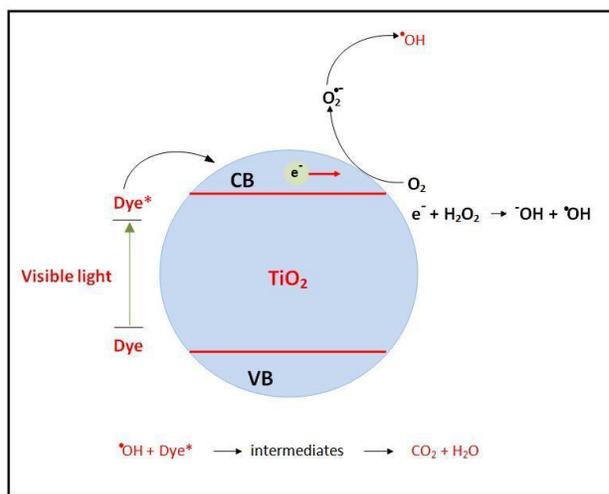


Fig. 9: Dye sensitization degradation on a TiO₂ semiconductor surface.

molecules at faster rate (Dorraj et al. 2009) with an optimum concentration of 9 × 10⁻⁶ mol dm⁻³. At this optimum concentration, the rate constant decreases due to absorption of sulphate ions on the surface of TiO₂ deactivating a section of photocatalyst.

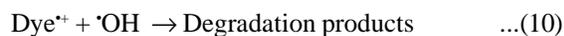
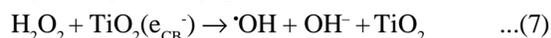
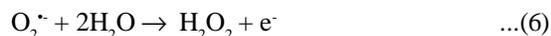
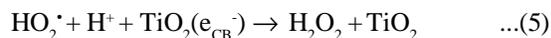
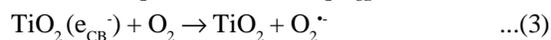
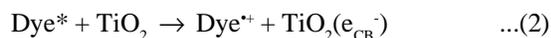
Mineralization studies of dyes: The results presented in Table 1 shows that the photocatalytic process leads, apart from decolorization, to a substantial decrease of COD of the solution. As the irradiation time increases, dye molecules are degraded to components of lower and lower molecular weight fractions and consequently complete mineralization which is observed from COD and CO₂ measurements. The chemical oxygen demand is widely used as an effective

Table 1: COD and CO₂ measurements for degradation of Acridine orange dye. Acridine orange concentration = 3.8 × 10⁻⁵ mol dm⁻³, TiO₂ = 300 mg/100 mL, Irradiation intensity = 15 × 10³ lux, pH = 9.0.

Irradiation time (h)	COD (mg/L)	CO ₂ (mg/L)	% Efficiency	pH
0	184	55	0	5.8
2	116	143	36	5.3
4	12	187	93	4.7
6	4	242	97	4.7

technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO₂ and H₂O. The COD of the dye solution was estimated before and after the treatment. The reduction in COD values of the treated dye solution indicates the mineralization of dye molecules along with colour removal. The aqueous solution of a mixture of Acridine orange dye (3.8 × 10⁻⁵ mol dm⁻³) was exposed separately to visible light in the presence of TiO₂ at a dose of 300 mg/L. Aliquots were taken at regular intervals and COD was measured using closed reflux titrimetric method (Kavitha & Palaisamy 2010). As the irradiation time increased dye molecule got degraded to compounds in which the COD values decrease from 184 mg/L to 0 mg/L and CO₂ value increases from 55 mg/L to 242 mg/L in 6 hours illumination. It indicates photodegradation of treated dye solution. The reduction in pH of solution is observed with increase in the extent of mineralization.

Mechanism of photocatalytic degradation: Photosensitized degradation of organic dyes has been carried out on TiO₂ where the organic dye serves as both a sensitizer and a substrate to be degraded (Chatterjee & Dasgupta 2005). Such type of electron transfer mechanism has been called photosensitizing oxidation. The mechanism of dye degradation under visible light irradiation can be described by following equations (1-10) (Hasnat et al. 2005).



This process of dye sensitization Fig. 9 has an advantage

in degradation of organic pollutants in presence of visible light.

CONCLUSION

The detailed observations and results revealed that TiO₂ catalysed photodegradation using visible irradiation is a suitable technique for removal of coloured wastewater from textile and leather industries. pH 9.0 was found to be the optimal under the given experimental conditions. The oxidizing agents such as hydrogen peroxide and persulphate ion have major role in the degradation efficiency of the Acridine orange dye. The additives such as sodium chloride and sodium carbonate are hindering the rate of photocatalytic degradation.

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