

Full Length Research Paper

Photodestruction and COD removal of toxic dye erioglaucine by TiO₂-UV process: influence of operational parameters

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Aqueous solutions of Erioglaucine, a hazardous dye, are photodegraded under ultraviolet light using TiO₂ as catalyst. The process has been carried out at different pHs, amounts of catalyst, concentrations of the dye, and effects of the electron acceptor H₂O₂. It is found that under the influence of TiO₂ as catalyst the coloured solution of the dye Erioglaucine becomes colourless and the process follows first-order reaction kinetics. The optimum conditions for the degradation of the dye have been found as 7.0 × 10⁻⁵ M dye concentration, pH 8.5, and 12 mg catalyst dose. In order to evaluate the effect of the electron acceptor, the effect of H₂O₂ on the degradation process is also monitored and it is found that generation of hydroxyl radicals and retardation of electron-hole recombination takes place. It was observed that photocatalytic degradation by TiO₂ is an effective, economic and faster mode of removing Erioglaucine from aqueous solution. Chemical oxygen demand and dye absorbance of the photodegraded dye solution substantially decreased. The adsorption trends of Erioglaucine at various initial concentrations followed the Langmuir isotherm trend.

Key words: TiO₂, photocatalytic degradation, Erioglaucine dye, COD, pollution, treatment, catalyst.

INTRODUCTION

The treatment of highly coloured wastewater containing hazardous industrial chemical effluents is one of the growing needs of the present time (Ruthven, 1984; Suzuki, 1993). Various physical and chemical techniques like coagulation, adsorption, chemical oxidation and froth flotation processes have been used by a number of research workers for the removal of organics as well as inorganics from wastewaters, as discussed in the review article of (Bailey et al., 1999). Recently, sophisticated instrumentation involving electrochemical, photochemical, chromatographic techniques, etc., has also been employed for this purpose (Gupta and Ali, 2002; Zhou and He, 2007). Several workers have also tried water treatment of dyes by adsorption over low cost materials (Gupta et al., 2005, 2006a, b, c, 2008; Mittal, 2006; Mittal

et al., 2006a, b, 2007a, b, 2008). Each method has its own advantages and disadvantages. For example, the use of charcoal is technically easy but has a high waste disposal cost. While in filtration, low-molar-mass dyes can pass through the filter system. Coagulation, using alum, ferric salts or lime is a low cost process. However, the disposal of toxic sludge is a severe drawback in all the above methods. The ozone treatment suffers from high cost. Photocatalytic degradation is considered a favoured, promising, cleaner, and greener technology for the removal of toxic organic and inorganic pollutants from water and wastewater (Pruden and Ollis, 1983). Our laboratories are also contributing in this direction with adsorption and electrochemical methods for the removal of some toxic textile and food dyes (Jain and Sikarwar, 2006; Jain et al., 2007a, b; Gupta et al., 2007).

For the present investigation water soluble Erioglaucine (molecular formula C₃₇H₃₈N₃NaO₉S₃ and molecular weight 787.91) was selected (Figure 1), which is an acid blue dye of the triphenyl methane class. Acid dyes are the best choice for dyeing the new fibers silk, Acid Blue

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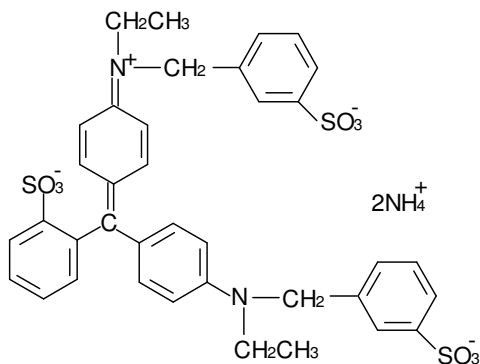
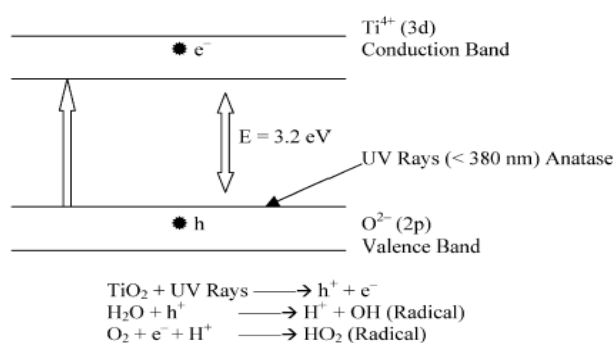


Figure 1. Structure of Erioglaucline



Crystal Structure	Band Gap (eV)	Absorption Edge (nm)
Anatase	3.2	388
Rutile	3.0	410

Scheme 1. Energy band gap created on anatase and rutile pigments.

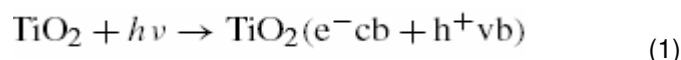
9/Erioglaucline is carcinogenic in rats after its subcutaneous injection: it produced fibrosarcomas following repeated injections. It also produced an increased incidence of kidney tumors in mice after its oral administration. Thus, keeping the hazardous nature and harmful effects in view, it was considered worthwhile to make systematic efforts to remove Erioglaucline from wastewaters using photochemical techniques. Photocatalysis has been successfully used to oxidize many organic pollutants and particularly to decolourize and mineralize dyes (Houas et al., 2001; Vautier et al., 2001; Lachheb et al., 2002; Puzenat et al., 2003; Guillard et al., 2003; Saquib et al., 2008; Baran et al., 2008; Chen et al., 2008).

There are three different types of titanium dioxide, anatase, rutile, and brookite. Most of the studies have been performed on the anatase and rutile types. The adsorptive affinity of anatase for decomposition of organic compounds is larger than that of rutile. Due to irradiation of anatase titanium dioxide particles by UV light ($\lambda < 300$ nm), it has a large band gap around 3.2 eV; rutile has a 3.0 eV band gap under wavelengths less than 410 nm (Scheme

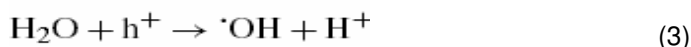
1). This provides for anatase comparably large numbers of electrons and holes produced in the conduction and valence bands respectively. Electrons have a high potential for reduction reactions on the catalyst surfaces. This mechanism in some respects is close to photosynthesis by plants. It can also be called artificial photosynthesis, although unlike photosynthesis titanium dioxide absorbs only UV light.

Mechanism

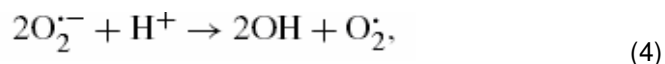
Irradiation of TiO_2 particles with photons of energy equal to, or greater than, the band gap energy results in the promotion of an electron from the valence band (vb) to the conduction band (cb) of the particle. The outcome of this process is a region of positive charge, termed a hole (h^+), in the vb and a free electron (e^-) in the cb:



The charge carrier species can recombine, with the absorbed energy dissipated as heat, or they can migrate to the particle surface, where the holes can react with surface-bound hydroxyl groups (OH^-) and adsorbed water molecules to form hydroxyl radicals (OH^\cdot):



In the absence of an electron acceptor, electron-hole recombination dominates. The presence of oxygen prevents recombination by trapping electrons through the formation of superoxide ions, maintaining electrical neutrality within the TiO_2 particle. The final product of the reduction is commonly hydroxyl radicals (OH^\cdot) and hydroperoxyl radical HO_2^\cdot :



Parra et al. (2000) suggested that hydrogen peroxide absorbs only UV light with a wavelength (λ) 300 nm. Hydroxyl radicals are known to be powerful, indiscriminate oxidizing agents and during the photocatalytic process they can react with organic compounds and bacterial species adsorbed onto, or very close to the semiconductor surface, resulting in degradation. The complete mineralization of the adsorbed organic substance has been observed. The results obtained show that the photocatalytic oxidation process is more efficient in the removal of pollutants from pretreated wastewater.

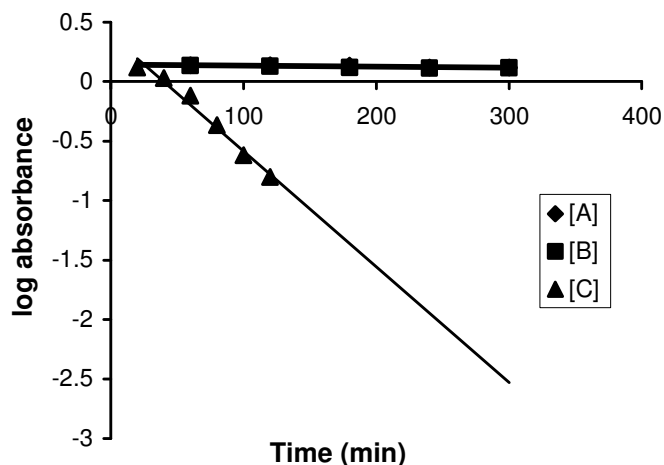


Figure 2. Photocatalytic degradation of Erioglaucine (a) in absence of UV light but in presence of TiO_2 (b) in presence of UV but in absence of TiO_2 (c) in presence of UV and TiO_2 both at dye conc. 7.0×10^{-5} M, temp. ($30 \pm 0.1^\circ\text{C}$).

EXPERIMENTAL

Materials

For the present studies the photocatalyst anatase titanium dioxide (325 mesh) and the dye Erioglaucine were obtained from M/s Merck. For photocatalytic degradation, 0.01 M stock solution of Erioglaucine was prepared in double-distilled water. Aqueous solutions of desired concentrations of pH 8.5 were prepared from the stock solution. Britton-Robinson Buffers in the pH range 2.5 to 9.0 were prepared by reported method (Britton, 1956). Double distilled water was used for necessary dilutions. All laboratory reagents were of analytical grade.

Instrumentation

Experiments were carried out in an ultraviolet photocatalytic reactor using a 6-W UV lamp, placed inside the wall of a quartz glass photoreactor of capacity 150 ml. To prevent UV radiation leakage the reactor was covered with black colour wooden box. The lamp emits predominantly UV radiation of 10 mW/cm^2 at wavelength of 254 nm.

pH metric measurements were made on Decibel DB 1011 digital pH meter fitted with a glass electrode, which was previously standardized with buffers of known pH in acidic and alkaline medium. For carrying out the COD experiments, reagents were prepared as per standard methods (APHA, 1995). Usual 2 h open reflux method was applied for the COD determination. Chemical oxygen demand (COD) of coloured and photocatalysed solutions was recorded using COD digestion apparatus (Spectra lab- 2015-S).

Procedures and analyses

To carry out the photocatalytic reactions, 100 ml of a dye solution of desired concentration was taken in a 250 ml flask and an appropriate amount (varying from 2 to 14 mg) of solid TiO_2 catalyst was added into it at 30°C . The mixture was then irradiated with UV light to provide energy to excite TiO_2 loading. To ensure thorough

mixing of the TiO_2 catalyst, oxygen was continuously bubbled from the side of the reactor. About a 5 ml aliquot of the dye was withdrawn after a specific time interval and analyzed spectrophotometrically at λ_{max} 632 nm after centrifugation. The rate of decrease of colour with time was continuously monitored and it was found that at all the pHs and concentrations of the dye a first-order kinetics was followed. Once the dye solution became completely colourless, the reaction was thought to be completed and the solution was withdrawn from the reactor.

RESULTS AND DISCUSSION

The photocatalytic degradation of Erioglaucine was studied at λ_{max} 632 nm. The optimum conditions for the removal of dye is conc. 7.0×10^{-5} M, pH 8.5, TiO_2 0.12 g/L and temperature ($30 \pm 0.1^\circ\text{C}$). The rate of reaction (k) was determined using the expression:

$$\text{Rate } (k) = 2.303 \times \text{Slope} \quad (6)$$

Preliminary observations

A preliminary photocatalytic study were carried out under three different conditions, that is, by keeping the TiO_2 containing solution in the dark, in presence of UV light but in absence of TiO_2 and in presence of both TiO_2 and O_2 was also investigated. It was observed that presence of TiO_2 only does not catalyze the degradation of the dye. Only a minor loss of the dye on to the TiO_2 surface could be observed due to the initial degradation of dye on TiO_2 surface. When solutions were irradiated by UV light no change in the absorbance was recorded. This finding is in agreement with the behaviour of other textile dyes (Pelgrini et al., 1999). However, better results were observed when small amount of TiO_2 is added to the solution in the presence of O_2 and UV light. About 88.7% of the dye was photodegraded within 2 h of experiment respectively. This clearly indicates that the rate of photodegradation of Erioglaucine in the presence of TiO_2 is very sensitive to the presence of UV light. A typical log (absorbance) versus contact time plot under the above mentioned three conditions is presented in Figure 2 at pH 8.5 and concentration 7.0×10^{-5} M of Erioglaucine.

Effect of the amount of catalyst on the colour removal

Assuming pseudo-first-order reaction kinetics for the photocatalytic oxidation process, the decolourization rate constant was determined from the equation.

$$\ln (C_t / C_0) = -kt, \quad (7)$$

Where C_0 and C_t are the dye concentrations (g/l) at times 0 and t , respectively, and k is the pseudo-first-order rate

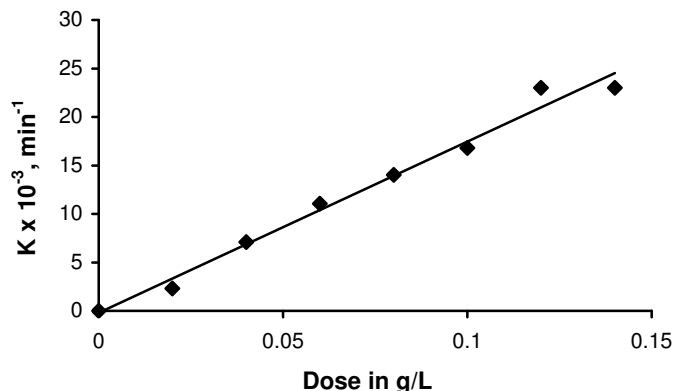


Figure 3. Variation of the rate constant with different concentration of TiO_2 at dye conc. 7.0×10^{-5} M, pH 8.5, temp. $(30 \pm 0.1^\circ\text{C})$.

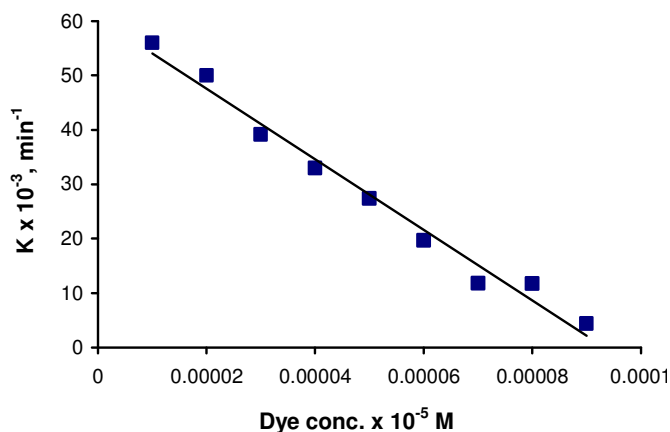


Figure 4. Variation of the rate constant with different concentration of dye pH 8.5, temp. $(30 \pm 0.1^\circ\text{C})$.

constant (time^{-1}). The effect of TiO_2 concentration on decolourization was investigated in the run (UV + TiO_2) (Muruganandham and Swaminathan, 2006). The decolourization rate constants were determined from the slopes of the plots of $\ln(C_t/C_0)$ vs time. Accordingly the colour removal rate was increased significantly by increasing the amount of catalyst. The increase in the amount of catalyst increases the number of active sites on the TiO_2 surface that in turn increases the number of OH^\cdot and $\text{O}_2^{\cdot-}$ radicals. The effect of photocatalyst concentration on the degradation kinetics of Erioglaucine was investigated employing different concentrations of the anatase TiO_2 varying from 0.02 to 0.14 g/l. It was observed that the rate of dye decolourization increases with increasing catalyst level up to 0.12 g/l and beyond this, the rate of reaction becomes constant (Figure 3). This may be due to the fact that, after a certain level of catalyst concentration with the same concentration of dye, further dye molecules are not available for adsorption. The additional catalyst particles therefore are

not involved in the catalytic activity. Hence the degradation remains constant. A similar trend has been observed in the case of Rhodamine 6 G dye (Mills et al., 1994). Optimum dose for efficient degradation of Erioglaucine dye is 0.12 g/l of TiO_2 .

Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the substrate concentration. It is generally noted that the degradation rate increases with the increase of dye concentration to a certain concentration and a further increase leads to a decrease in the dye degradation rate (Sakthivela et al., 2003). The decrease of dye degradation as the dye concentration increase is as a result that the generation of OH^\cdot radicals on the catalyst surface are reduced since the active sites are covered by dye ions (Poulios and Tsachpinis, 1999). Hence the effect of substrate concentration on the degradation of Erioglaucine was studied at different concentrations varying from 1.0×10^{-5} M to 9.0×10^{-5} M at fixed conc. of TiO_2 0.12 g/l, pH 8.5 (Figure 4). It is interesting to note that highest efficiency was observed at lower concentration, which decreased with the increase in substrate concentration from 1.0×10^{-5} M to 7.0×10^{-5} M and then it becomes almost constant at conc. 7.0×10^{-5} M and 8.0×10^{-5} M and thereafter it further decreases. Increase in the dye concentration from 1.0×10^{-5} to 9.0×10^{-5} M decreases the percentage removal of Erioglaucine from 95.96 to 45.45%. This may be due to the fact that with the increase in initial concentration of the dye, while the UV light irradiation period and catalyst dose are kept constant, more dye molecules are adsorbed onto the surface of TiO_2 (Subramani et al., 2007). Thus, an increase in the number of substrate ions accommodating in interlayer spacing inhibits the action of the catalyst, which thereby decreases the reactive OH^\cdot and $\text{O}_2^{\cdot-}$ free radicals attacking the dye molecules and photodegradation efficiency.

Effect of pH

The pH of the reaction medium has a significant effect on the surface properties of the TiO_2 catalyst, which include the surface charge of the particles, the size of the aggregate of catalyst particles it forms, and the band edge position of TiO_2 . Because a photocatalytic degradation reaction takes place on the surface of the catalyst, the photocatalyst reaction in general is pH dependent, although the rate varies by less than first order of magnitude between pH 2 and 12 (Fox and Dulay, 1993; Mills and Lehunte, 1997). The number of positive charges on the TiO_2 surface decreases with increasing pH and reaches zero at pH_{zpc} . Therefore, pH significantly affects

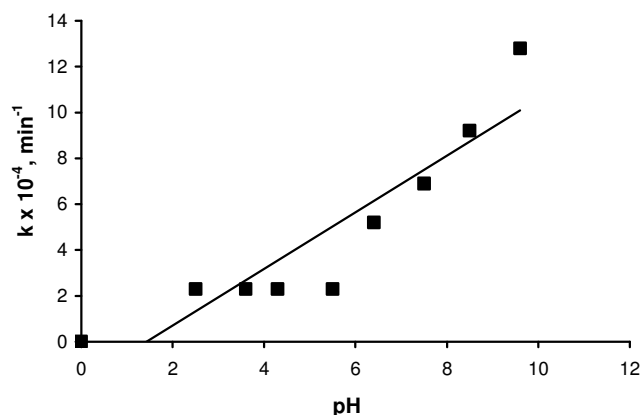


Figure 5. Variation of rate constant with different pH at conc. 7.0×10^{-5} M, temp. $(30 \pm 0.1^\circ\text{C})$.

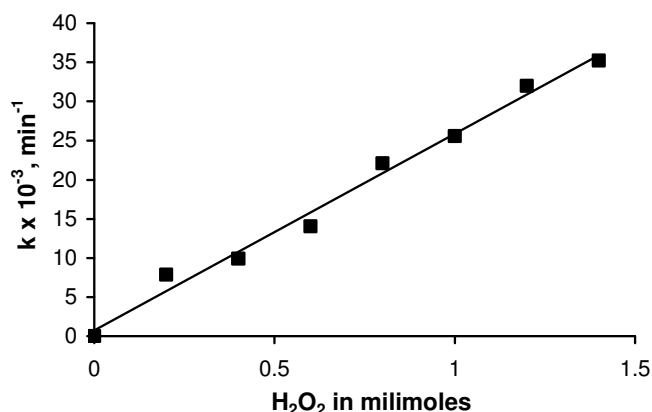


Figure 6. Variation of rate constant with different concentrations of H_2O_2 at conc. 7.0×10^{-5} M, pH 8.5, and temp. $(30 \pm 0.1^\circ\text{C})$.

affects the adsorption–desorption properties of the model compounds on the surface of the catalysts. The photocatalytic degradation experiments with erioglaucine on TiO_2 were conducted in the pH range 2.5 – 9.6 and at a fixed loading of TiO_2 (0.12 g/l) (Figure 5). It was observed that the rate of degradation increases in the neutral to alkaline range, as compared to the acidic pH conditions. Enforcement of the reaction rate under alkaline condition could be attributed to the increase of hydroxyl ions, which induces more hydroxyl radical formation. The formed OH radicals initiate the degradation reaction.

Effect of catalyst and oxidizing agent on the photocatalytic degradation

In photocatalytic degradation studies, it has been observed that H_2O_2 molar concentration is a key factor that can significantly influence the degradation of the dye.

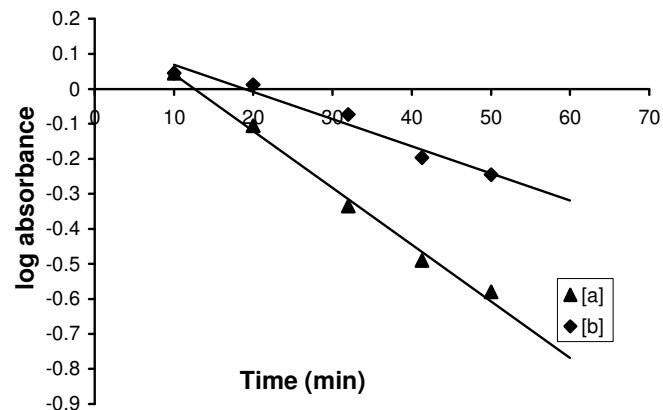
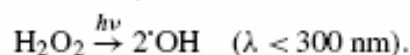
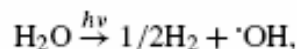


Figure 7. Photocatalytic degradation of Erioglaucine (a) in presence of H_2O_2 and TiO_2 (b) in presence of H_2O_2 only.

Direct UV light irradiation was insufficient to decolorize this dye. The addition of H_2O_2 as oxidant together with the UV light was more effective for colour removal. However, the colour removal in the experiment (UV + TiO_2) was much more efficient (Figure 6). This is attributed to the adsorption of the dye molecules on the surface of the catalyst, where water molecules adsorbed on the surface of the catalyst generate $\cdot\text{OH}$ radicals efficiently. In the presence of H_2O_2 , the UV light induces the formation of $\cdot\text{OH}$ radicals from H_2O_2 . H_2O_2 absorbs only the UV light with a wavelength <300 nm.



Combination of TiO_2 and H_2O_2 is necessary to obtain high colour removal within a short illumination period in the photooxidation process. The maximum colour removal efficiency was observed for the combination (UV + H_2O_2 + TiO_2). The fact that the decolorization efficiency is higher with (UV + TiO_2 + H_2O_2) than with (UV + H_2O_2) shows that TiO_2 acts as a photocatalyst (Figure 7). Dye molecules are oxidized by $\cdot\text{OH}$ radicals on the surface of the catalyst and within the bulk of the solution. It is explained by Fujishima et al. (2000), that photocatalytic degradation can take place at a distance of as much as $500 \mu\text{m}$ away from the TiO_2 surface and with the reaction rate decreasing with distance. In addition, they show that both oxidation and reduction reactions can take place on the illuminated TiO_2 surface. Thus, experiments were conducted with different amounts of H_2O_2 ranging from 0.2 to 1.4 mM at fixed dye concentration, catalyst amount, and temperature. Increase in the addition of H_2O_2 from 0.2 to 1.4 mM increases the removal rate from 45.2 to 90%. This phenomenon clearly explains the effect of H_2O_2 as electron acceptor (Gerixhac, 1993), which may be due to retardation of the electron–hole recombina-

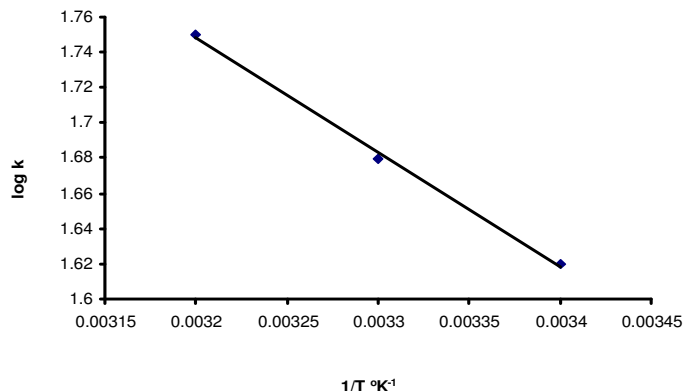


Figure 8. Plot of temperature variations for the photocatalytic degradation of Erioglaucine at conc. 7.0×10^{-5} M, pH 8.5, and temp. ($30 \pm 0.1^\circ\text{C}$).

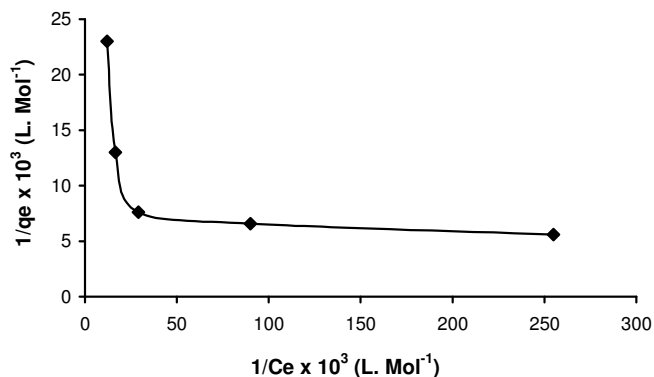
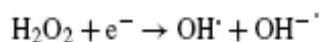


Figure 9. Erioglaucine adsorption isotherm on TiO_2 (pH 8.5, temperature 30°C).

recombination process after generation of hydroxyl radicals by H_2O_2 on absorption of an electron from the conduction band, and can be understood by the following equation:



Effect of temperature

The photocatalytic degradation was studied at various temperatures at range $293 - 313^\circ\text{K}$ and rate constant k was determined from the first order plots. An increase in temperature helps the reaction to compete more efficiently with e^-/h^+ recombination (Byrappa et al., 2006). The energy of activation E_a , was calculated from the Arrhenius plot of $\log k$ Vs $1/T$ °K (Figure 8). From the figure, the calculated activation energy 'Ea' is 12 KJ/mole.

Adsorption isotherm

Figure 9 illustrates the adsorption isotherm of erioglaucine over TiO_2 , where q_e is plotted as a function of C_e in the presence of UV light. C_e is the concentration of erioglaucine remaining in the bulk solution upon the attainment of adsorption equilibrium in the presence of UV light and q_e is the concentration of erioglaucine adsorbed in the solid. The isotherm showed a type of L shape (Figure 9) according to the classification of Giles et al. (1974). The L-shape isotherms mean that there is no strong competition between the solvent and the dye to occupy the TiO_2 surface sites. The data obtained from the adsorption experiments were fitted to the Langmuir equation (Langmuir, 1916)

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0} \frac{1}{C_e}$$

Where C_e is the concentration of the dye in solution at equilibrium, q_e is the amount of dye adsorbed per unit weight of the catalyst at equilibrium, b is the Langmuir adsorption constant, and Q_0 is the amount of dye adsorbed corresponding to monolayer coverage.

Chemical oxygen demand

The chemical oxygen demand test is widely used as an effective 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 CO_2 and water. In the present work results of chemical oxygen demand were taken as one of the parameter to judge the feasibility of the photochemical process for the degradation of Erioglaucine dye solution. The open reflux method was applied for COD determination and the treated solution showed a significant decrease in the COD value of the initial colour solution from 1460 to 262.0 mg/l of the treated solution indicating the high potential of the TiO_2 -catalyzed photodegradation process for the removal of Erioglaucine from wastewater. The photodegradation efficiency was found to be 82.0%.

Conclusion

A detailed feasibility study has been carried out on photocatalytic degradation of erioglaucine using TiO_2 powder as a photocatalyst under UV radiation at 30°C . It was observed that pH, catalyst concentration, substrate concentration and electron acceptor (H_2O_2) all significantly affect the photocatalytic degradation of erioglaucine. The results of the study indicate that anatase TiO_2 is very effective in enhancing the photocatalytic degradation of the dye erioglaucine. The best reaction dosage of TiO_2 catalysts is about 0.12 g/l. The electron acceptor H_2O_2 also played an important role in degradation of the dye. The maximum degradation efficiency of dye was achieved with the combination of UV + H_2O_2 + TiO_2 .

The photodegradation efficiency of erioglaucine dye is

82.0%. The photocatalytic kinetics follows first order.

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