

Solar photocatalytic degradation of Vat Yellow 4 dye in aqueous suspension of TiO₂ - optimization of operational parameters

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Abstract. The photocatalytic decolourisation and degradation of an anthraquinone dye Vat Yellow 4 in aqueous solution with TiO₂-P25 (Degussa) as photocatalyst in slurry form has been investigated under solar irradiation and UV irradiation. The study on the effect of various photocatalysts on the degradation reveals that TiO₂ is the best catalyst in comparison to other commercial photocatalysts. The effects of various operational parameters such as catalyst loading, initial dye concentration and pH on the decolourisation and degradation under solar irradiation in TiO₂ suspension have been investigated to find out the optimum conditions. The decolourisation and degradation kinetics have been analysed. Both follow first-order kinetics. A study on the effect of electron acceptors on photo oxidation reveals that both decolourisation and degradation increase in the presence of the electron acceptors such as H₂O₂ and (NH₄)₂S₂O₈ up to an optimum dosage beyond which the enhancement effect is negligible. The comparison between thin-film coating of TiO₂ and aqueous slurry method reveals that slurry method is more efficient.

Key Words: photocatalytic degradation, Vat Yellow 4, TiO₂.

Introduction. Treatment of colored wastewater from textile or other industries continues to be a serious problem that has attracted the attention of many researchers during last decades. In general the methods for treatment of wastewater containing dyes can be divided into two main groups (Slokar et al 1981, cited by Slokar & Le Marechal 1998), chemical or physical methods and biological methods. The physical methods include different precipitation methods, adsorption, filtration, reverse osmosis etc. Among chemical methods of dye removal, there are processes such as reduction, oxidation, complexometric methods, ion exchange and neutralization. Biological methods include different aerobic and anaerobic processes. Each of the methods has its own advantages and disadvantages. Photocatalysis using a semiconductor is an alternative to conventional methods. Heterogeneous photocatalysis using UV and solar irradiation has been found promising for the degradation of dyes (Al-Ekabi et al 1991; Neppolian et al 1999). Many semiconductor catalysts such as TiO₂ (Degussa P25), ZnO, ZnS, Hombikat UV100, ZrO₃, CdS, Fe₂O₃ have been attempted for the photocatalytic degradation of a wide variety of organic contaminants.

Since sunlight is abundantly available natural source of energy, utilizing it for the irradiation of semiconductors in the photodegradation of pollutants can make the process economically more viable. Solar energy has been successfully used for photocatalytic degradation of pollutants (Kruzler et al 1999). The use of photocatalyst in suspension causes the problem of leaching and makes the separation of photocatalyst from the reaction mixture after degradation a tedious process. Hence many researchers have studied the feasibility of coating the photocatalyst on inert surfaces like glass, polythene fibres and cement surface (Peill & Hoffmann 1995). Fixing the catalyst on a stationary support could circumvent the need to recover the catalyst from the reaction mixture without any leaching.

In the present study the degradation of the anthraquinone dye Vat Yellow 4 was investigated using solar and UV irradiation and the efficiencies of various commercial catalysts were compared. Then using TiO₂-P25 as the photocatalyst under solar irradiation the effect of different operational parameters on the degradation and the effect of immobilization of the catalyst were studied.

Materials and Method. The commercial sample of the dye Vat Yellow 4 (C.I. 59100) was obtained from Sivasakthi Dyeing unit, SIPCOT Industrial Estate, Perundurai, India. It is also known as Golden Yellow GK and is a group 3 carcinogen according to IARC. It was used without any purification. The commercial photocatalysts TiO₂-P25 was obtained from Degussa, Germany. It has an average particle size of 30nm and BET specific surface area of 55 m²/g. Hombikat, ZnO (Merck), CdS, ZnS, Fe₂O₃ and SnO₂ (S.D Fine Chemicals) and analytical grade H₂O₂ and (NH₄)₂S₂O₈ (Merck) were used as received. Double distilled water was used to prepare the experimental solutions.

(a) Solar Irradiation Experiments

An open cylindrical reactor of 200ml capacity made up of borosilicate glass having 8 cm height and 4.5 cm diameter with ports at the top for air purger was used as the reaction vessel. Solar light was used as the energy source for catalyst excitation. The reactor assembly was placed on a magnetic stirrer for enhancing the agitation. Samples were drawn from the reactor at periodic intervals and analysed after centrifugation for decolorization and degradation. The decolorization of the dye was determined by measuring the absorbance at λ_{max} 490nm using spectrophotometer (Model: Hitachi U-2001) and the degradation of the dye was measured by COD tests performed according to the standard methods. pH adjustments for the solution were carried out by measuring the pH using ELICO, India LI 120-pH meter.

(b) UV Irradiation Experiments

The reaction vessel was an immersion well photoreactor consisting of double walled cylinder of 0.75 L, made of pyrex glass, with ports at the top for air sparger. Water was circulated in between the two walls of the reactor to arrest the heat produced during the reaction and to eliminate the IR radiation and short wavelength radiation. Irradiations were carried out using a 125 W medium pressure mercury lamp. The slurry composed of dye solution and catalyst was placed in the reactor and stirred magnetically. The samples were withdrawn from the reactor vessel periodically for the analysis of decolourisation and degradation.

(c) Solar Irradiation in Thin-Film Coated Photoreactor

The photocatalyst was thoroughly mixed with Portland cement in the ratio 1:1 by grinding. The mixture was then transformed into a semisolid mass by adding double distilled water. The semisolid mass was applied physically as a thin coating, to the inner surface of a Petri dish of size 2cm height and 15cm diameter. It was then allowed to set for 2 hours. The dye solution was taken in the dish and exposed to sunlight. The progress of the photocatalytic degradation was monitored by withdrawing definite quantity of aliquots at regular intervals and measuring the absorbance in the UV spectrophotometer for decolorization and the degradation was determined by COD method.

Results and Discussion

(i) Photocatalytic Degradation of the Dye under Solar and UV Irradiation

Photodegradation experiments were carried out under the following conditions. (i) irradiation of the dye solution under solar/UV light in the absence of TiO₂ (ii) irradiation of the dye solution with TiO₂ in dark and (iii) irradiation of the dye solution under solar/ UV light in the presence of TiO₂. The results of the studies as given in Fig.1 show that direct photolysis did not cause any significant degradation both under solar as well as UV irradiation. In the presence of TiO₂ without irradiation, slight loss was observed due to the adsorption of the dye on the surface of TiO₂. The irradiation under UV light in the

presence of catalyst caused 84% degradation in 120 minutes whereas the solar irradiation in the presence of catalyst resulted in 78% degradation in 300 minutes.

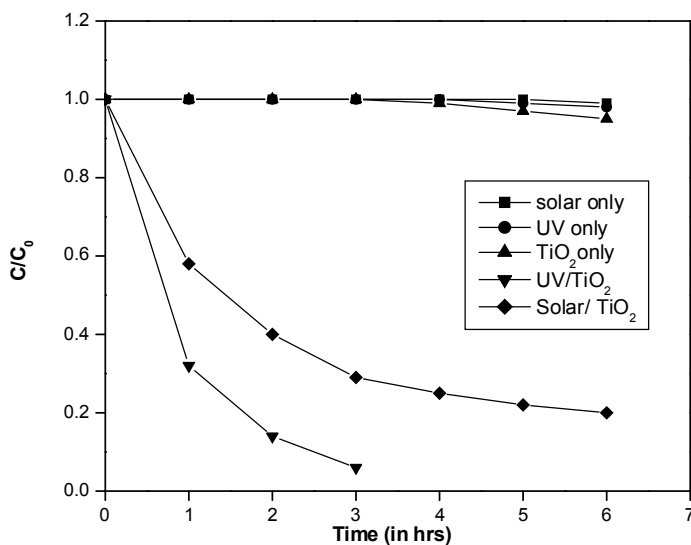


Fig.1. Effect of Solar/ UV irradiation on the degradation of Vat Yellow 4 in the presence and absence of TiO₂

The observed difference in the rate of degradation under solar and UV irradiation as shown in Fig.2 is attributed to the difference in the input energy. The energy of UV irradiation is large compared to the band gap energy of the catalysts.

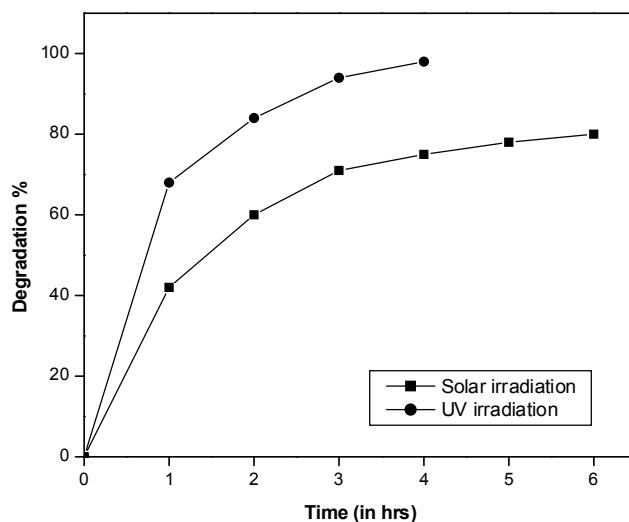


Fig.2. Effect of Solar/UV irradiation on the degradation of VY 4

Hence the electron-hole recombination problem, which is more common in semiconductor oxide mediated heterogeneous photocatalysis, is largely avoided, though not fully, with UV irradiation source. But in sunlight, only 5% of the total irradiation possesses the optimum energy for the band gap excitation of the electrons (Maruthamuthu & Murugesan 1995). Hence the percentage degradation is found to be less in solar irradiation of textile dyes (Neppolian et al 2002). Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately for the degradation of textile

dyes, it could be a safe and cost effective source. UV source is not only hazardous but also expensive because of the large input of electric power to generate UV irradiation. Since intense sunlight is available throughout the year in tropical countries like India, it could be effectively used for the photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation sunlight would be the ultimate source. Moreover there is no material deterioration in case where sunlight is used as a radiation source. But UV light source may effect the catalyst decomposition (Domenech & Prieto 1986).

(ii) Comparison of Photocatalytic Activity of Commercial Catalysts

The photocatalytic activity of various commercial photocatalysts was investigated under both solar and UV irradiation. TiO₂-P25 and ZnO were found to be more efficient as shown in Fig.3 and the order of activities of the photocatalysts is TiO₂>ZnO>Hombikat>CdS. Other catalysts such as ZnS, SnO₂ and Fe₂O₃ have negligible activity. In general, semiconductors with large band gap have strong photocatalytic activity. TiO₂-P25 and ZnO have a band gap of 3.2eV and hence show strong activity.

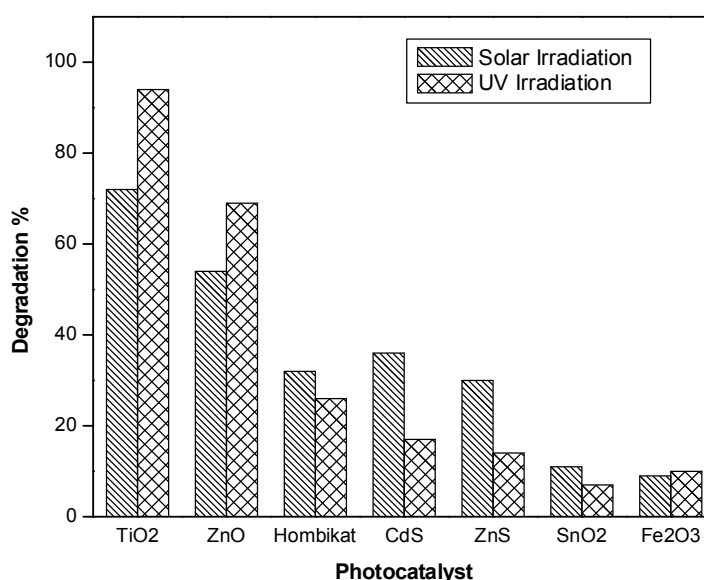
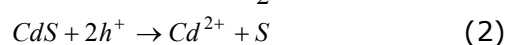
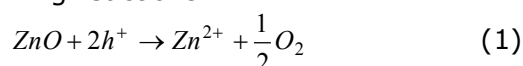


Fig.3.Effect of various photocatalysts on the degradation of VY 4
C₀ = 100 mg/L,Irradiation time: 3 hrs

TiO₂ is the most promising photocatalyst as it is chemically inert and stable with respect to photocorrosion and chemical corrosion (Matthews 1989 and Nishimoto et al 1985). The high photoreactivity of TiO₂-P25 compared to Hombikat (TiO₂ anatase) is due to the slow recombination of the electron-hole pair and large surface area. The surface area of TiO₂-P25 is six times as high as that of TiO₂ anatase (Weller 1993). ZnO is unstable due to incongruous dissolution to yield Zn(OH)₂ on the ZnO particle surfaces and thus leading to catalyst inactivation (Bahnemann et al 1987). Moreover, ZnO and CdS suffer from photocorrosion induced by self-oxidation and they can react with the photogenerated holes giving the following reactions:



These competing reactions lead to decrease in photocatalytic activity (Neppolian et al 2002). The occasional release of Cd²⁺ metal ions into the aqueous medium may cause heavy metal pollution (Kakuta et al 1985). Hence TiO₂ proves to be more a suitable bench mark catalyst for photodegradation of textile dyes due to its high photoactivity,

high surface area and resistance to photocorrosion and was used in this present study for the degradation of the dye Vat Yellow 4 under solar irradiation.

(iii) Effect of TiO₂ Loading

The effect of TiO₂ loading on the percentage removal of the dye under solar irradiation has been examined by varying the amount of catalyst from 1-6g/L of the catalyst at 100mg/L dye concentration and the results are given in Fig.4. The results indicate that the increase in catalyst dose from 1 to 4g/L increase the decolorisation from 63.5 to 98% in 120 min and the degradation percentage increases from 56 to 72.9% in 300min. At concentrations higher than 4g/L the decolorisation and degradation efficiencies are almost constant. Hence the optimum concentration of 4g/L was fixed as the catalyst load for the present study.

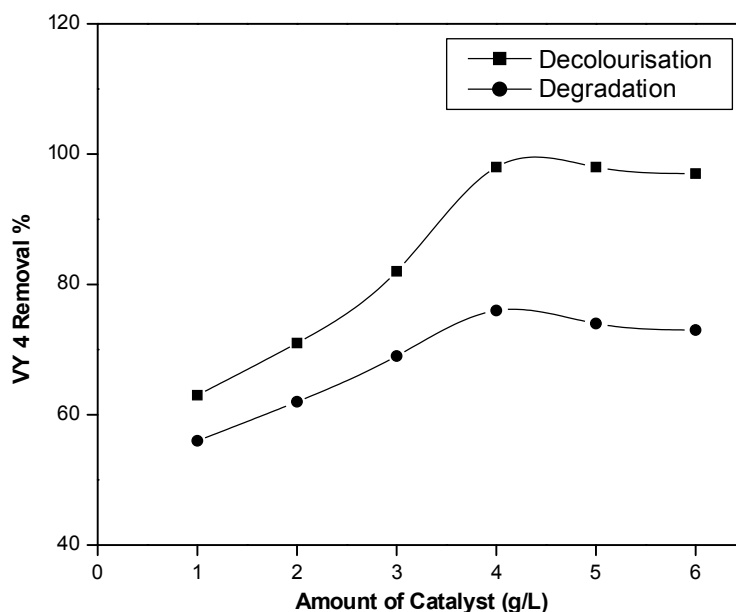


Fig.4. Effect of Catalyst loading on the decolourisation and degradation of VY 4
 $C_0 = 100\text{mg/L}$, Irradiation time: Decolourisation = 2 hrs, Degradation = 4 hrs

The lower percentage degradation at lower TiO₂ loading can be attributed to the fact that more light is transmitted through the reactor and the transmitted light is not utilized in the photocatalytic reaction (Stafford et al 1997). The increase in removal rate with increasing amount of the catalyst can be rationalized in terms of the availability of active sites on TiO₂ surface and the penetration of the photoactivating light into the suspension. The availability of active sites increases with the suspension of catalyst loading, but the light penetration and hence the photoactivated volume of the suspension shrinks. The trade-off between these two effects is that at low catalyst concentration, the balance between the opposing effects is evenly poised and the degradation is at lower rate. When the catalyst concentration increases, the availability of excess active sites outweighs the diminishing photoactivated volume and photodegradation percentage increases significantly (Matthews 1990). Above a certain level the number of substrate molecules is not sufficient to fill the surface active sites of TiO₂ and hence further addition of catalyst does not lead to the enhancement of the degradation rate. The slight decrease in degradation rate at higher concentrations of the catalyst may also be due to the aggregation of TiO₂ particles at higher concentrations causing decrease in the number of surface active sites and also due to the increase in opacity and light scattering of TiO₂ particles (Kaur & Singh 2007).

Different amount of photocatalysts have been reported as the optimum catalyst loading for the degradation of various pollutants (Toor et al 2006; Garcia & Takashima 2003). This shows that the optimum catalyst loading is not common for all photocatalytic reactions and it is dependent on various experimental parameters.

(iv) Effect of Concentration of the Dye

The effect of initial concentration of the dye on the percentage decolorisation and degradation was studied by varying the initial concentration of the dye from 50 mg/L to 250 mg/L. The results as shown in Figs 5-6 show that the increase in dye concentration decreases the removal rate. Increase in concentration of the dye from 50 mg/L to 100 mg/L results in the decrease of decolorisation from 100 to 84% in 120 min and the decrease of degradation from 95% to 64% in 300 min.

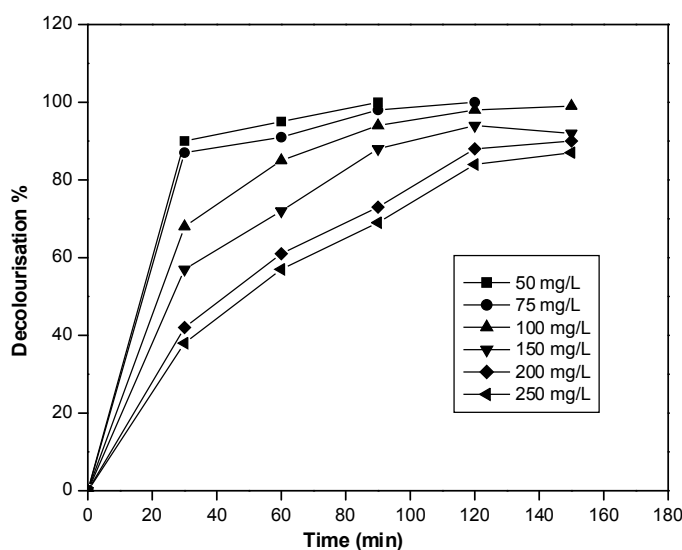


Fig.5. Effect of initial dye concentration on the decolourisation of VY 4. Amount of $TiO_2 = 4$ g/L

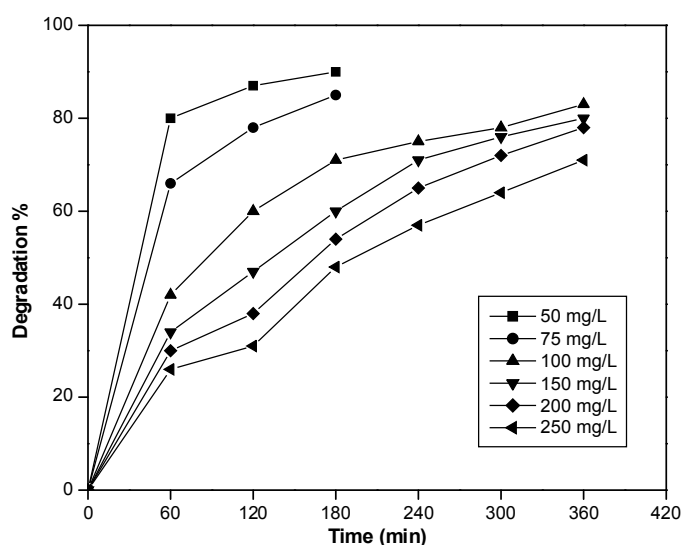


Fig.6. Effect of initial concentration on the degradation of VY 4. Amount of $TiO_2 = 4$ g/L

The rate constants for decolourisation and degradation are given in Table 1. The possible explanation for the decrease in removal rate is that as the initial concentration of the dye increases, the path length of the photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration (Neppolian et al 2002). Moreover, at high dye concentration, a significant amount of solar light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency (Mills et al 1993).

Table 1

Rate constants of VY 4 decolourisation and degradation

<i>Initial concentration mol/l</i>	<i>Decolourisation k' (min⁻¹)</i>	<i>Degradation k (min⁻¹)</i>
50 mg/L	0.0521	0.01383
75 mg/L	0.0416	0.00972
100 mg/L	0.0307	0.00472
150 mg/L	0.0183	0.00454
200 mg/L	0.0152	0.00421
250 mg/L	0.0129	0.0033

The photocatalytic decolourisation and degradation of the dye obey pseudo-first-order kinetics. At low initial concentrations the rate expression is given in Eq. (3)

$$-\frac{d[C]}{dt} = k'[C] \quad (3)$$

where k' is the pseudo-first-order rate constant. The dye is adsorbed on to TiO₂ surface and the adsorption-desorption equilibrium is reached in 20 min. The equilibrium concentration of the dye solution after adsorption is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (3) with the limit of C = C₀ at t = 0 gives Eq. (4)

$$\ln\left[\frac{C_0}{C}\right] = k't \quad (4)$$

where C₀ is the equilibrium concentration of the dye and C is the concentration at time t.

The plots of lnC₀/C versus t for photodecolorisation and degradation are shown in Figs 7-8. The linear fit between lnC₀/C and irradiation time supports the conclusion that the decolourisation and degradation follow first-order kinetics.

(v) Effect of pH

The wastewater from textile industries usually has a wide range of pH values. The generation of hydroxyl radicals responsible for photodegradation is also a function of pH. Hence pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Therefore attempt has been made to study the influence of pH on the degradation of the dye Vat yellow 4. Photodegradation under solar irradiation was examined at pH values ranging from 2 to 12. Adjustment of pH was done by adding appropriate amount of 0.02N H₂SO₄ or 0.02N NaOH solution. The results are shown in Fig.9.

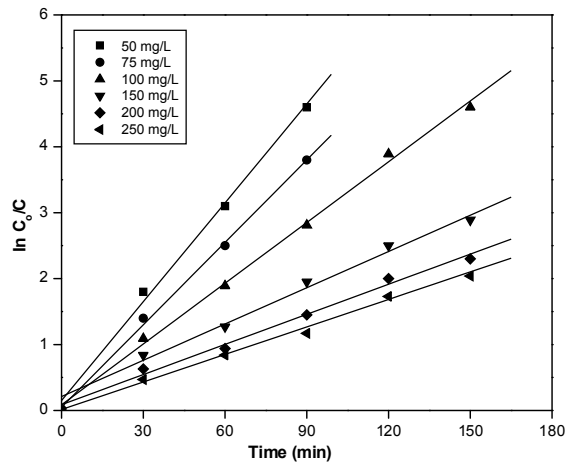


Fig.7. Kinetics of VY 4 decolourisation for different initial concentrations

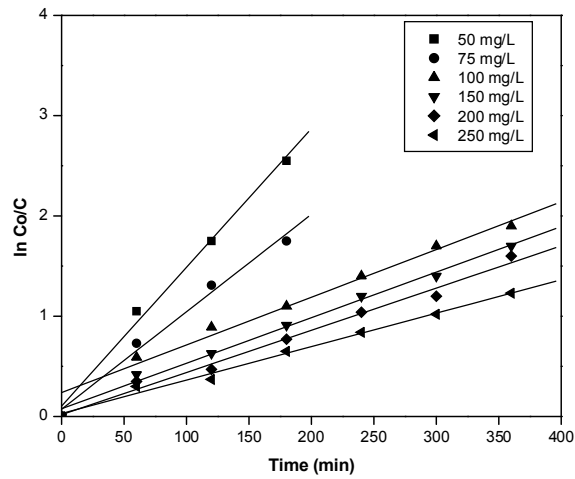


Fig.8. Kinetics of degradation of VY 4 for different initial concentrations

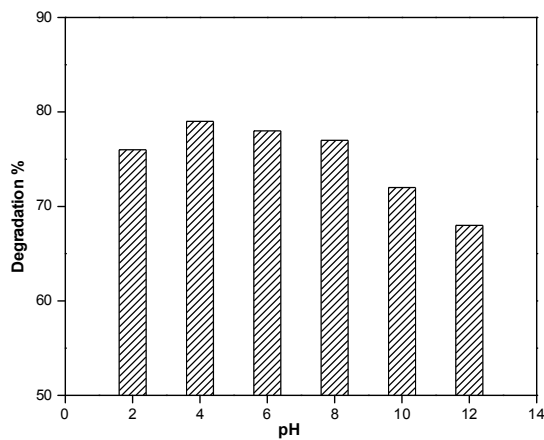


Fig.9. Effect of pH on the degradation of VY 4.
 $C_0=100$ mg/L, $[TiO_2]=4$ g/L, Time = 4 hrs

The percentage degradation of the dye remained unchanged with increase in pH up to 10 and the degradation decreased on further increase in pH. The inhibitory effect seems to be more pronounced in the alkaline range. At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes (Neppolian et al 2003). The pH affects not only the surface properties of TiO_2 , but also the dissociation of dyes and formation of hydroxyl radicals. The interpretation of the effect of pH on the efficiency of the photodegradation process is a very difficult task, because three possible reaction mechanisms can contribute to the dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band. The importance of each mechanism depends on the nature and pH of the substrate (Tang et al 1997). It can be presumed in the present case that the main reaction is due to the hydroxyl attack, which can be favoured by the high concentration of the hydroxyl radicals at around natural pH.

(vi) Effect of Electron Acceptors

The major energy wasting step in the photocatalytic reaction of TiO_2 is the electron-hole recombination. As leads to low quantum yield, the prevention of electron-hole recombination is very essential. This can be achieved by the addition of suitable irreversible electron acceptors such as H_2O_2 , $\text{S}_2\text{O}_8^{2-}$ and BrO_3^- to the system (Kormann et al 1988; Poulios & Tachpinis 1999). The added oxidants can enhance the rate of degradation by several ways: (i) preventing the electron hole recombination by accepting the conduction band electron, (ii) increasing the hydroxyl radical concentration and (iii) producing other oxidising species to accelerate the intermediate compound oxidation rate.

(vi) (a) Effect of Addition of H_2O_2

To keep the efficiency of the added H_2O_2 at the maximum, it is necessary to choose the optimum concentration of H_2O_2 according to the type and concentration of the pollutants. The effect of addition of H_2O_2 in the range of 0.5 to 2.5mL on the photocatalytic oxidation has been investigated. The results are shown in Fig.10.

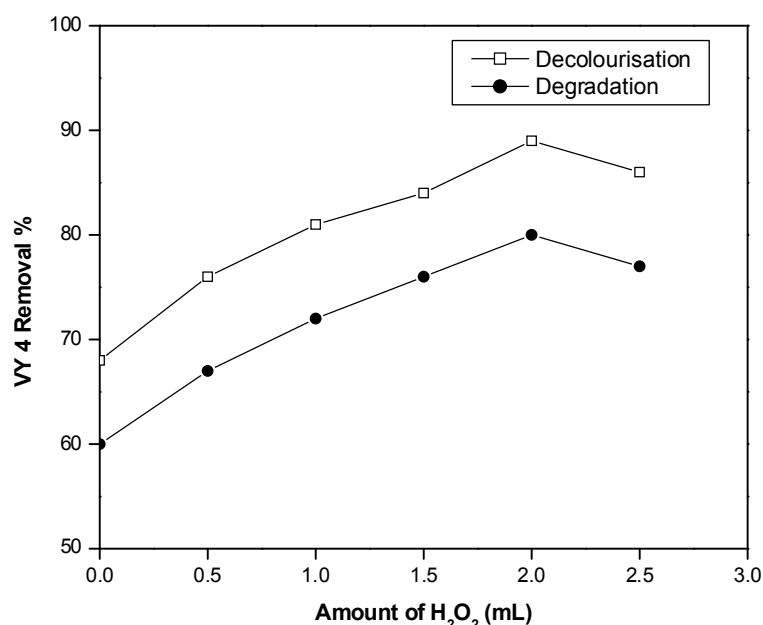
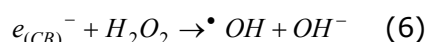
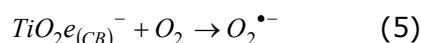


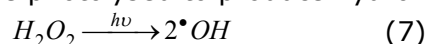
Fig.10. Effect of addition of H_2O_2 on the decolorisation and degradation of VY 4. $C_0 = 100\text{mg/L}$, $[\text{TiO}_2] = 4\text{ g}$. Irradiation time: Decolourisation=30 min, Degradation = 120 min

The addition of H₂O₂ in the range 0.5 to 2.0ml/L increases the decolourisation from 68.1 to 88.6% in 30 min and degradation from 60.1 to 79.8% in 120 min. Further increase in the H₂O₂ concentration limits the removal rate. Hence, 2.5ml H₂O₂ concentration appears to be optimal for the degradation. An increase in H₂O₂ level enhances the degradation rate up to the optimal load beyond which inhibition occurs. Similar observation had been reported in dye degradation and organic pollutant degradation (Malato et al 1998). The enhancement of decolourisation and degradation by addition of H₂O₂ is due to increase in the hydroxyl radical concentration by the following ways:

(i) Oxygen is the primary acceptor of the conduction band electron with formation of superoxide radical anion (Eq. (5)). H₂O₂ can compensate for the O₂ lack and play a role as an external electron scavenger according to Eq. (6). It can trap the photogenerated conduction band electron, thus inhibiting the electron-hole recombination and producing hydroxyl radicals as shown by the equations:

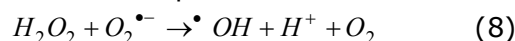


(ii) H₂O₂ may also be photolysed to produce hydroxyl radicals directly (Eq. (7))

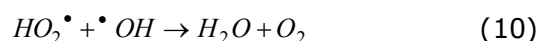
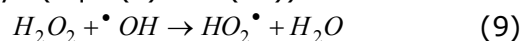


H₂O₂ has extremely low absorption of solar light. Hence, the oxidation of the dye by photolytic H₂O₂ (Eq. (7)) will be insignificant.

(iii) H₂O₂ may also reacts with super oxide anion to form •OH radical (Eq. (8)).



The inhibition of the degradation of the dye beyond the optimum load of H₂O₂ may be due to the hydroxyl radical scavenging effect of H₂O₂. The reaction between excess hydrogen peroxide and hydroxyl radical (•OH) forms hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of the dye (Eqs. (9) and (10)).

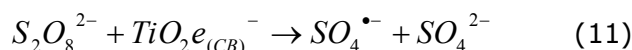


(vi) (b) Effect of S₂O₈²⁻

The effect of addition of S₂O₈²⁻ on the photocatalytic oxidation of VY 4 has been investigated by varying the amount of (NH₄)₂S₂O₈ from 1 to 4 g/L. The results are shown in Fig. 11.

Addition of 1–3 g/L of (NH₄)₂S₂O₈ increases the decolourisation from 68.1 to 94.0% in 30 min and degradation from 60.1 to 78% in 120 min. Further increase in the addition (4 g/L) decreases the decolourisation. Further increase in the addition above 4g/L increases the decolourisation by 1.39% and degradation by 0.91% only. Similar enhancements by the addition of S₂O₈²⁻ have been reported earlier (Bekholet et al 1996). Addition of persulphate to photocatalytic processes enhances the decolourisation rate by the following ways:

(i) Persulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidising species namely sulphate radical anion (Eq. (11)).



(ii) S₂O₈²⁻ can generate sulphate radical anion (SO₄^{•-}) both thermally and photolytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following ways:

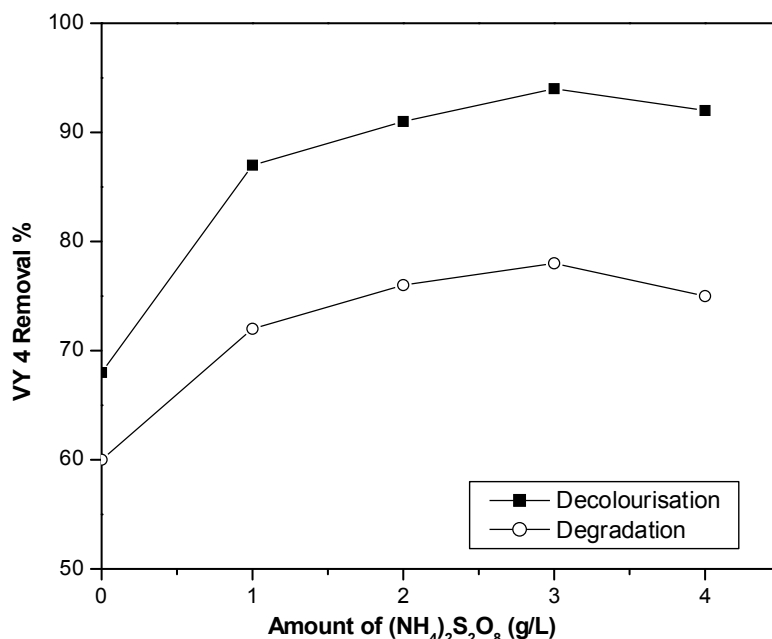
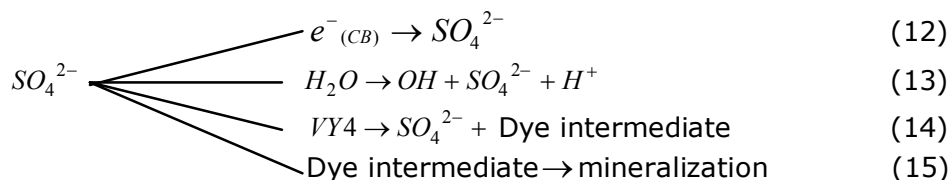


Fig.11. Effect of addition of (NH₄)₂S₂O₈ on the decolourisation and degradation of VY 4. C₀ = 100 mg/L, [TiO₂]=4 g/L, Irradiation time:Decolourisation=30 min, Degradation=120 min.



(iii) At high dosage of S₂O₈²⁻ the inhibition of reaction occurs due to the increase in concentration of SO₄²⁻ ion (Eq. (11)). The excess of SO₄²⁻ ion is adsorbed on the TiO₂ surface and reduces the catalytic activity. The adsorbed SO₄²⁻ ion also reacts with photogenerated holes (Eq. (16)) and with hydroxyl radicals (Eq. (17)).



Since SO₄^{•-} is less reactive than •OH radical and h⁺, the excess SO₄²⁻ reduces the photodegradation of the dye.

(vii) Effect of Immobilization of the Catalyst

To determine the effect of immobilization of the catalyst on the degradation of the dye under solar irradiation, experiments were carried out in the thin-film coated photoreactor in which the mixture of the catalyst and cement had been coated.

The result of the study on immobilized catalyst as given in Fig.12 indicate that the degradation is significantly low compared to the degradation of the dye irradiated in TiO₂ suspension. After 6 hours of exposure to solar irradiation the degradation achieved was only 45%. But for the same irradiation time in TiO₂ suspension the degradation was 80%. Similar result has been reported by Neppolian et al (2002) in the study of solar/UV induced photocatalytic degradation of three commercial textile dyes.

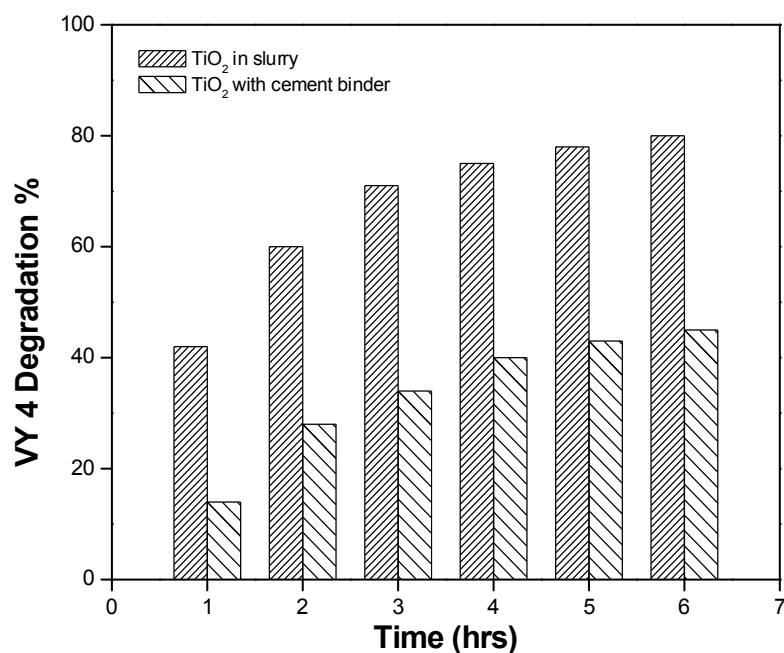


Fig.12. Effect of immobilisation of TiO₂ with cement binder.

The reason for the slower rate of degradation of the dye solution is that the particles are only half-exposed to light when irradiation induces band gap excitation of electrons. They may not be available for the degradation in the solution side, if they migrate towards the support, namely, TiO₂ cement film. This would largely favour electron-hole recombination rather than dye degradation. Particles are bound to one another and, hence, free movement of particles is restricted. Only particles on the surface alone are exposed to light irradiation. Even though the concentration of dyes employed is low, the problem of leaching and separation of photocatalyst after the reaction are fairly minimized in this method. The photocatalyst can be used for a number of cycles without loss of its photocatalyst activity. Hence, it may be a viable technique for large volume of textile dye wastes degradation provided strong binding of the photocatalyst particles on the surface of the reactor is possible.

Though the degradation takes place at comparatively slower rate the thin-film coating study of TiO₂ indicate that this method can be upgraded to large volume of textile wastes of low concentration. If the concentration is high, dilution to the appropriate level is a prerequisite.

Conclusions. The photocatalytic decolorisation and degradation of the dye Vat Yellow 4 in the presence of different commercial catalysts in slurry under solar and UV irradiation revealed that TiO₂ is the more efficient catalyst. Though the degradation in the presence of TiO₂ under solar irradiation takes place to lesser extent compared to UV irradiation, the process is economically viable than degradation under UV irradiation. It can be considered as an alternative cost effective method because of the abundance and non-hazardous nature of solar light. The optimum catalyst loading for the degradation of 100 mg/L solution of the dye was 4 g/L and the degradation was maximum at neutral pH range. The addition of electron acceptors H₂O₂ and ammonium persulphate increase the decolorisation and degradation upto the optimum dosage of 2.5ml/L and 3g/L respectively and beyond the optimum dosage the enhancement is not significant. Thin film coating of the catalyst, though comparatively less efficient than slurry method, may resolve the problems of leaching and separation of the catalyst.

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