

Photocatalytic Degradation of Vat Yellow 4 Using UV/TiO₂

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Abstract

The photocatalytic degradation of an anthraquinone dye Vat Yellow 4 in aqueous solution with TiO₂-P25 (Degussa) as photocatalyst has been investigated under solar and UV irradiation. The study on the effect of various photocatalysts reveals that TiO₂ is the best catalyst in comparison to other commercial photocatalysts. The effect of operational parameters such as catalyst loading and initial dye concentration on the decolourisation and degradation under UV irradiation in TiO₂ suspension has been investigated to find out the optimum conditions. The decolourisation and degradation kinetics was found to follow first-order kinetics. A study on the effect of electron acceptors reveals that both decolourisation and degradation increase in the presence of the electron acceptors such as H₂O₂, (NH₄)₂S₂O₈ and KBrO₃ up to an optimum dosage beyond which the enhancement effect is negligible. The presence of inorganic additives was found to decrease the degradation.

Keywords: Photocatalytic degradation, UV, TiO₂, Vat yellow 4

1. Introduction

The development of organic chemical industry has lead to the synthesis of more and more organic compounds. While they offer people better and easier life, they also pose serious environmental problems. Biological treatment of domestic wastewater has been used worldwide because of its cost effectiveness and versatility in handling a variety of organic pollutants. However biological treatment methods find their own difficulty to be used for the treatment of toxic and refractory chemicals in the wastewater. Especially the colour due to commercial dyes in the wastewaters is extremely difficult to remove. Hence, chemical oxidation methods have been extensively studied because they can provide the ultimate solution for the destruction of commercial dyes in wastewater. For example, Advanced Oxidation Processes (AOPs) have been developed to meet the increasing need of effective wastewater treatment. Studies have shown that toxic and refractory organics including dyes in wastewater could be destroyed by most AOPs (Huang et al., 1993).

Photocatalytic oxidation of toxic organic compounds by semiconductors has emerged as one of the important AOP (Fox et al., 1993; Hoffmann et al., 1995). Upon irradiation by photons, such as UV, electrons on the surface of the semiconductor are excited to the conduction band and positive holes are formed in the valence band. The electrons and holes can either recombine and produce thermal energy, or interact with other molecules (Venkatadri and Peters, 1993). The holes react with the electron donors in the solution to produce powerful oxidising free radicals such as hydroxyl radicals, which oxidize the organics on the surface. The holes can also oxidize the substrate by direct electron transfer. (Kormann et al., 1988).

Anthraquinone dye is the second most important class of commercial dyes after azo dye. These dyes are characterized by their brightness and good fastness and they gain wide applications in textile industry. On the other hand , serious environmental problems are also associated with this class of dyes. Therefore a commercial anthraquinone dye Vat Yellow 4 is photodegraded by a batch reactor in this study, using solar and UV irradiation and the efficiencies of various commercial catalysts were compared. Then using TiO₂-P25 as the photocatalyst under UV irradiation the effect of different operational parameters on the degradation, the effect of addition of electron acceptors and the effect of the presence of inorganic ions were studied.

2. Experimental

2.1 Materials

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.

2.2 Methods

2.2.1 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. 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 test. pH adjustments for the solution were carried out by measuring the pH using ELICO, India LI 120-pH meter.

2.2.2 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.

3. Results and Discussion

3.1 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.

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. 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. Hence the percentage degradation is found to be less in solar irradiation of textile dyes (Nepolian et al., 2002).

3.2 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 Table.1, the activities of the photocatalysts were found to follow the order TiO₂>ZnO>Hombikat>CdS>ZnS>SnO. 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. TiO₂ is the most promising photocatalyst as it is chemically inert and stable with respect to photocorrosion and chemical corrosion (Nishimoto et al., 1985; Matthews, 1989). 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, 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 (Nepolian et al., 2002). Since band gap of SnO_2 is 3.87eV, activation of the catalyst under irradiation does not take place easily. CdS and Fe_2O_3 have smaller band gap of 2.4eV and 2.3eV respectively. The smaller band gap permits rapid recombination of electron-hole and so electron in these semiconductors cannot move into the electron acceptors in the solution rapidly. Hence very low photocatalytic activity is observed in these catalysts. TiO_2 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 hence the same was used in this present study for the degradation of the dye Vat Yellow 4 under UV irradiation.

3.3 Effect of TiO_2 loading

Addition of optimum amount of TiO_2 is essential in order to avoid the usage of excess catalyst and also to ensure total absorption of radiation photons for efficient photodegradation. The reaction rate as a function of catalyst loading in photocatalytic oxidation process has been investigated by several authors (San et al., 2001; Saquib and Muneer, 2002). The effect of TiO_2 loading on the percentage removal of the dye under UV irradiation has been examined by varying the amount of catalyst from 1-6g/l of the catalyst at 3×10^{-4} mol/l dye concentration. The results as given in Fig.3 indicate that the increase in catalyst dose from 1 to 4g/l increase the decolorisation from 76 to 98% in 60 min and the degradation percentage increases from 62 to 84% in 120 min. At concentrations higher than 4g/l the decolorisation and degradation efficiencies are almost constant.

The lower percentage degradation at lower TiO_2 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, 1997). The enhancement of removal rate at higher catalyst loading is due to the increase in amount of the catalyst weight which increases the number of dye molecules absorbed on the active sites and also due to the increase in the density of particles in the area of illumination. Above a certain level, since the dye concentration is kept constant the number of substrate molecules is not sufficient to fill the surface active sites of TiO_2 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 TiO_2 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 TiO_2 particles (Kaur and Singh, 2007).

Toor et al. (2006) reported the optimum catalyst concentration for the degradation of Direct yellow dye to be 2.0 g/l. Garcia and Takashima (2003) found that 8g/l of TiO_2 loading was most efficient in degradation of imazaquin in UV radiation. Alhakimi et al. (2003) reported that a catalyst loading of 3g/l was found to be optimum for potassium hydrogen phthalate degradation using TiO_2 under sunlight. These results clearly indicate that the optimum catalyst loading is not common for all photocatalytic reactions. In the present study the optimum amount of catalyst loading for the degradation of the dye Vat yellow 4 was found to be 4 g/l and hence the same dosage was used for the study of other parameters.

3.4 Effect of initial dye concentration

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 1×10^{-4} to 6×10^{-4} mol/l. The results as shown in Fig.4 and Fig.5 show that the increase in dye concentration decreases the removal rate. Increase in concentration of the dye from 1×10^{-4} to 6×10^{-4} mol/l results in the decrease of decolorisation from 100 to 81% in 60 min and the decrease of degradation from 98 to 64% in 120 min. 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. Further when the dye concentration increases the amount of dye adsorbed per molecule of the catalyst increases. This affects the active sites of the catalyst and thereby decreases the efficiency of the catalyst. Moreover, at high dye concentration, a significant amount of radiation may be absorbed by the dye molecules rather than the catalyst and this may also reduce the efficiency of the catalyst (Mills et al., 1993).

The photocatalytic decolorisation 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 TiO_2 surface and the adsorption-desorption equilibrium is reached in 5 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 $C = C_0$ at $t = 0$ gives Eq. (4)

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

where C_0 is the equilibrium concentration of the dye and C is the concentration at time t .

The plots of $\ln C_0/C$ versus t for photodecolorisation and degradation are shown in Figs. 6 and 7. The linear fit between $\ln C_0/C$ and irradiation time supports the conclusion that the decolorisation and degradation follow first-order kinetics. The rate constants for decolorisation and degradation are given in Table 2.

3.5 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 and Tsachpinis, 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.

3.5.1 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 aqueous solution of 50% 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.8. The addition of H_2O_2 in the range 0.5 to 2.0ml/l increases the decolourisation from 68.1 to 88.2% in 20 min and degradation from 42 to 63.8% in 20 min. Further increase in the H_2O_2 concentration limits the removal rate. Hence, 2.5ml H_2O_2 concentration appears to be optimal for the degradation. An increase in H_2O_2 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 H_2O_2 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)). H_2O_2 can compensate for the O_2 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) H_2O_2 may also be photolysed to produce hydroxyl radicals directly (Eq. (7))



H_2O_2 has extremely low absorption of solar light. Hence, the oxidation of the dye by photolytic H_2O_2 (Eq. (7)) will be insignificant.

(iii) H_2O_2 may also reacts with super oxide anion to form $\cdot OH$ radical (Eq. (8)).



The inhibition of the degradation of the dye beyond the optimum load of H_2O_2 may be due to the hydroxyl radical scavenging effect of H_2O_2 . The reaction between excess hydrogen peroxide and hydroxyl radical ($\cdot OH$) forms hydroperoxy radical. These hydroperoxy radicals are much less reactive and do not contribute to oxidative degradation of the dye (Eqs. (9) and (10)).





3.5.2 Effect of addition of $S_2O_8^{2-}$

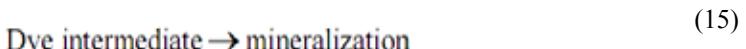
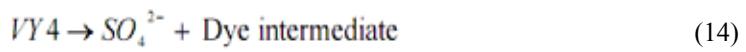
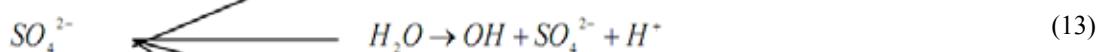
The effect of addition of $S_2O_8^{2-}$ on the photocatalytic oxidation of VY 4 has been investigated by varying the amount of $(NH_4)_2S_2O_8$ from 1 to 4 g/l. The results are shown in Fig.9. Addition of 1–3 g/l of $(NH_4)_2S_2O_8$ increases the degradation rate from 42 to 81.5% in 20 min. Further increase in the addition (4 g/l) decreases the degradation slightly. Similar enhancements by the addition of $S_2O_8^{2-}$ have been reported earlier (Bekholet et al., 1996; Minero 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) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet-}$) both thermally and photolytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following ways:



(iii) At high dosage of $S_2O_8^{2-}$ the inhibition of reaction occurs due to the increase in concentration of SO_4^{2-} ion (Eq. (12)). The excess of SO_4^{2-} ion is adsorbed on the TiO_2 surface and reduces the catalytic activity. The adsorbed SO_4^{2-} ion also reacts with photogenerated holes (Eq. (16)) and with hydroxyl radicals (Eq. (17)).



Since $SO_4^{\bullet-}$ is less reactive than $\cdot OH$ radical and h^+ , the excess SO_4^{2-} reduces the photodegradation of the dye.

3.5.3 Effect of addition of BrO_3^-

The rate of photocatalytic degradation increases considerably by the addition of BrO_3^- ion since it is an efficient electron acceptor (Sanchez et al., 1998; Poulios et al., 1999)

The effect of addition of $KBrO_3$ on the degradation of the dye Vat Yellow 4 is given in Fig.9. The addition of $KBrO_3$ from 1-3 g/l increases the degradation percentage from 42 to 73% in 20 minutes of irradiation time. The degradation percentage does not increase considerably on addition further of $KBrO_3$. The increase in removal rate by the addition of BrO_3^- is due to the electron scavenging effect caused by its reaction with the conduction band electron (Eq.18)



Negligible increase in the degradation percentage on further addition of $KBrO_3$ may be due to the adsorption of Br^- ion TiO_2 surface which affects the catalytic activity of TiO_2

3.6 Effect of the presence of inorganic ions

The waste water from dyeing operations normally contains considerable amount of carbonate ions as sodium carbonate is the common auxiliary chemical used in textile processing operations for adjusting the pH of the dye bath. Therefore it is important to study the influence of carbonate ion on the treatment efficiency. Sodium chloride also usually comes out in the effluent from textile mills as the dyeing process often requires high concentrations of sodium chloride for the transfer of dyestuff to the fabric. The study of the influence of NaCl is important in photocatalysis, because the NaCl may reduce reaction rates by poisoning the TiO_2 active sites or by scavenging radicals via the chloride ion (Abdullah et al., 1990; Arslan et al., 2000 'a')

3.6.1 Effect of Na_2CO_3

The effect of addition Na_2CO_3 on the photocatalytic degradation of Vat Yellow 4 is shown in Fig.10. The degradation percentage of the dye gradually decreased with increasing carbonate ion concentration. This is due to the hydroxyl scavenging property of carbonate ion, which can be accounted from the following eqs.(19) and (20)



Thus the free hydroxyl radical which is a primary source for the photocatalytic degradation decreases gradually with increase in the carbonate ion concentration resulting in the ultimate decrease in the percentage degradation of the dye significantly. Similar trend has been reported by Nansheng and Shizhong (1996).

3.6.2 Influence of NaCl

The results of the studies carried out with the addition of NaCl revealed that the degradation percentage of the dye decreased with increase in the amount of chloride ion as shown in Fig.10. Since the iso – electric point (IEP) of Degussa P25 TiO_2 is 6.6 (Abdullah et al.,1990) it is positively charged at pH below 6.6. In the presence of NaCl the Cl^- ions migrate to the positively charged TiO_2 surface and scavenge for h^+ and OH^\bullet . The $\text{h}^+/\text{OH}^\bullet$ scavenging reactions of Cl^- ions at $\text{pH} < \text{pH}_{\text{IEP}}$ of TiO_2 are as follows (Arslan et al.,2000 'b')



The $\text{Cl}_2^{\bullet-}$ formed is capable of oxidising the organic compounds, but at a lower rate than OH^\bullet radicals (Minero et al.,1993). In the presence of O_2 , $\text{dye}^{\bullet+}$ is further oxidized into lower molecular weight organics and carbon dioxide as shown in Eq (24). Thus at $\text{pH} < 6.6$ the degradation reaction should be less favorable in the presence of NaCl as already reported in previous studies (Tanaka and Saha, 1994; Bekbolet et al.,1998)

4. Conclusion

The anthraquinone dye Vat Yellow 4 is resistant to direct photolysis. The photocatalytic degradation of the dye in the presence of different commercial catalysts in slurry under solar and UV irradiation revealed that TiO_2 is the more efficient catalyst. Degradation of the dye in the presence of TiO_2 under solar irradiation takes place to lesser extent compared to UV irradiation. The optimum catalyst loading for the degradation of 3×10^{-4} solution of the dye under UV irradiation was 4 g/l and the degradation rate decreases with increase in the initial concentration of the dye. The decolorisation and degradation obey first order kinetics. The addition of electron acceptors H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KBrO_3 increases the decolorisation and degradation up to the optimum dosage of 2.5ml/l, 3g/l and 3 g/l respectively and beyond the optimum dosage the enhancement is not significant. Degradation percentage was found to decrease due to the presence of NaCl and Na_2CO_3 .

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Table 1. Photocatalytic activity of various commercial catalysts for the degradation of VY4

Catalyst	Degradation %	
	Solar Irradiation	UV Irradiation
TiO ₂	72	94
ZnO	54	69
Hombikat	32	26
CdS	36	17
ZnS	30	14
SnO ₂	11	7
Fe ₂ O ₃	9	10

Table 2. Rate constants of VY 4 decolourisation and degradation

Initial concentration mol/l	Decolourisation		Degradation	
	k' (min ⁻¹)	R	k' (min ⁻¹)	R
1 x 10 ⁻⁴	0.1150	0.9947	0.0336	0.9639
2 x 10 ⁻⁴	0.0799	0.9829	0.0229	0.9453
3 x 10 ⁻⁴	0.0651	0.9974	0.0157	0.9957
4 x 10 ⁻⁴	0.0542	0.9865	0.0133	0.9846
5 x 10 ⁻⁴	0.0374	0.9834	0.0109	0.9913
6 x 10 ⁻⁴	0.0321	0.9889	0.0098	0.9943

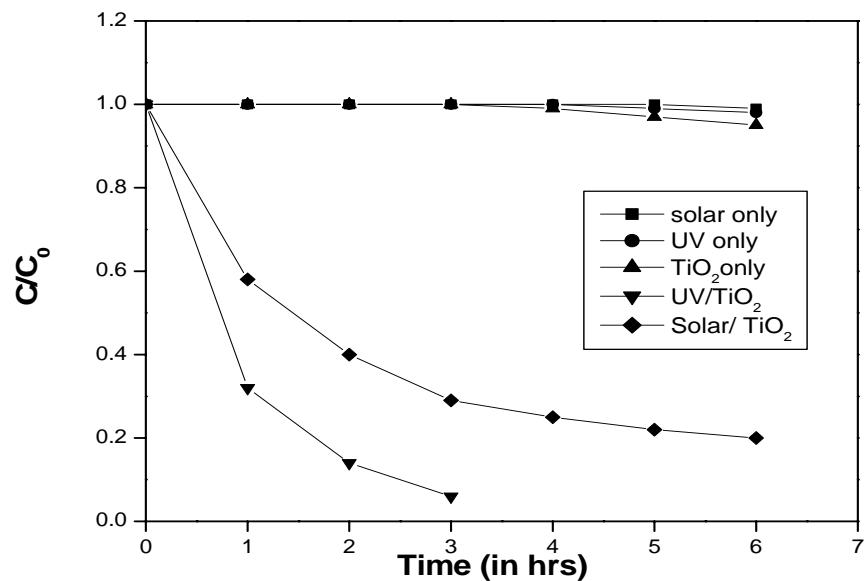


Fig.1. Effect of Solar/ UV irradiation on the degradation of Vat Yellow 4 in the presence and absence of TiO_2

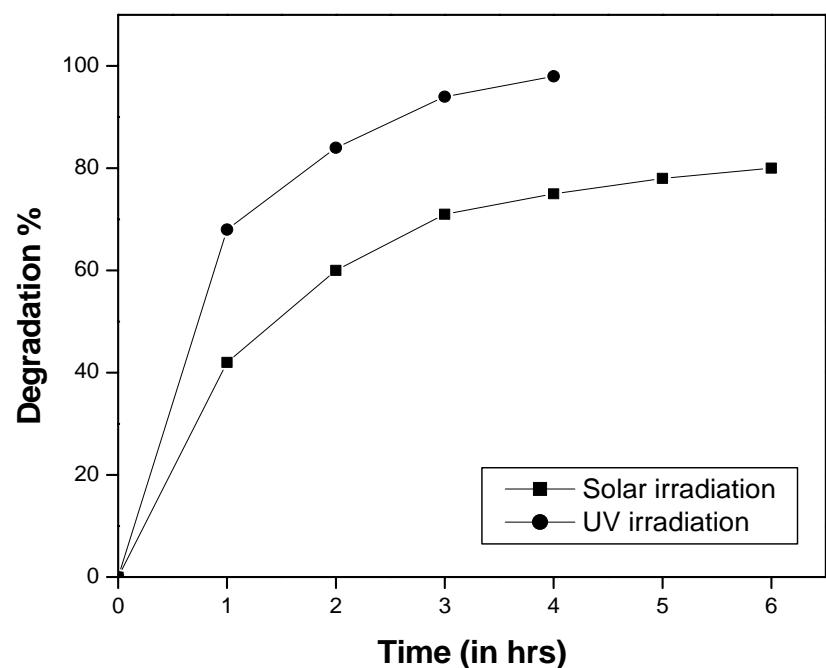


Fig.2. Effect of Solar/UV irradiation on the degradation of VY 4

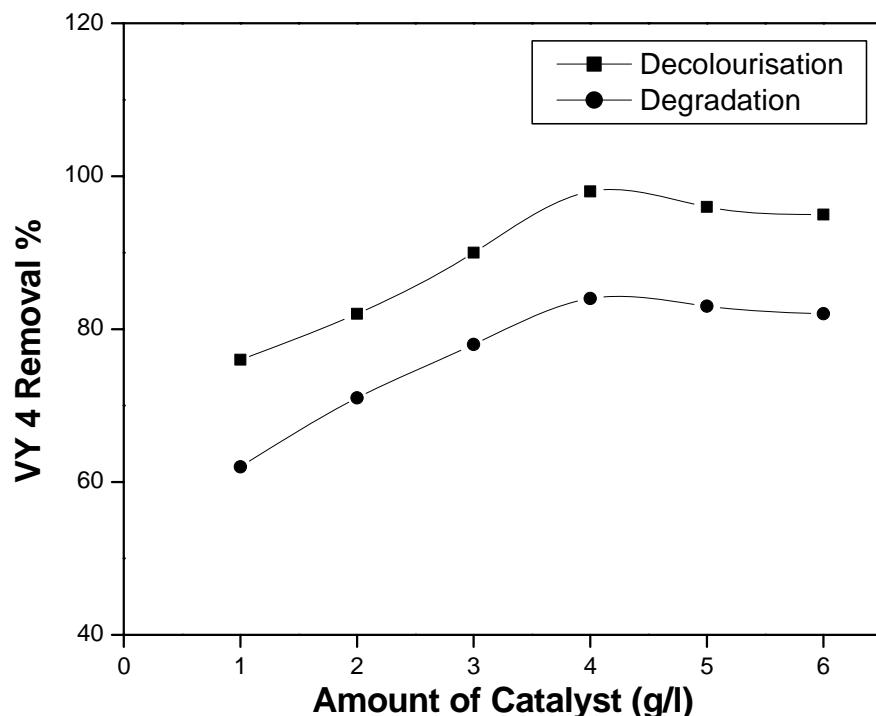


Fig.3. Effect of Catalyst loading on the decolourisation and degradation of VY 4
 $[VY\ 4]=3\times 10^{-4}\ mol/l$, Irradiation time: Decolourisation = 60 min, Degradation = 120 min

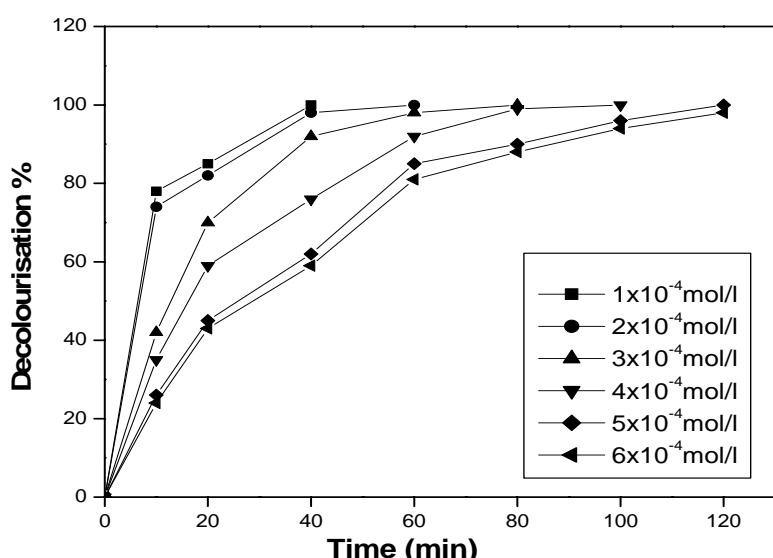
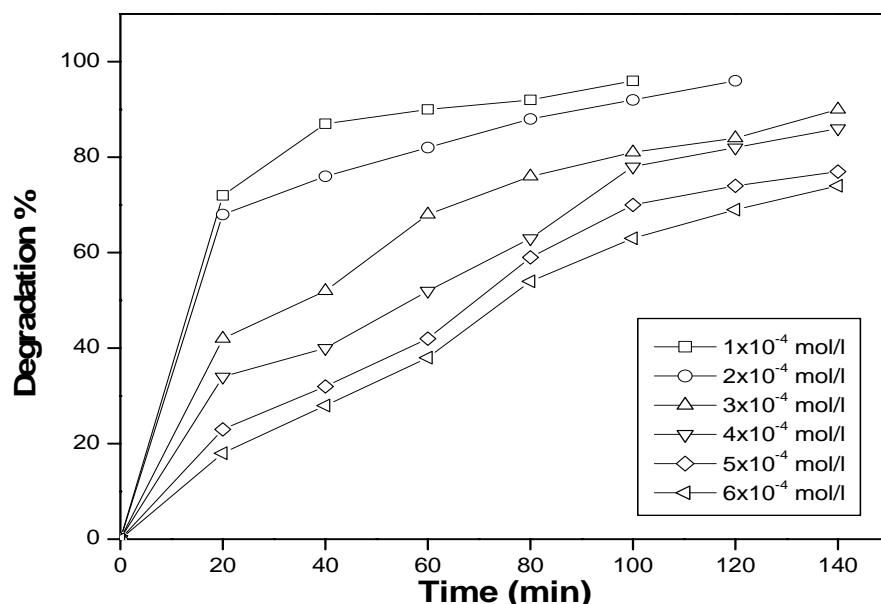


Fig.4. Effect of initial dye concentration on the decolourisation of VY 4.
 $\text{Amount of } TiO_2 = 4\ g/l$



**Fig.5. Effect of initial concentration on the degradation of VY 4
Amount of $\text{TiO}_2 = 4 \text{ g/l}$**

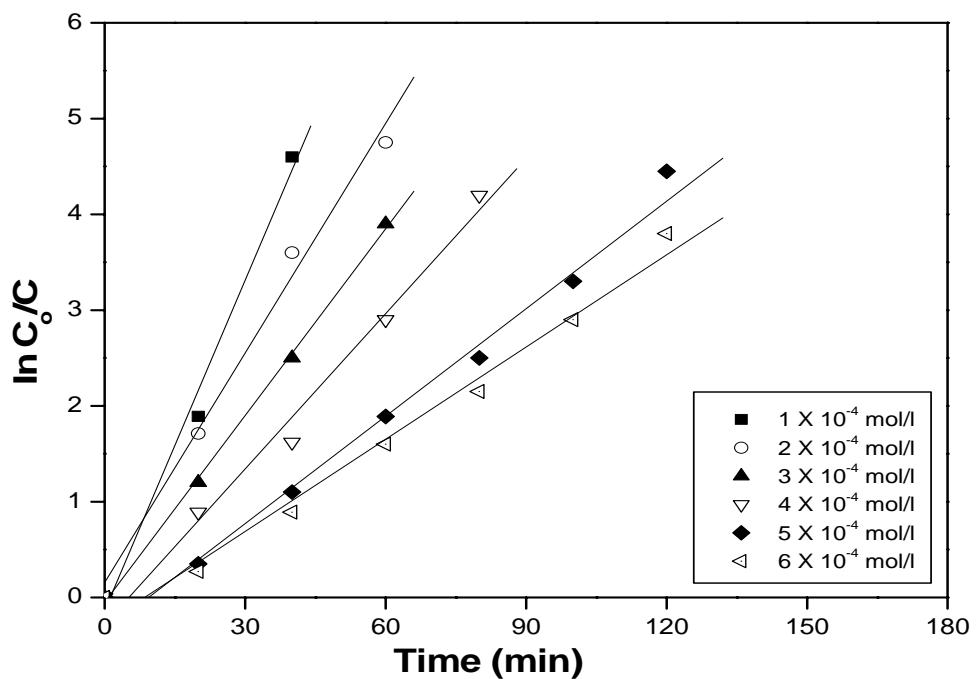


Fig.6. Kinetics of VY 4 decolourisation for different initial concentrations

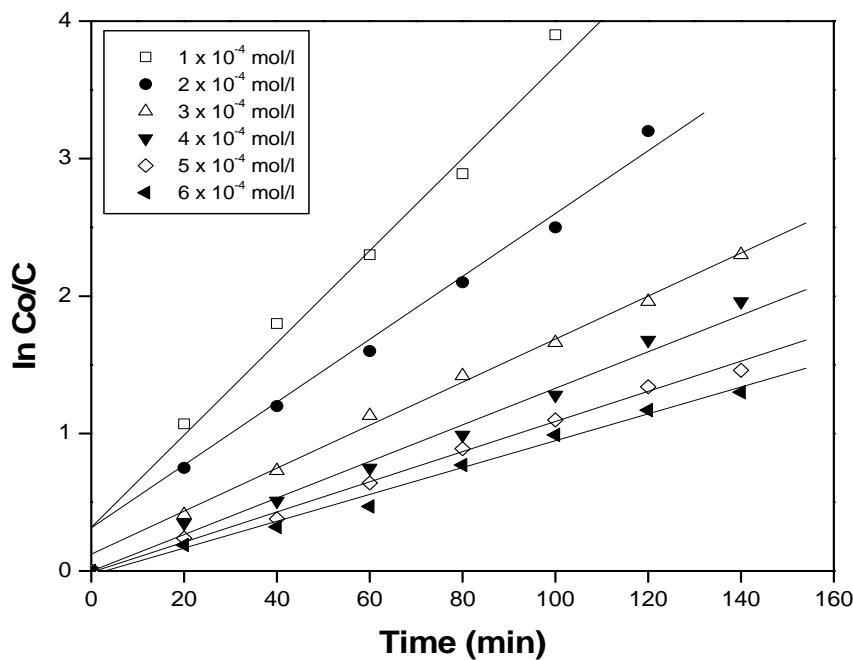


Fig.7. Kinetics of degradation of VY 4 for different initial concentrations

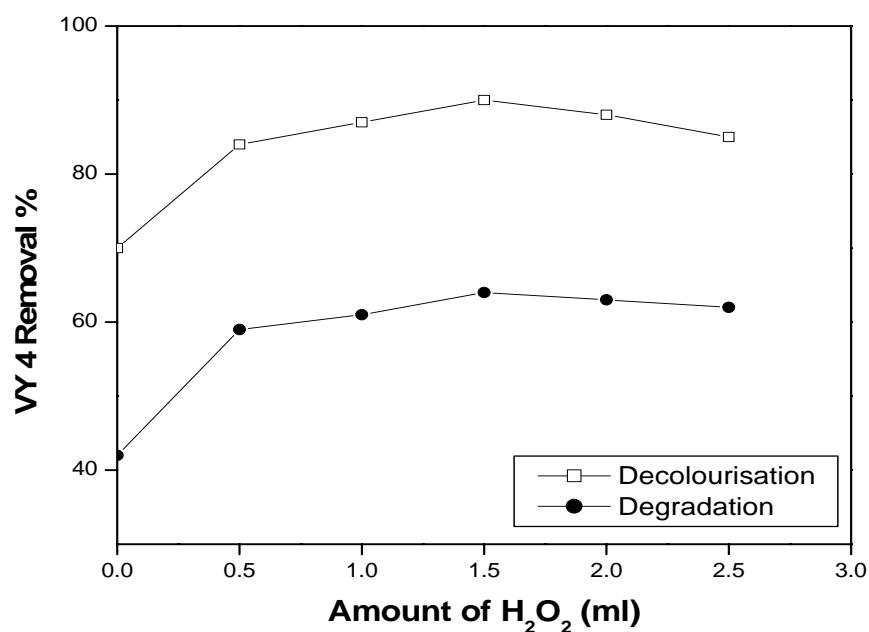


Fig.8. Effect of addition of H_2O_2 on the decolourisation and degradation of VY 4. $[VY\ 4]=3\times 10^{-4}\ \text{mol/l}, TiO_2=4\ \text{g/l}$, Irradiation Time:20 min

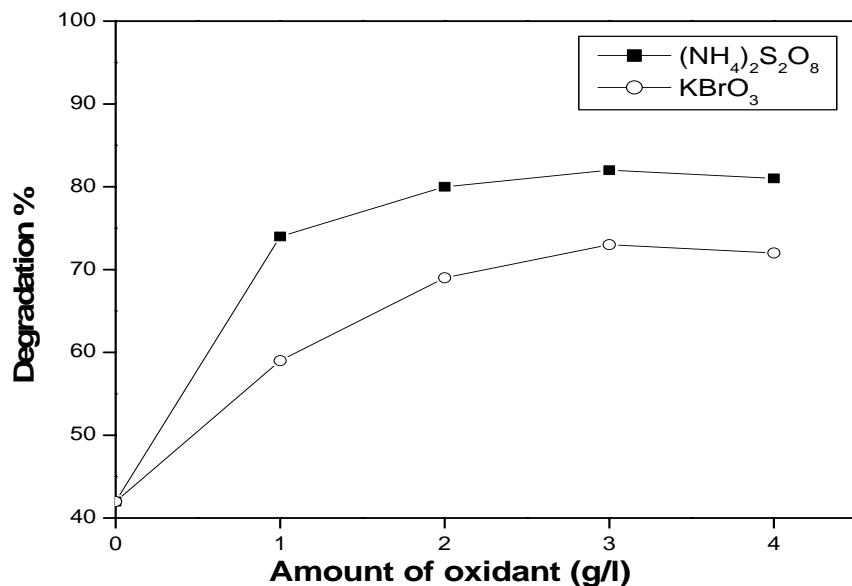


Fig.9. Effect of addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KBrO_3 on the degradation of VY 4. $[\text{VY } 4]=3 \times 10^{-4}$ mol/l, $\text{TiO}_2=4$ g/l, Irradiation time:20 min.

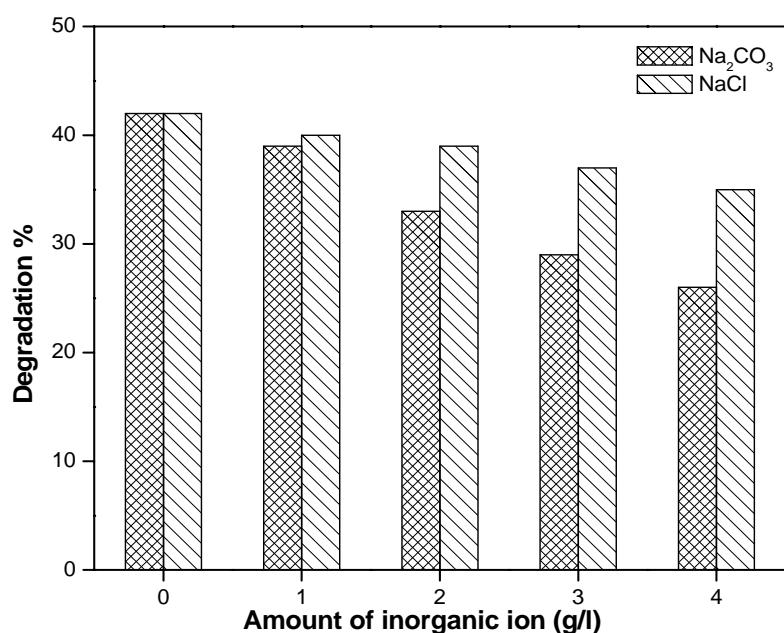


Fig.10. Effect of the presence of Na_2CO_3 and NaCl on the degradation of VY4. $[\text{VY } 4]=3 \times 10^{-4}$ mol/l, Amount of TiO_2 4 g/l, Irradiation time = 20 min