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CATALYSED DEGRADATION OF INDANTHRENE GOLDEN ORANGE RG IN SUNLIGHT WITH VANADIUM - DOPED TiO_2

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ABSTRACT

Nano sized particles of TiO_2 were synthesized by gel to crystalline conversion and doped suitably with vanadium by solid state method. Semiconductor mediated photocatalysed degradation of indanthrene golden orange RG (IGORG) under sunlight and UV light has been investigated as a function of irradiation time under various conditions like pH, catalyst concentration and substrate concentration using TiO_2 and vanadium- doped TiO_2 in presence of different electron acceptors. Doped TiO_2 was found to be more efficient under sunlight than TiO_2 under various experimental conditions. The trend of degradation rates for the two photocatalysts however appear to be similar though they are experimented under different sources of light. The extent of degradation and degradation products for the enhanced degradation were analyzed by UV-visible, IR and Gas chromatography-Mass spectrometry (GC-MS) techniques. The probable pathways for the formation of products is proposed.

Key words : Photocatalysis, Vanadium-doped TiO_2, Indanthrene golden orange, UV/ Sunlight.

INTRODUCTION

Dyeing or printing of textiles releases a vast amount of unused and unfixed synthetic colorant into the environment in the form of waste and wash liquor[1, 2]. Although most commercial dyes are not directly toxic, the colored wastewater is subjected to rigorous environmental legislation due to their negative impact on the surrounding environment. The classical techniques like flocculation, electrolysis and activated sludge do not work efficiently due to high solubility of these synthetic dyes in water. In addition, an incomplete chemical oxidation or partial biodegradation can be environmentally detrimental[3-5] because of generation of toxic aromatic amines and phenols. Ozone/UV, H_2O_2/UV and TiO_2 photocatalysis have already been used to decolorize natural and

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synthetic dyes[6-24]. Photoexcitation of semiconductors (titanates) leads to the formation of electron–hole pair, which can eventually initiate redox reactions of organic substrates.

Indanthrene golden orange-RG (IGORG) is a water-soluble dye and is resistant to chemical oxidation due to its aromatic anthraquinone strength, which is highly stabilized by resonance. Since these dye derivatives are becoming a class of concerning water pollutants and are accumulating in the environment, there is a strong need to determine optimum conditions for rapid degradation of this dye. The present investigation involves the practical application of photocatalysed degradation of this dye with the utilization of most environmentally available and abundant energy source, the sunlight. Thus, a comparative and a detailed study has been done on the photodegradation of anthraquinone dye, using TiO_2 and vanadium-doped TiO_2.

EXPERIMENTAL

The experimental equipment used in this study consists of a reactor vessel into which the UV or sunlight is focused directly. The exposure area is 176.62 cm^2.The UV light source equipment is a medium pressure Hg vapor lamp source whose wavelength peaks around 400 nm and the photon flux is found to be 7.75 mW/cm^2 as determined by ferrioxalate actinometry[25-27]. While using the natural source, the sunlight is concentrated using a high powerful convex lens of 6-inch diameter directing the concentrated sunlight into the reactor. In a study, in which only titanate photocatalysis was used to degrade different dyes, IGORG was observed to be the most recalcitrant to discoloration. Therefore, an optimum amount of $(NH_4)_2S_2O_8$, was used as an oxidizing agent in all experiments,s wherever the photocatalyst was used, since the extent of degradation was very low without it. Any increase or decrease of $(NH_4)_2S_2O_8$ was observed to affect the reaction adversely. The suspensions in each experiment were continuously stirred under atmospheric oxygen, since no degradation took place in absence of oxygen.

Sunlight experiments were carried out between 10 : 30 am to 2 : 30 pm during the month of March at Bangalore city [130 00.57’ N and 770 34.15’ E) which is about 1800 Km from New Delhi, the capital of India. Exactly, same experimental conditions were maintained for both; sunlight and UV light reactions. The extent of degradation of this dye was studied by withdrawing samples for analysis at any desired time interval during irradiation. Samples withdrawn were centrifuged for complete removal of photocatalysts and analyzed. The residual concentration of the dye was estimated from calibration curves of absorbance versus concentration of dye at a constant value of λ_{max}.

The particle size of the photocatalysts prepared was calculated by X-ray diffraction studies (Phillips PW/1050/70/76). Stereo scan 440 Cambridge-UK, energy dispersive X-ray analyzer used in conjunction with SEM confirmed the percentage composition of each element. The analysis was done by UV-Visible, (Shimadzu 1650 PC UV-Vis spectrophotometer), IR (Nicolet impact 400D FTIR spectrophotometer) and Mass (GCMS-QP 5000 Shimadzu mass spectrometer) techniques.

Materials and methods

Indanthrene golden orange RG was obtained from BASF and used without any further purification. The dye had two values of λ_{max}; one at 460 nm and the other at 207 nm. The water employed in all studies was double distilled. The photocatalyst TiO_2 and vanadium-doped TiO_2 used for comparative studies were synthesized in the laboratory. The other chemicals used in this study like titanium tetrachloride, NaOH, H_2SO_4, $(NH_4)_2S_2O_8$, $K_2S_2O_8$, H_2O_2 and V_2O_5 are obtained from Merck chemicals.

Procedure

Fine-grained powders of anatase form of TiO_2 were prepared by precipitation method[28-30]. Anatase form of TiO_2 is then allowed to undergo solid-state reaction with calculated amounts of vanadium pentoxide (V_2O_5). Then the doped titanate was annealed at 600 °C for 6 hours and then milled well for completion of solid-state reaction and annealed further for 3 hours and used.

RESULTS AND DISCUSSION

Characterization of photocatalyst

The crystallite size is measured from Scherrer's equation[31-33] relating pure diffraction breadth (half band width) to crystallite size normal to plane hkl as $D_{hkl} = \frac{K\lambda}{\beta Cos\theta}$ where D_{hkl} is mean dimension in Å, λ is the wavelength, β the pure diffraction line broadening and θ the Bragg angle of the reflection hkl and K is a constant approximately equal to unity. The crystallite size of doped titanate was calculated to be 173.63 Å as against the undoped TiO_2 of particle size 164.4 Å from Scherrer's equation. The EDX analysis data of TiO_2 and vanadium-doped TiO_2 are shown in the Table 1. Fig. 1 represents the plot of $(1-R_\infty)^2/2$. R_∞ versus wavelength where R_∞ = Ratio of relative reflectance to reflectance of non-absorbing medium. Band gap; thus, calculated from the above plot is 3.01eV for TiO_2. In addition of having a band gap of 3.01eV, doped TiO_2, has

many mid band gaps of which 2.60 eV appears prominent in the plot, thus facilitating the photocatalyst to respond to sunlight.

Table 1. EDX analysis data

Catalyst	Element (%)	Atom (%)
TiO_2	Ti – 59.95	Ti – 33.25
	O – 40.05	O – 66.75
Vanadium – doped TiO_2	V– 34.70	V – 19.631
	Ti – 32.617	Ti – 23.848
	O – 32.67	O – 56.521

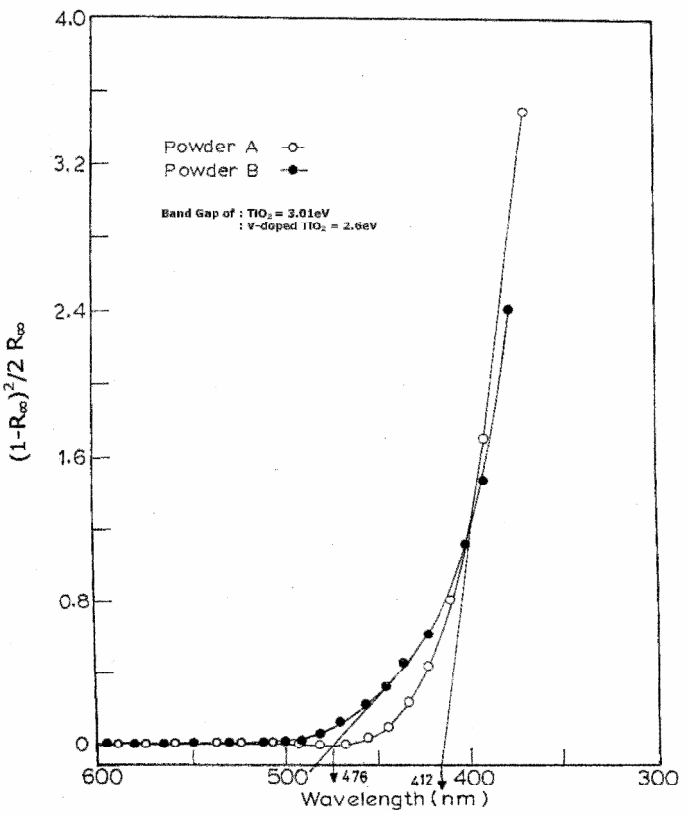


Fig. 1 : A plot of $(1-R_\infty)^2/2\ R_\infty$ versus wavelength to calculate the band gaps of TiO_2 and vanadium doped TiO_2

Photocatalytic degradation kinetics

Fig. 2. shows the plot of C/C_0 versus time (where C_0 is the initial concentration and C is the concentration at any desired time interval) for the degradation of IGORG in presence and absence of photocatalyst both; under UV and sunlight. There was no observable loss of the dye, when the irradiation was carried out in absence of photocatalyst and oxidizing agent, both in UV-light and in sunlight. Efficient degradation of almost 100% was observed, when TiO_2 /vanadium-doped TiO_2 were used with oxidizing agent for photocatalysis.

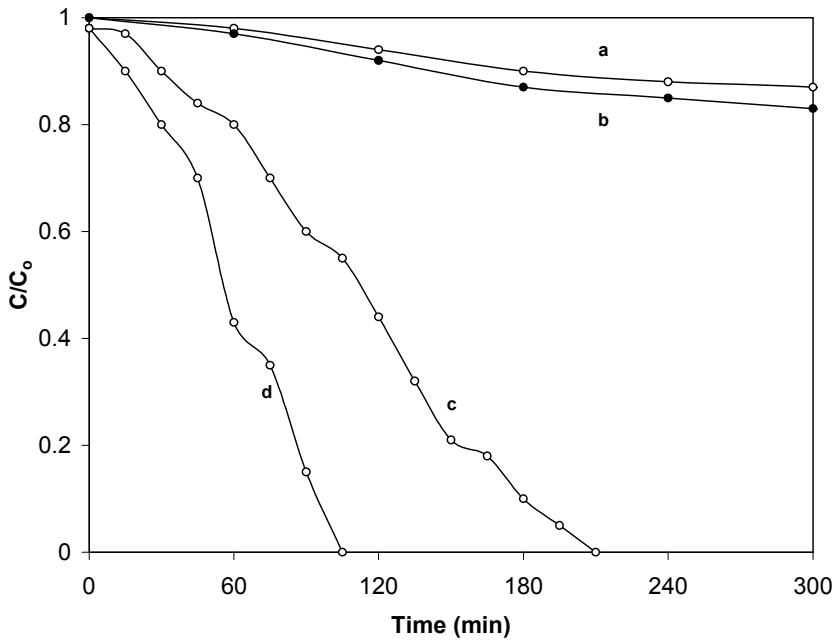


Fig. 2 : A plot of C/C_0 versus irradiation (C_0 =10 ppm) time for the following experimental conditions

(a) Sunlight photolysis without catalyst or oxidizing agent.
(b) UV-Photolysis without catalyst or oxidizing agent.
(c) Sunlight-photolysis with TiO_2.
(d) Sunlight photolysis with vanadium-doped TiO_2.

Further, Table 2 substantiates degradation rate for the decomposition of dye in presence of different photocatalysts under sunlight as well as in UV light in presence of $(NH_4)_2S_2O_8$ as oxidizing agent. It is observed that the photocatalytic activity of doped

TiO_2 enhanced to almost thrice as compared to that of TiO_2 in sunlight, whereas the difference is not observed in UV light.

Table 2. Degradation rate for the decomposition of dye in presence of different photocatalysts

Experimental condition	Source of light	Degradation rate K (min^{-1})
Dye + $(NH_4)_2S_2O_8$ + TiO_2	UV light	0.0270
	Sunlight	0.0060
Dye + $(NH_4)_2S_2O_8$ + Vanadium-doped TiO_2	UV light	0.0270
	Sunlight	0.0160

Therefore, it is important to mention that all (i) UV light irradiated experiments were conducted with the photocatalyst TiO_2 and sunlight irradiated experiments were conducted with the photocatalyst vanadium-doped TiO_2, for the comparative studies; henceforth. This was also necessary to study the difference in trend of their degradation rates when the two catalysts were used. (ii) The degradation rates for all comparative studies were calculated for the results obtained with respect to λ_{max} = 460 nm. The course of the reactions was followed systematically by UV, IR and mass spectroscopy.

Effect of substrate and catalyst concentration

In a view to study the dependence of photocatalytic reaction rate on the substrate concentration, the degradation kinetics of IGORG has been investigated employing different concentrations of dye. Fig. 3 shows the degradation rate of the dye as a function of substrate concentration, employing TiO_2 and doped TiO_2 in UV light and sunlight, respectively. It is interesting to note that degradation rate under UV light source increases with increase in substrate concentration from 5 ppm to 10 ppm. A further increase from 10 ppm to 15 ppm leads to a decrease in degradation rate.

The effect of photocatalyst concentration on the degradation kinetics of IGORG has been observed with TiO_2/UV and doped TiO_2/sunlight varying from 0.2 g/L to 1.0 g/L. As expected, the degradation rate for the decomposition of IGORG in both light sources has been found to increase with increase in concentration of the photocatalyst (Fig. 4), which is characteristic of heterogeneous photocatalysis.

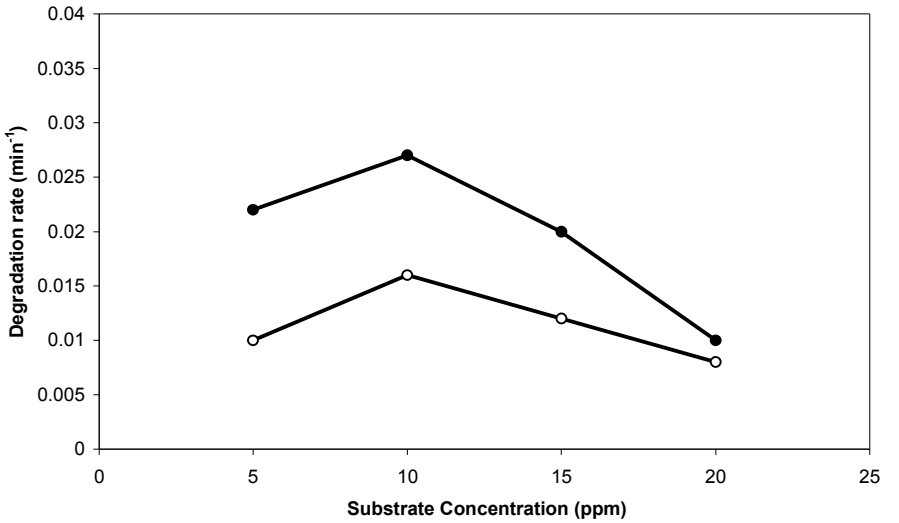


Fig. 3 : Influence of substrate concentration on the degradation rate using 0.6 g/L of photocatalyst with 0.1M of 2 mL $(NH_4)_2S_2O_8$ for an irradiation time of 105 minutes

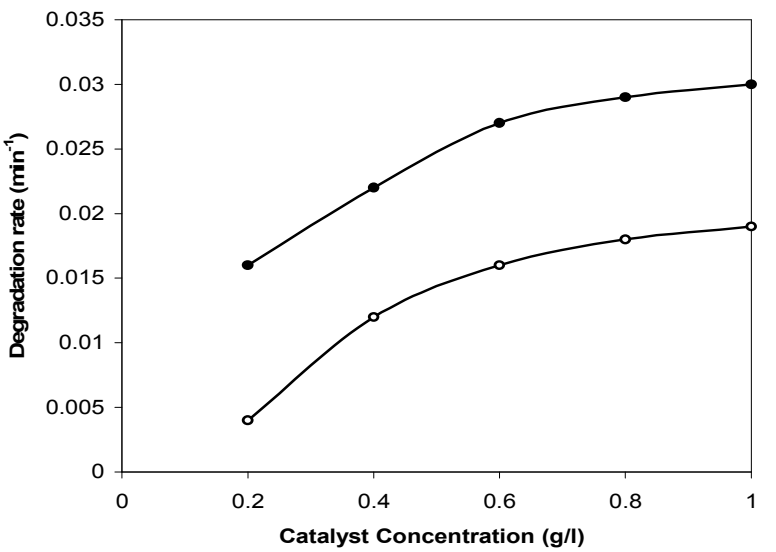


Fig. 4. Influence of catalyst concentration on the degradation rate for the decomposition of IGORG (10 ppm) using 0.1M of 2 mL $(NH_4)_2S_2O_8$ for an irradiation time of 105 minutes

Effect of pH

Employing TiO_2 and vanadium-doped TiO_2, as photocatalysts, the degradation of the dye was studied at the following pH values; 2.0, 3.5, 6.0, 9.0 and 12.0 both; under UV light and sunlight source. Fig. 5 shows the degradation rate as a function of reaction pH. It is important to mention that pH of the solution was adjusted before irradiation by adding suitable amounts of 1M H_2SO_4 and 1M NaOH and pH is not followed in the course of the reaction. However, the pH of the solution decreased slightly at the end of reaction. Higher efficiency was observed at very low pH (pH < 4) and also at very high pH (pH > 10) for both TiO_2 and vanadium-doped TiO_2.

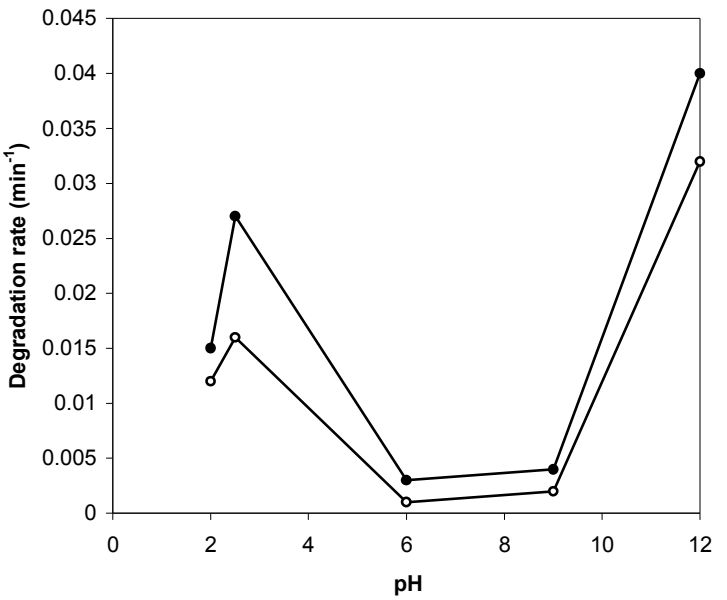


Fig. 5. Influence of pH on the degradation rate for the decomposition of IGORG (10 ppm) with photocatalyst (0.6 g/L) and $(NH_4)_2S_2O_8$ (2 mL and 0.1 M) for an irradiation period of 105 minutes

Effect of electron acceptors

Since hydroxyl radicals appear to play a very important role in photocatalysis, the effect of electron acceptors such as hydrogen peroxide and persulphate ions on the photocatalysis is investigated. The comparative photodegradation rates in presence of various electron acceptors are as given in Table 3. All the additives showed a beneficial

effect on the degradation of the dye to a greater extent in UV light than in sunlight. Further $(NH_4)_2S_2O_8$ shows highest activity, when compared to H_2O_2 and $K_2S_2O_8$.

Table 3. Degradation rate for the decomposition of dye in presence of different electron acceptors

Electron acceptor	Source of light	Degradation rate k (min^{-1})
$(NH_4)_2S_2O_8$	UV light	0.0273
	Sunlight	0.016
$K_2S_2O_8$	UV light	0.0241
	Sunlight	0.010
H_2O_2	UV light	0.0179
	Sunlight	0.007

Photocatalytic degradation of dyes employing irradiated TiO_2 is well documented in literature[34]. The initial step in TiO_2 mediated photocatalysed degradation is proposed to involve the generation of electron–hole pair leading to redox reactions causing degradation of the dye as observed in Fig. 2. The degradation takes place only in presence of oxygen. Adsorbed oxygen traps electron; thereby causing delay in electron–hole recombination in the illuminated semiconductor particle. The preadsorbed molecular oxygen scavenges the electron carrier to give superoxide radical anion $O_2^{-\bullet}$ that can be reduced to peroxide dianion[35], which are good oxidizing species. From Table 2, it is observed that the photocatalytic activity of vanadium-doped TiO_2 enhances to almost three times to that of TiO_2 in sunlight. Doping causes the creation of new energy levels at 445 nm (2.79 eV), 480 nm (2.57 eV) and 530 nm (2.33 eV) with an energy difference of 0.22 eV, 0.24 eV and 0.46 eV between them. The above three mid band gaps could be due to the distortion related to modified defect centers, which may have been caused due to the doping. The high photoreactivity of doped TiO_2 can thus be owed to (i) TiO_2 has a band gap of 3.01 eV (Fig. 1), because of which it responds to only light of UV range and the narrow mid bands observed in doped TiO_2 adds in decreasing the band gap to a range of 2.6 eV, and thus, extending the light absorption from UV to visible range. (ii) The increased particle size on doping may have decreased the band energy to visible region causing an increased response in sunlight (iii) The active energy levels formed during photocatalytic reactions promote an easy and fast interfacial charge transfer and (iv) Electron–hole pairs generated from the photocatalyst sometimes recombine and this recombination becomes

inefficient/slow with created energy levels acting as electron traps; thus, avoiding a major energy wasting step. However, the concept of slow recombination and charge transfer seems to have less importance, since the response of doping is very much prominent only in sunlight and not in both sources of light.

In Fig. 3, initially, when the substrate concentration increases from 5 ppm to 10 ppm, the catalytic sites may be sufficient enough to withstand the increased concentration leading to higher rate of photodegradation. With further increase in concentration of pollutant, more and more molecules of the compound gets adsorbed on the surface of the photocatalyst, because of which, the requirement of catalyst surface needed for the degradation also increases. However, the generation of relative amount of $^{\bullet}OH$ and $O_2^{-\bullet}$ on the surface of catalyst do not increase as the intensity of the light, irradiation time, amount of catalyst and quantity of oxidizing agent are constant. Consequently the rate of photodegradation decreases with increase in concentration of pollutant. This holds good for both the sources of light.

The degradation rates were found to be directly proportional to catalyst concentration indicating heterogeneous regime (Fig. 4). However, it has been observed that above a certain concentration, the rate levels off and becomes independent of catalyst concentration[36] and this limit depends on working conditions of the photoreactor, factors like scattering of light by particles and efficiency of absorption of photons. Further, when the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given reaction, the optimum catalyst concentration has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons. From the studies, 0.6 g/L of the photocatalyst was observed as optimum concentration for all heterogeneous photocatalysis performed.

The pH of the reaction mixture is an important factor to be considered, since it affects the surface charge properties of the photocatalyst, size of the aggregate it forms and band edge positions of valence and conduction band with respect to the redox potentials of adsorbate. Fig. 5 indicates that the degradation rate is strongly influenced by pH. The isoelectric point of photocatalyst TiO_2 in dye solution is at pH 6.0[37-39], while isoelectric point of TiO_2 in water is at pH 8.0. Sulphuric acid and sodium hydroxide were used to obtain desired low and high pH values accordingly. Hence, at more acidic pH values, the TiO_2 particle surface is positively charged, while at pH values greater than 6.0 it is negatively charged. Due to the low pKa value of the sulfonic acid group, whole dye molecule will be in anionic form and the degradation rate below pH 6 is quiet high. At isoelectric point charge range pH = 6 – 8, the degradation rate is very low because of

catalyst being almost neutral. At higher pH, the degradation rate again increases. Dye seems to have better degradation rate at a pH, of 2.5 with respect to both sources of light. However, in the present study, both the semiconductor fine powders show good response at very high or low pH.

One of the methods to inhibit electron-hole pair recombination is to add some electron acceptors to the reaction. They not only increase the number of trapped electrons and consequently avoid recombination but also generate more radicals accelerating photodegradation. These acceptors are known to generate hydroxyl radicals, which are thought to be primary oxidizing species[40, 41]. They are then known to react very rapidly with aromatic hydrocarbons to yield hydroxylated radicals and subsequent reaction of these adduct radicals can lead to mineralization of polynuclear hydrocarbons[36]. Thus, the density of hydroxyl groups on catalyst surface affect the adsorption behavior of the pollutant.

$$K_2S_2O_8/(NH_4)_2S_2O_8 + e^- \longrightarrow SO_4^{2-\bullet} + SO_4^{-\bullet}$$

$$SO_4^{2-\bullet} + e^- \longrightarrow SO_4^{-\bullet}$$

$$SO_4^{-\bullet} + H_2O \longrightarrow SO_4^{2-} + {}^{\bullet}OH + H^+$$

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^-$$

It is clear from Table 3 that $(NH_4)_2S_2O_8$ shows highest activity, when compared to H_2O_2 and $K_2S_2O_8$. $SO_4^{2-\bullet}$ radical can further give $SO_4^{-\bullet}$; thus producing more hydroxyl radicals. Therefore compounds with $S_2O_8^{2-}$ are better oxidants compared to H_2O_2 and further $(NH_4)_2S_2O_8$ is much better oxidant than $K_2S_2O_8$ as it provides better acidic pH of 2.5. The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed species on its surface is governed by band edge positions of the semiconductor and the redox potentials of the adsorbate. The relevant potential level of the acceptor species is thermodynamically required to be lower (more positive) than the conduction band potential of the semiconductor and the potential level of the donor needs to be higher (more negative) than the valence band position of the semiconductor in order to donate an electron to the vacant hole. The reagents like $(NH_4)_2S_2O_8$; thus, influences the pH, which in turn influences the band edge positions of semiconductor, together with surface charge of titanate particles. Thus, the efficiency of the reaction increases.

Spectroscopic analysis

UV-Visible spectral analysis

UV-visible spectra for the photodegradation of IGORG under different experimental conditions after an irradiation time of 105 min are shown in Fig. 6.

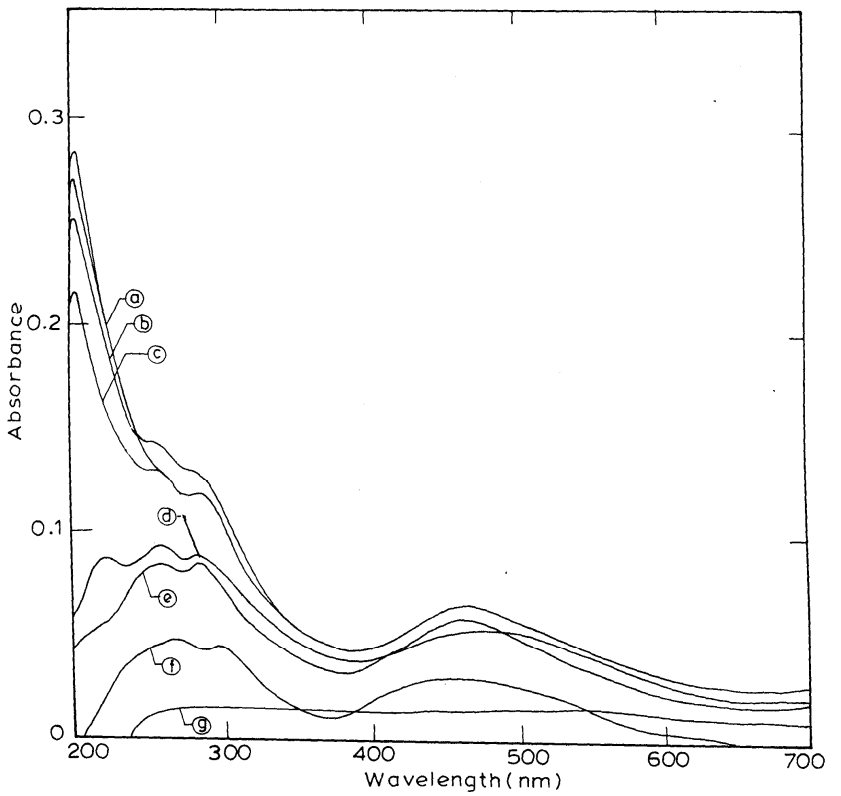


Fig. 6 : UV–Visible spectra of IGORG dye (10 ppm) taken during the process of degradation under different experimental conditions for an irradiation time of 105 minutes

Curve **a** represents the spectra of original compound before any irradiation. It shows four prominent peaks at 207 nm, 270 nm, 290 nm and 460 nm. The peak at 207 nm is because of the E band resulting from $\pi \rightarrow \pi^*$ transition in the high symmetrically fused benzene molecule[42]. The peak at 270 nm is the B-band of an alcohol arising due to keto-enol tautomerism in dye molecule. The peak at 290 nm is clearly the B-band of an extended ketone. It is important to specify that this peak at 290 nm appears more

prominently with degradation, which could also be explained as a secondary band of benzoic acid, formed as an intermediate. The high conjugation present in the molecule gives a peak at 460 nm, which is also the working λ_{max} of the present investigations. Curve **b** indicates the system where photodegradation was performed without photocatalyst and without oxidizing agent. Not much change in spectra is observed even after 105 minutes of illumination. Curve **c** indicates the marginal decrease in intensities of peak with respect λ_{max} = 207 nm, on addition of $(NH_4)_2S_2O_8$ even before any irradiation. Curves **d** and **f** imply homogeneous and direct photolysis of the dye taking place in presence of only $(NH_4)_2S_2O_8$ in sunlight and UV light, respectively. Anthraquinone dyes, which are known for not favoring the donation from excited state, do not allow sensitization[36]. This means only $(NH_4)_2S_2O_8$ is responsible for this partial degradation. It has been well known that $S_2O_8^{2-}$ is decomposed to $SO_4^{-\bullet}$ radical under UV irradiation, which is a strong oxidant. $SO_4^{-\bullet}$ radical itself oxidizes the dye leading to partial degradation of dye in homogenous reaction. Not much difference is observed between the two photocatalysts in UV light irradiation. Curve f indicates the UV photolysis of the dye with TiO_2/ vanadium doped TiO_2. Curve **e** and **g** depicts sunlight photolysis, when TiO_2 and vanadium-doped TiO_2 are used respectively along with $(NH_4)_2S_2O_8$. The figure clearly indicates the most efficient system to be that of curve **g** for which, there is a sharp decrease in intensities of all peaks including λ_{max} = 460 nm, which is quite resistant (because of huge concentration) and complete dissappearence of peak at λ_{max} = 207 nm, within 105 minutes of illumination indicating complete destruction of IGORG.

IR and GC-MS spectral studies were analysed for the most enhanced system to confirm the intermediates, completion and pathway of degradation.

IR spectroscopy

The complete analysis of IR bands[43] for the solid sample, reaction mixture before irradiation, midway of the irradiation and the after complete irradiation are given in Table 4. IR spectrum of the sample before any irradiation exhibits a strong prominent band in finger print region at 1640 cm^{-1} and 1610 cm^{-1} representing C=O stretching of the extended quinine (Fig. 7). Keto-enol tautomerism (existing), because of high conjugation in continuation with –C=O group in the dye is responsible for γO-H stretch at 3514 cm^{-1}. The very low intense band observed at 2076 cm^{-1} is because of 1, 2, 3 – tri substituted phenyl groups, where usually number of such low intense bands could be observed between 2000 cm^{-1} – 1660 cm^{-1}).

Table 4. Diagnostic bands in IR spectra at different time intervals for the most enhanced degradation

Comp.	νenol (O–H)	νCOOH(O-H)	ν aryl (C-H)	νCO_2	ν (C=O)	ν bend (O-H)	ν (C-O-C)	Puckered ring structure
Solid dye	3514	-	2940	2334	1640, 1610	1316	1040, 1052	664
Sample before irradiation	3441 (High intensity)	-	2934	2334	1636, 1590	-	1119	-
Sample after 45 min. of irradiation	3412 (Low intensity)	2572 (Low intensity)	(Neg. intensity)	-	1641 (Low intensity)	1316	-	-
Sample after 105 min. of irradiation	(Negligible intensity)	(Very low intensity)	-	Persists	(Negligible intensity)	-	-	-

The band at 2572 cm^{-1}, which appears at mid way of degradation, is characteristic of the benzoic acid (dimer). The spectra taken after 105 min of irradiation show no intense bands except for the band at 2340 cm^{-1} (antisymmetric stretching band in fine structure of O=C=O). This band becomes stronger with degradation implying the formation of the product CO_2.

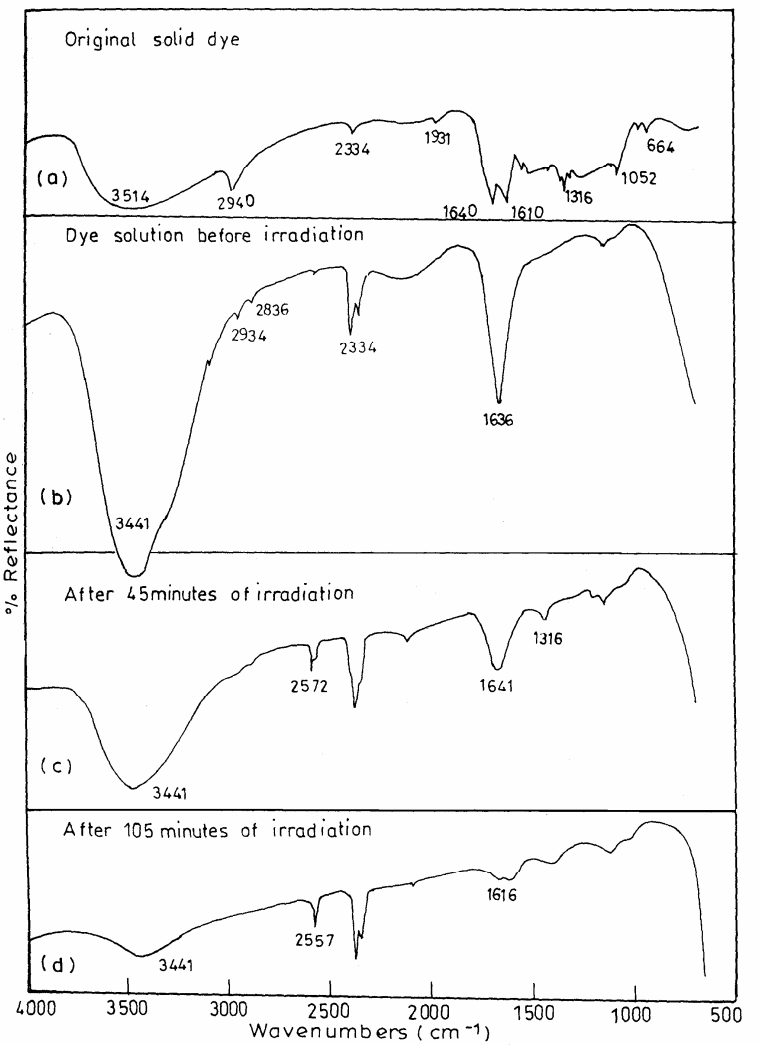
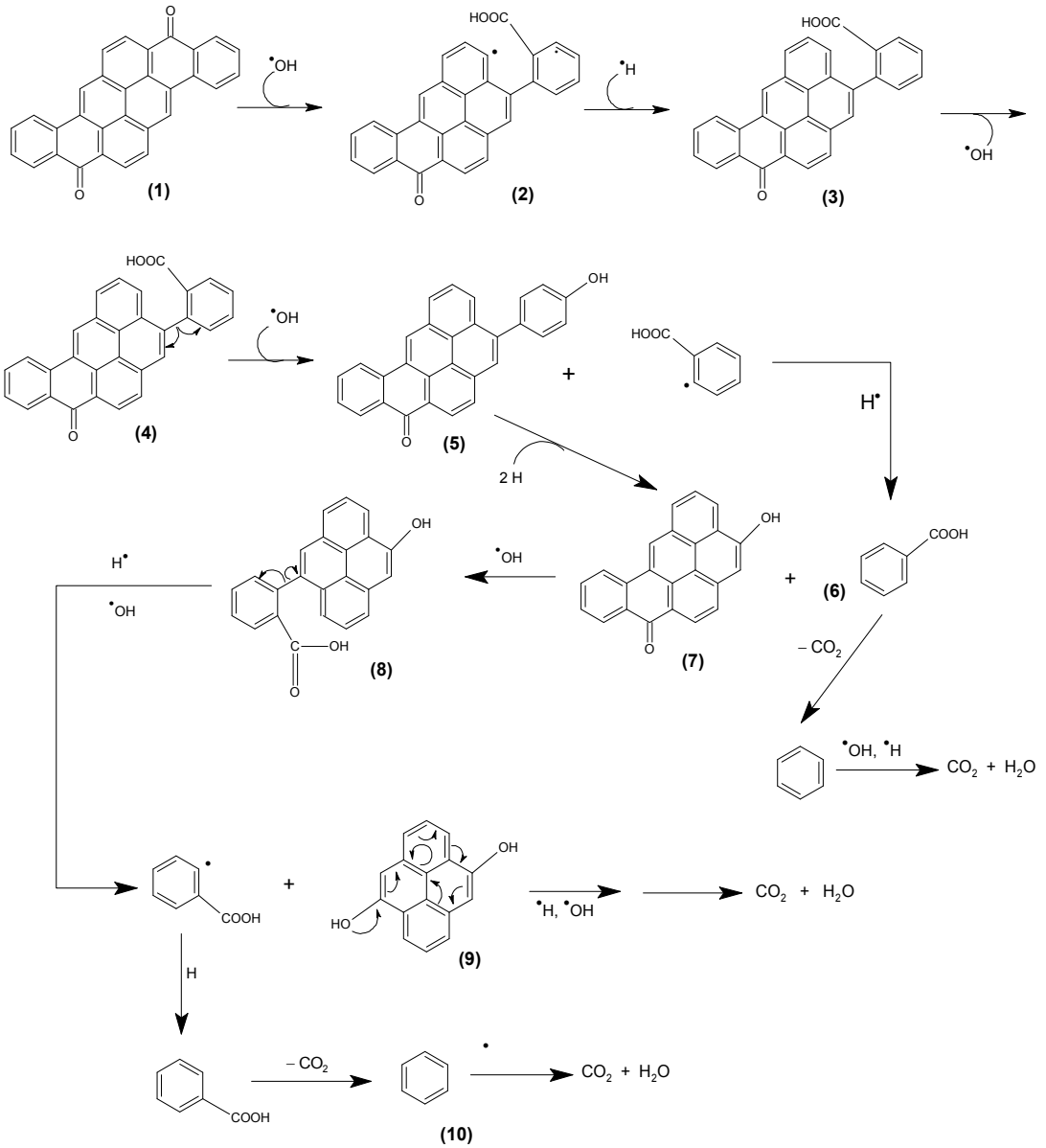


Fig. 7: (a) IR spectrum of the solid dye (b) IR spectrum before irradiation (c) and (d) IR spectrum after 45 minutes and 105 minutes of irradiation, respectively

Mass spectrometry

The probable mechanism for the formation of different products in the most efficient system of photodegradation of dye is proposed in **Scheme 1.**



Scheme 1 : Reaction mechanism for the photocatalytic degradation of IGORG dye

The GC-MS analysis[44] of the irradiated mixture taken at midway of irradiation showed formation of two products compound **6** and compound **9** appearing at retention times 4.983 and 8.842 minutes, respectively with the following m/z values.

Compound **6** (R_t = 4.9823) : 105 (M+), 85, 77, 54 and 51

Compound **9** (R_t = 8.842) : 233 (M+), 196, 149, 133, 121, 83, 57 and 44.

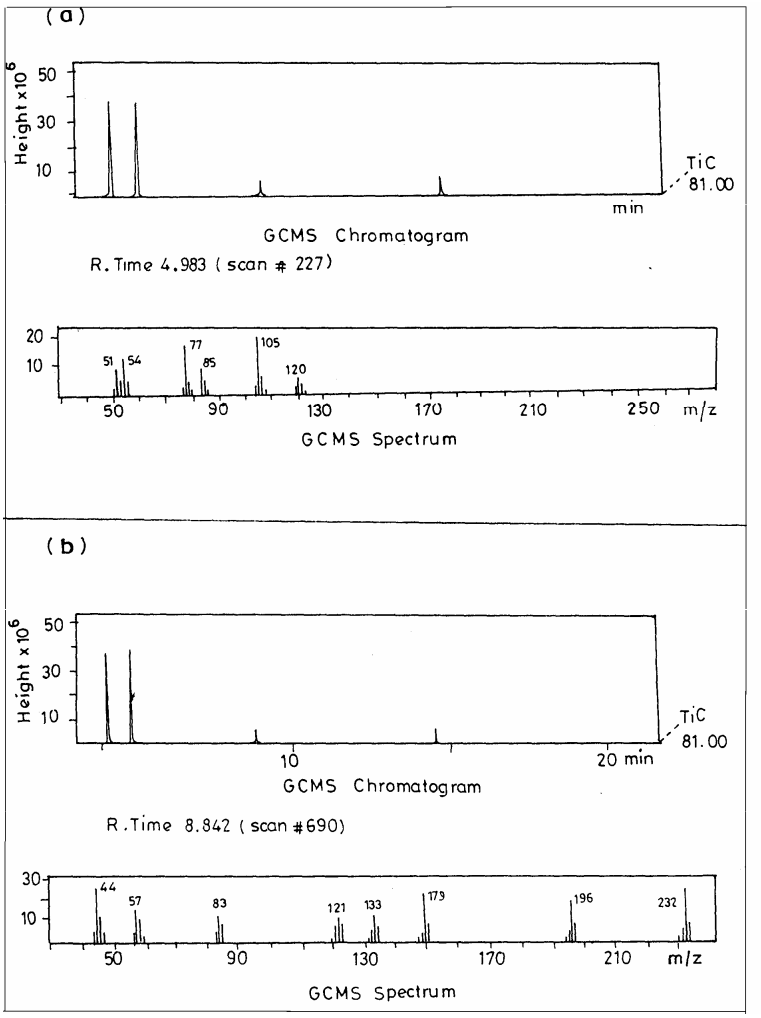


Fig. 8: GCMS analysis of the sample withdrawn at midway of photodegradation of the most enhanced system (a) m/z peaks of intermediate product corresponding to compound 6 appearing at a retention time of 4.983 minutes (b) m/z peaks of intermediate product corresponding to compound 9 appearing at a retention time of 8.842 minutes

The products were identified based on their molecular ion and mass spectrometric fragmentation peaks[44]. Benzoic acid, which is one of the important intermediate identified by UV visible and IR spectroscopy is further substantiated by GCMS. The point of cleavage on irradiation is found to be =C-C=O in the fused benzene ring by addition of OH radicals to get compound **2** as in **Scheme 1**. Further separation of benzoic acid i. e. compound **6** gives ion fragmentation peaks with m/z values at 105, 77, 85, 54 and 51 as being evident from the Fig. 8(a). Separation of one more group of benzoic acid with addition of hydroxyl group and proton abstraction gives compound **9**, which shows m/z peak at 233 and ion fragmentation peak at m/z value 196. Further breaking of fused ring gives m/z peaks at 83 and 57 (Fig. 9(b)).

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