

Solar assisted photocatalytic and photochemical degradation of Reactive Black 5

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Abstract

The photocatalytic oxidative degradation of Reactive Black 5 (RB 5) has been investigated using TiO₂-P25 as photocatalyst and sunlight as irradiation source in slurry form. The degradation was carried out at different experimental conditions to optimize the parameters such as amount of catalyst, concentration of dye and pH. A complete degradation of 3.85×10^{-4} M dye solution under solar irradiation was observed in 3.5 h. The photochemical degradation using hydrogen peroxide results in the partial removal of the dye.

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1. Introduction

Dyes are the major industrial pollutants and water contaminants [1]. During the dyeing process about 20% of the dye is not fixed on the fabric and enters into the environment. Due to their complicated structure most of the dyes are resistant to biodegradation [2]. So the concentration of the dye pollutants remains constant in the effluent. A variety of physico-chemical methods are presently available for the treatment of textile wastewater [3]. But these processes are ineffective on pollutants which are not readily absorbable or volatile and also they simply transfer the pollutants to another phase rather than destroying them. Numerous studies on the application of photocatalytic oxidation (PCO) for the removal of dyes have been reported [4–6]. Heterogeneous photocatalysis through illumination of light to aqueous suspension of TiO₂ offers an attractive advanced oxidation process. This photocatalytic process is receiving great attention because of its mild operating conditions and it can be powered by sunlight.

Another advanced oxidation process for the degradation of dyes is the UV photolysis in presence of H₂O₂. Several studies have been reported the successful application of UV/H₂O₂ process for the treatment of dye industrial wastewater [7–9]. The combination of UV light and H₂O₂ produce very reactive species hydroxyl radical which can oxidise most of the organic pollutants. The use of high energy UV light is not only costly but also can be hazardous [10]. Reeves et al. [11] suggested that the potential exists for the use of highly concentrated sunlight in the removal of textile dyes from wastewater. Nogueira and Jardim [12] demonstrated how the photobleaching of some dye could be achieved by solar light irradiation using TiO₂ as a photocatalyst. In our earlier work, we had reported the photodegradation of Reactive Orange 4 using sunlight and UV-A light [13,14]. The water soluble Reactive Black 5 (RB5) has been extensively used for dyeing cotton fabrics.

Poulios and Tsachpinis have investigated the photocatalytic degradation of Reactive Black 5 (RB 5) using TiO₂-P25 in UV light [15]. Though they had reported that the RB 5 photodegradation is more effective in UV-A light than sunlight, a detailed investigation in sunlight had not been carried out. Hence in the present work we have investigated photocatalytic and photochemical degradation of Reactive Black 5 in sunlight under various experimental conditions. The structure of the dye is shown in Fig. 1.

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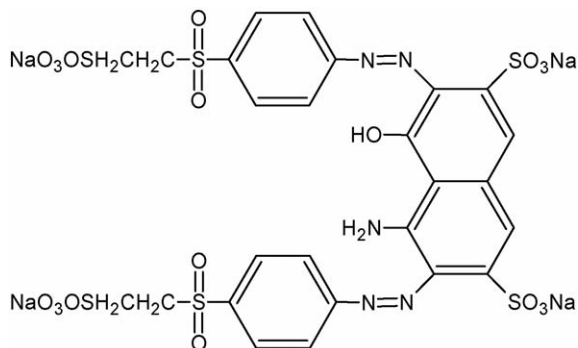


Fig. 1. Structure of Reactive Black 5.

2. Experimental

2.1. Material

The commercial azo dye RB 5 (C.I. No. 20505) obtained from Colour Chem, Pondicherry was used as such. A gift sample of TiO₂-P25 was obtained from Degussa (Germany). TiO₂-P25 is a mixture of anatase and rutile form (70:30) and synthesised specially for the photocatalytic degradation of xenobiotics. The commercially available photocatalysts ZnO (Merck), SnO₂, CdS, Fe₂O₃, ZnS (s.d. fine) and TiO₂ anatase (Aldrich) were used as received. TiO₂ anatase (Aldrich) had a medium particle size of approximately 1 μm with a specific surface area of 8.9 m²/g. The other chemicals such as NaOH, H₂SO₄ and H₂O₂ (30%, w/w) (Merck) were used as such. The double distilled water was used for the preparation of experimental solutions. The pH of the solutions was adjusted using H₂SO₄ or NaOH.

2.2. Irradiation experiments

All photocatalytic and photochemical experiments were carried out under similar conditions on sunny days between 11 a.m. to 2 p.m. in the months of May–June (2003). An open borosilicate glass tube of 50 ml capacity, 40 cm height and 20 mm diameter was used as the reaction vessel. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between dye and TiO₂. Irradiation was carried out in the open air and continuously aerated by a pump to provide oxygen and for the complete mixing of reaction solution. During the illumination time no volatility of the solvent was observed. For photochemical experiments a desired molar ratio of dye/H₂O₂ at pH 3 was prepared freshly before the experiment. In all cases, 50 ml of reaction mixture was irradiated. At specific time intervals, 1–2 ml of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the sample was suitably diluted and their absorbance at 310 nm was measured.

2.3. Solar light intensity measurements

Solar light intensity was measured for every 30 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set in the position of maxi-

imum intensity. The intensity of solar light was measured using LT Lutron L × 10/A Digital Lux meter and of 1000 × 100 lx. The intensity was nearly constant during the experiments. During May–June (2003) the intensity of sunlight was high.

UV spectral analysis was done using Hitachi U–2001 spectrophotometer. The pH of the solution was measured by using HANNA phev (model H 198107) digital pH meter.

3. Results and discussion

The time dependent UV–Vis spectrum of RB 5 (3.85×10^{-4} M) solution during photocatalytic degradation is shown in Fig. 2. The absorption peaks in UV and visible region decrease and finally disappear under reaction indicating the complete degradation of the dye.

3.1. Photodegradability

The results of photodegradation with and without TiO₂ are shown in Fig. 3. The dye is not degradable by direct photolysis and by TiO₂ in dark. The 9% decrease in dye concentration with TiO₂ in dark is due to the adsorption of dye; about 99% of dye

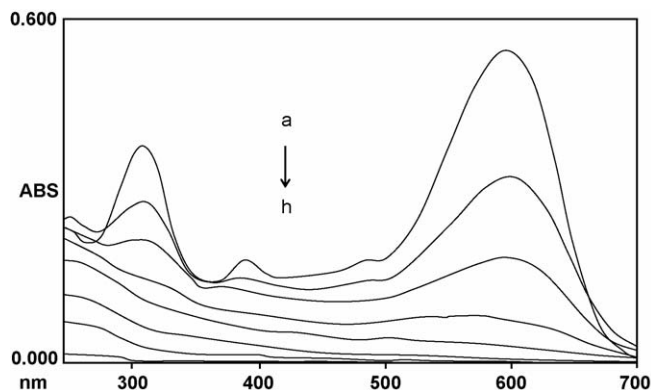


Fig. 2. Time dependent UV visible spectrum of RB 5. [RB 5] = 3.85×10^{-4} M, TiO₂-P25 = 2 g/dm³, pH 6.5 ± 0.1. (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min, (f) 150 min, (g) 180 min and (h) 210 min.

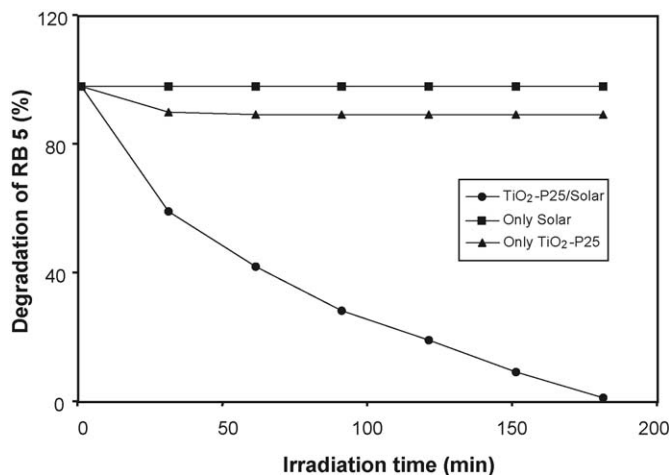


Fig. 3. Effect of solar light and TiO₂-P25 on photocatalytic degradation of RB 5. [RB 5] = 3.85×10^{-4} M, TiO₂-P25 = 2 g/dm³, pH 6.5 ± 0.1.

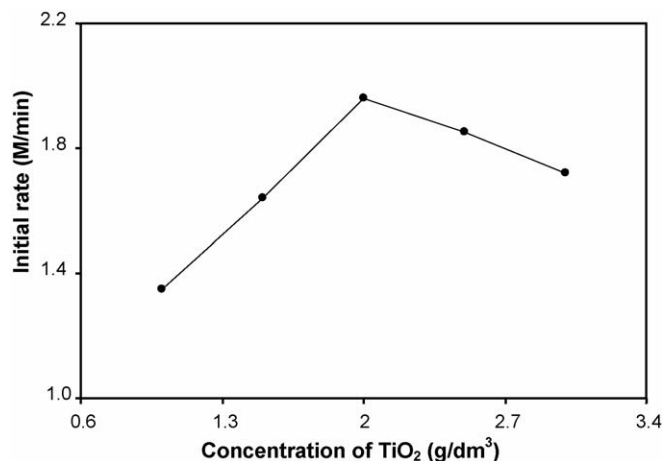


Fig. 4. Effect of TiO₂ catalyst weight on the initial rate of photocatalytic degradation of RB 5. [RB 5] = 3.85×10^{-4} M, pH 6.5 ± 0.1 .

is removed after 180 min of solar irradiation. This reveals that the dye can be degraded only in the presence of TiO₂ and solar light.

3.2. Effect of catalyst loading

The amount of catalyst is one of the main parameter for the degradation studies. The effect of catalyst weight (TiO₂-P25) on the initial rate of photodegradation of RB 5 is presented in Fig. 4. The degradation efficiency increases with increase in the catalyst weight up to 2 g/dm^3 . When the amount of catalyst exceeds 2 g/dm^3 , the degradation efficiency decreases. As the amount of catalyst increases, the number of available adsorption and catalytic sites on TiO₂ also increases. Hence the degradation efficiency increases. But at concentrations above 2 g/dm^3 of the catalyst, the decrease in degradation efficiency may be due to the enhancement of light reflectance by the catalyst. The light penetration decreases and subsequently the photoactivated volume of the catalyst shrinks [16,17]. The optimum concentration of the catalyst for efficient solar photomineralisation of RB 5 is found to be 2 g/dm^3 .

3.3. Effect of dye concentration

It is important both from the mechanistic and from the application point-of-view, to study the dependence to the photocatalytic reaction on the substrate concentration. The effect of initial dye concentration on the degradation was investigated from 0.77×10^{-4} to 6.93×10^{-4} mol/l. The results are given in Table 1. Increase in the dye concentration from 0.77×10^{-4} to 6.93×10^{-4} mol/l decreases the percentage removal of RB 5 from 98.74 to 20.37% in 60 min of irradiation time. When the dye concentration increases the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of TiO₂ [18,19]. The increase in dye concentration also decreases the path length of photon entering into the dye solution at high dye concentration. The dye molecule rather than the catalyst may absorb a significant amount of solar light and this may also reduce the catalytic efficiency.

Table 1

Effect of initial dye concentration on the photocatalytic degradation of RB 5

Concentration of dye (10^{-4} M)	Percentage removal of RB 5
0.77	98.74
2.31	70.19
3.85	57.64
5.39	36.59
6.93	20.37

Irradiation time: 60 min, TiO₂-P25 (2 g/dm^3), pH 6.5 ± 0.1 .

3.4. Effect of pH

The most important parameter that influences the photocatalytic degradation is the solution pH. The efficiency of the catalyst is affected by pH of the solution [20,21]. The effect of pH on the photocatalytic degradation of RB 5 as a function of time is given in Fig. 5. Increase of pH of the dye solution from 3 to 9 increases the decolourisation from 74.8 to 97.6% at the time of 150 min. The surface charge property of TiO₂-P25 changes with change in pH of the solution. The point of zero charge (PZC) for TiO₂-P25 is 6.8 [15]. When pH is lower than PZC, the TiO₂ surface is positively charged. In basic solution the surface is negatively charged.

Due to the low pK_a value of the sulphonic group, RB 5 was fully in the anionic form within the pH range studied. With increasing pH, the negative charges on TiO₂ are expected to repel the dye, and a decrease in the efficiency of photodegradation with increasing pH is expected. However, it was observed that the removal efficiency increased with an increase in pH. Similar results were reported earlier for the acid blue 40 dye degradation [22]. This effect may be attributed to more efficient generation of hydroxyl radicals by TiO₂ with an increasing concentration of hydroxide ion.

3.5. Effect of various photocatalyst

The efficiencies of the various photocatalysts such as TiO₂-P25, TiO₂ anatase, ZnO, ZnS, SnO₂, Fe₂O₃, CdS have been

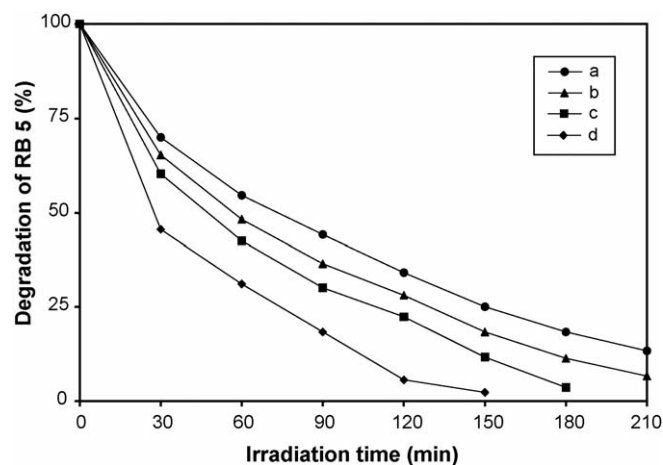


Fig. 5. Effect of pH on the photocatalytic degradation of RB 5. [RB 5] = 3.85×10^{-4} M, TiO₂-P25 = 2 g/dm^3 . (a) pH 3, (b) pH 5, (c) pH 7 and (d) pH 9.

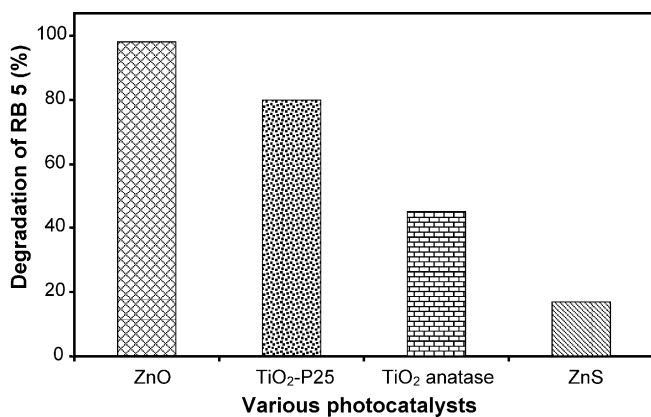


Fig. 6. Effect of various photocatalyst on the photocatalytic degradation of RB 5. [RB 5] = 3.85×10^{-4} M, catalyst dosage = 2 g/dm^3 , pH 6.5 ± 0.1 , irradiation time 120 min.

investigated. The results for 2 h irradiation with 2 g/dm^3 of the catalysts are shown in Fig. 6. SnO_2 , Fe_2O_3 , CdS have negligible activity on RB 5 degradation. The order of activities of other photocatalysts are $\text{ZnO} > \text{TiO}_2\text{-P25} > \text{TiO}_2 \text{ anatase} > \text{ZnS}$. ZnO is more efficient than $\text{TiO}_2\text{-P25}$ in solar photodegradation. According to Kormann et al. [23] the quantum yield of H_2O_2 production in illuminated aqueous suspension of ZnO was found to be one order of magnitude higher than the corresponding values of TiO_2 . It was also reported that ZnO absorbs a large fraction of solar spectrum than $\text{TiO}_2\text{-P25}$ [24]. But ZnO has the disadvantage of undergoing photocorrosion. Fe_2O_3 absorb sunlight more than ZnO or TiO_2 but it has less photocatalytic activity. This may be due to fast recombination of electron–hole pair. The physico-chemical parameters such as particle size and surface area of all the catalysts are reported in Table 2. $\text{TiO}_2\text{-P25}$ is more active than TiO_2 anatase. The high photoreactivity of the $\text{TiO}_2\text{-P25}$ is due to (i) slow recombination of electron–hole pair and (ii) large surface area. Another reason for the better efficiency of the Degussa P25 photocatalyst can be explained by the fact that Degussa P25 is a mixture of 30% rutile and 70% anatase. Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [25,26]. However, TiO_2 anatase (Aldrich, surface area = $8.9 \text{ m}^2/\text{g}$) has the surface area six times less than that of TiO_2 Degussa P25 (surface area = $55 \text{ m}^2/\text{g}$) and hence, its photocatalytic activity is less compared to Degussa P25 grade which is biologically and chemically inert.

Table 2
The physico-chemical parameters of various catalysts

Catalyst	Average particle size (μm)	Surface area (m^2/g)	Band gap energy (eV)
ZnO	4.80	5.05	3.17
$\text{TiO}_2\text{-P25}$	1.25	55.00	3.10
SnO_2	10.00	155.79	3.54
CdS	11.50	43.88	2.26
Fe_2O_3	10.30	33.72	2.20
TiO_2 anatase	1.00	8.9	3.10

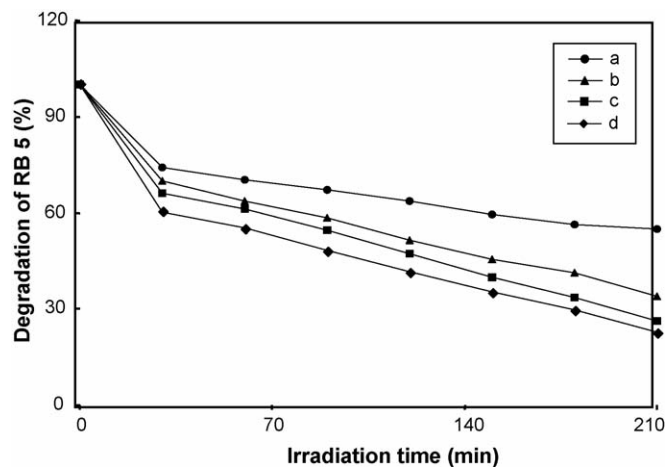
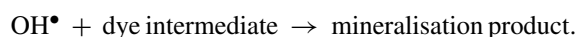
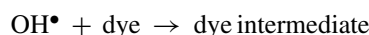
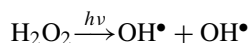


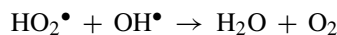
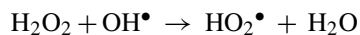
Fig. 7. Photochemical degradation of RB 5. [RB 5] = 3.85×10^{-4} M, pH 3.0 ± 0.1 . (a) 0.01 M H_2O_2 , (b) 0.025 M H_2O_2 , (c) 0.1 M H_2O_2 and (d) 0.05 M H_2O_2 .

3.6. Solar/ H_2O_2 process

The result of solar photolysis of RB 5 in the presence of H_2O_2 is shown in Fig. 7. The dye undergoes degradation by the addition of H_2O_2 . Increase in the addition of H_2O_2 from 0.01 to 0.05 M increases the removal rate from 40.5 to 61.2%. The increase in the dye degradation by the addition of H_2O_2 is due to the production of hydroxyl radical by photodissociation of H_2O_2 .



Further increase of H_2O_2 from 0.05 to 0.1 M, the removal efficiency decreases. This is due to hydroxyl radical scavenging effect of H_2O_2 [27].



3.7. Comparison of solar/ TiO_2 process with solar/ H_2O_2 process

The results of comparative study of photocatalytic and photochemical process are shown in Fig. 8. At the time of 90 min the removal efficiency is 70 and 57% for photocatalytic and photochemical process. The higher efficiency of photocatalytic process is due to the higher production of hydroxyl radicals. The Photolysis of H_2O_2 is caused only by UV light since H_2O_2 has absorption only up to 300 nm. But in this case we observed significant dye removal with solar/ H_2O_2 process. H_2O_2 in dark has no effect on the degradation. The observed degradation of dye by solar/ H_2O_2 process might have been caused by certain UV component of sunlight. Bleaching and photodegradation of some textile dyes by H_2O_2 with solar and UV radiation had

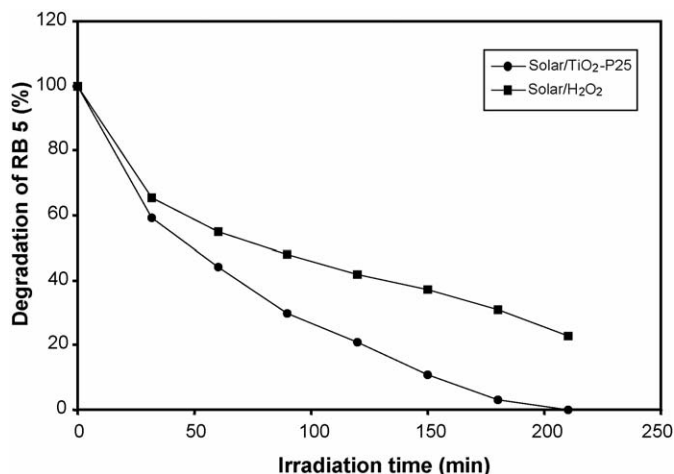


Fig. 8. Comparison of Solar/TiO₂-P25 (2 g/dm³) with Solar/H₂O₂ (0.05 M) process. Solar/TiO₂ process: [RB 5] = 3.85 × 10⁻⁴ M; TiO₂-P25 = 2 g/dm³, pH 6.5 ± 0.1. Solar/H₂O₂ process: [RB 5] = 3.85 × 10⁻⁴ M, H₂O₂ = [0.05 M], pH 3.0 ± 0.1.

been reported [28]. With TiO₂-P25 the solar energy is sufficient to activate the catalyst hence higher efficiency was observed. It is reported that the main oxidizing species involved in the photocatalytic oxidation by TiO₂ are hydroxyl radicals (OH•) and positive holes (h⁺). The superoxide ion radical O₂^{•-} seems to play a minor role in the oxidation process [29,30]. The oxidation by OH• is the main process at low substrate concentration whereas the oxidation by positive holes (h⁺) is considered as the main process at high substrate concentration [31].

4. Conclusions

This study reveals that RB 5 can be completely degraded by TiO₂-P25 Degussa sensitized photooxidation process using solar energy. The optimum concentration of the catalyst is 2 g/dm³. The main oxidising species involved in the photodegradation is hydroxyl radicals. The solar photochemical degradation using H₂O₂ is not as effective as solar photocatalytic degradation. The solar assisted photocatalysis with TiO₂-P25 can be used as a viable technique for the treatment of textile dye wastewater containing RB 5.

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