Solar/UV-induced photocatalytic degradation of three commercial textile dyes

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Abstract

The photocatalytic degradation of three commercial textile dyes with different structure has been investigated using TiO_2 (Degussa P25) photocatalyst in aqueous solution under solar irradiation. Experiments were conducted to optimise various parameters viz. amount of catalyst, concentration of dye, pH and solar light intensity. Degradation of all the dyes were examined by using chemical oxygen demand (COD) method. The degradation efficiency of the three dyes is as follows: Reactive Yellow 17 (RY17) > Reactive Red 2 (RR2) > Reactive Blue 4 (RB4), respectively. The experimental results indicate that TiO_2 (Degussa P25) is the best catalyst in comparison with other commercial photocatalysts such as, TiO_2 (Merck), ZnO, ZrO_2, WO_3 and CdS. Though the UV irradiation can efficiently degrade the dyes, naturally abundant solar irradiation is also very effective in the mineralisation of dyes. The comparison between thin-film coating and aqueous slurry method reveals that slurry method is more efficient than coating but the problems of leaching and the requirement of separation can be avoided by using coating technique. These observations indicate that all the three dyes could be degraded completely at different time intervals. Hence, it may be a viable technique for the safe disposal of textile wastewater into the water streams. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Textile dyes are an abundant source of coloured organic compounds that present an increasing environmental danger. During dye production and textile manufacturing processes

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a large quantity of wastewater containing dyestuffs with intensive colour and toxicity can be introduced into the aquatic systems. Due to the large degree of organics present in these molecules and stability of modern textile dyes, conventional biological treatment methods are ineffective for their decolourisation and degradation [1–10]. This led to the study of other effective methods. Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds using semiconductor photocatalysts under light irradiation [11–16].

Many catalysts like TiO_2 (Degussa P25), TiO_2 (Merck), ZnO, ZrO_2, WO_3, SrO_2, Fe_2O_3, CeO_2, CdS and ZnS have been attempted for the photocatalytic degradation of a wide variety of environmental contaminants. However, only a handful of studies have been attempted which compare the efficiency of different catalysts for a particular organic compound under identical experimental conditions. Serpone and Pelizzetti [17] have reported that TiO_2 and ZnO are the two most active catalysts in the degradation of pentachlorophenol under the identical experimental conditions. Hence, attempts have been made to study the activity of different photocatalysts such as TiO_2 (Degussa P25), TiO_2 (Merck), ZnO, WO_3, ZrO_2 and CdS in the photocatalytic degradation of three commercial textile dyes.

Since sunlight is abundantly available natural energy source, its energy can be conveniently exploited for the irradiation of semiconducting materials. UV irradiation is yet another high energy source for degradation of organics present in the effluents. In photocatalytic process, electron–hole recombination is a major problem to circumvent. In photocatalysis, UV irradiation source stands up among other sources to avoid this problem. So it was decided to study the influence of solar light and UV light independently on the photocatalytic degradation of dyes.

In recent years, vast majority of investigations in the area of photocatalytic degradation of pollutants have employed suspension of the semiconducting particles. However, from practical point of view it may not be possible to completely recover the photocatalysts used in the reactor. The use of catalyst as slurry, after photocatalytic degradation, has been a problem of leaching and separation of photocatalysts from the degraded reaction mixture. This needs either long time settlement or centrifugation. Hence, many researchers have decided to study the feasibility of coating the photocatalyst on inert surfaces like glass, polythene fibres and cement surface [18–21]. Fixation of the catalyst on a stationary support could circumvent the need to recover the catalyst from the reaction mixture without any leaching.

The purpose of this study was to investigate the degradation of the three dyes with photocatalytic system and the effects of different parameters such as catalyst loading, concentration of dye, pH, intensity of solar light, coating of catalyst with cement binder and the role of different commercial catalysts on the degradation efficiencies.

2. Experimental

2.1. Chemicals

The commercial samples of common textile dyes, Reactive Yellow 17 (RY17), Reactive Blue 4 (RB4) and Reactive Red 2 (RR2) obtained from Vanavil (India) Ltd., were used as such. The commercially available photocatalysts such as TiO_2 (Degussa P25 grade,

Germany), TiO_2, ZnO (Merck) and other photocatalysts such as ZrO_2, WO_3 and CdS (S-d Fine Chemicals) were used as received.

2.2. Chemical oxygen demand (COD)

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic content in a sample that is susceptible to oxidation by a strong oxidant. The dichromate reflux method is adapted to estimate COD [22].

2.3. Solar and UV light intensity measurements

The intensity of solar light was measured using Lux meter (Lutron Lx-101, Lux, Taiwan) at various time intervals of 2 h between 8 a.m. and 4 p.m. The intensity of six UV lamps (6×8 W low-pressure mercury vapour lamps) was measured using potassium ferrioxalate acti-nometry [23] and the intensity of incident light was found to be 1.514×10^{-9} Einstein/cm^2 s.

2.4. UV source photocatalytic reactor

The cylindrical photochemical reactor was made up of quartz having dimensions 30 cm × 3 cm (height × diameter) and provided with water circulation arrangement in order to maintain the temperature. The top portion of the reactor has ports for sampling, gas purger and gas outlet. The irradiation was carried out using 6×8 W low-pressure mercury arc lamp built into a lamp housing with polished anodised aluminium reflectors and placed 6.5 cm away from the reactor in order to prevent light radiation. The lamps emit predominantly UV radiation at a wavelength of 254 nm. During the photolysis experiments, the dye solution containing the appropriate quantity of the photocatalyst powder was magnetically stirred before and during illumination. After specific time intervals of irradiation, suitable aliquots of the sample were withdrawn and analysed after centrifugation.

2.5. Solar photocatalytic reactor

The cylindrical reactor of 200 ml capacity was made up of borosilicate glass having dimensions 8 cm × 4.5 cm (height × diameter) with ports at the top for sampling, gas purger and gas outlet. The experiments were performed at ambient temperature. Solar light was used as the energy source for catalyst excitation. The reactor assembly was placed on a magnetic stirring plate to further enhance the agitation, and at periodic intervals samples were drawn from the reactor and analysed after centrifugation for degradation.

2.6. Thin-film coated photocatalytic device

The photocatalyst powder was thoroughly mixed with Portland cement in the ratio 1:1 by grinding. The mixture was then transformed into a semisolid mass with suitable addition of distilled water. The semisolid mass was applied physically to the inner surface of the Petri dish as a thin coating. It was then allowed to set for 2 h. The dye solution was taken in the dish and exposed to direct sunlight. The Petri dish used in this study is 15.5 cm × 1.8 cm

(diameter $\times$ height). The progress of photocatalytic degradation of the dye was monitored by withdrawing definite quantity of aliquots at regular intervals and measuring the absorbance in the UV–VIS spectrophotometer for decolourisation and degradation using COD method.

3. Results and discussion

3.1. Batch studies

Experiments were performed with aqueous solution of dyes RY17, RR2 and RB4 in batch studies. Some of 100 ml of each dye solution of different concentration was taken in the batch reactor and maintained at the respective natural pH of the dye solution. The natural pH of RY17, RR2 and RB4 were 3.5, 4.65 and 4.20, respectively. The required amount of photocatalyst was added and the dye solutions were equilibrated for few minutes with continuous stirring using a magnetic stirrer. Additional experiments were conducted to verify that the observed reaction was indeed photocatalysis. The dye samples were first irradiated with solar/UV light without adding photocatalyst, and then it was slurred with photocatalyst in the absence of solar/UV light. After 8 h irradiation, direct photolysis contributed less than 3% degradation in solar irradiation, whereas 5% degradation was observed in the case of UV irradiation within 6 h for the optimised concentration of dyes. There was strong adsorption of dyes on TiO_2 (Degussa P25, the extent of adsorption at optimised concentrations approximately 10–15%). During the reaction, the adsorbed dyes were completely oxidised from the TiO_2 surface.

3.2. Effect of TiO_2 loading

The effect of TiO_2 loading on percentage degradation of the dyes has been examined by varying its amount from 100 to 600 mg/100 ml of the dye solution and the results are presented in Table 1. The percentage degradation increases rapidly with the increase in the

Table 1
Effect of TiO_2 loading[a,b]

| Amount of TiO_2 (mg/100 ml) | Name of the dye | | | | | |
| | RY17 | | RR2 | | RB4 | |
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
100	277	42	142	37	43	60
200	56	88	117	48	31	71
300	9	98	21	91	18	83
400	9	98	18	92	17	85
500	9	98	12	95	13	88
600	28	94	12	95	13	88

[a] Irradiation time: 8 h.
[b] Initial concentration: RY17, 1×10^{-3} M; RR2, 1.04×10^{-3} M; RB4, 4×10^{-4} M. Initial COD (mg/l): RY17, 476; RR2, 225, RB4, 108.

amount of TiO_2 from 100 to 300 mg/100 ml for all the three dyes. The minimum 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 utilised in the photocatalytic reaction [24]. Beyond 300mg of TiO_2, the percentage degradation increases only slightly in the case of RR2 and RB4 dyes up to 500 mg. But in the case of RY17, percentage degradation was found to be constant with increase of TiO_2 loading suggesting that upper level for catalyst effectiveness exists. Similar trends were reported previously in other photocatalytic reactions over TiO_2 catalyst [25,26]. Further increase in the amount of TiO_2 from 500 to 600 mg in RY17, the percentage degradation decreases [27]. This can be rationalised in terms of availability of active sites on TiO_2 surface and the light penetration of 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 solute concentration, when there are excess active sites, the balance between the opposing effect is evenly poised and change in suspension loading makes little difference on the percentage degradation. At high solute concentration availability of excess active sites outweighs the diminishing photoactivated volume and significantly greater percentage is achieved at increased TiO_2 loading [28].

Thus, the decreased percentage degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules. Shielding by TiO_2 may also take place (Eq. (1)).

$$TiO_2{}^* + TiO_2 \rightarrow TiO_2{}^\# + TiO_2 \tag{1}$$

where $TiO_2{}^*$ is the TiO_2 with active species adsorbed on its surface and $TiO_2{}^\#$ the deactivated form of TiO_2.

Hence, an optimum catalyst has to be added in order to avoid unnecessary excess catalyst and also to ensure total absorption of solar light photons [29] for efficient photomineralisation.

3.3. Effect of concentration of dye

The effect of initial concentration of dyes on the percentage degradation was studied by varying the initial concentration from 8×10^{-4} to 1.2×10^{-3} M in the case of RY17 dye, from 4.16×10^{-4} to 1.25×10^{-3} M in the case of RR2 dye and from 1×10^{-4} to 5×10^{-4} M in the case of RB4 dye with optimum catalyst loading. It can be seen in Table 2 that percentage degradation decreases with increasing initial concentration of the dye. The possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of 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 [25]. The same effect was observed by Matthews [30] during the photocatalytic degradation of methylene blue dye with TiO_2 catalyst.

This suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of TiO_2 is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst [31]. The major portion of degradation

Table 2
Effect of concentration of dyes on percentage degradation[a,b]

Name of the dye											
RY17				RR2				RB4			
Concentration of dye (M)	Initial COD (mg/l)	Final COD (mg/l)	Degradation (%)	Concentration of dye (M)	Initial COD (mg/l)	Final COD (mg/l)	Degradation (%)	Concentration of dye (M)	Initial COD (mg/l)	Final COD (mg/l)	Degradation (%)
8×10^{-4}	381	0	100	4.16×10^{-4}	90	0	100	1×10^{-4}	27	0	100
9×10^{-4}	428	26	94	6.24×10^{-4}	135	0	100	2×10^{-4}	54	0	100
1.0×10^{-3}	476	56	88	8.32×10^{-4}	180	7	96	3×10^{-4}	81	10	88
1.1×10^{-3}	524	178	66	1.04×10^{-3}	225	21	91	4×10^{-4}	108	20	82
1.2×10^{-3}	572	246	57	1.25×10^{-3}	270	120	56	5×10^{-4}	135	86	36

[a] Irradiation time: 8 h.
[b] Amount of TiO_2 (mg/100 ml): RY17, 200; RR2, 300; RB4, 250.

occurs in the region (termed as reaction zone) near to the irradiated side, since the irradiation intensity in this region is much higher than that at the other side [32]. Hence, at higher concentration, degradation decreases at sufficiently longer distances from the light source or reaction zone due to the retardation of penetration of light. Thus, the rate of degradation decreases with increase in concentration of dyes.

3.4. Effect of pH

The wastewater from textile industries usually have a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. Thus, pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dyes in the solar light irradiation. Photodegradation process was examined at pH values ranging from 3 to 13 for all the three dyes. In all the experiments pH was adjusted by adding appropriate amount of 0.02N H_2SO_4 or 0.02N NaOH solution. The effect of pH on the degradation is shown in Table 3.

At optimum concentration of dyes in both acidic and alkaline pH, it seems to decrease the percentage degradation of the dyes. The inhibitory effect seems to be more pronounced in the alkaline range (pH 11–13). At high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes [33,34]. 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 pH effects on the efficiency of the photodegradation process is a very difficult task, because three possible reaction mechanisms can contribute to 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 one

Table 3
Effect of pH on the degradation of dyes[a]

pH	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
3	56	88	21	91	20	80
4	56	88	21	91	20	82
5	56	88	6	97	16	85
6	12	98	6	97	16	85
7	9	99	6	97	16	85
8	5	95	6	97	16	85
9	24	95	6	97	16	85
10	24	95	6	97	16	85
11	38	92	19	92	20	82
12	60	87	19	92	24	78
13	60	87	19	92	30	72

[a] Initial concentration: RY17, 1×10^{-3} M; RR2, 1.04×10^{-3} M; RB4, 4×10^{-4} M. Initial COD (mg/l): RY17, 476; RR2, 225, RB4, 108. Amount of TiO_2 (mg/100 ml): RY17, 200; RR2, 300; RB4, 250.

Table 4
Effect of solar light intensity[a,b]

Solar light intensity ($\approx$lx $\pm$ 10)	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
83000	398	16	194	14	97	10
95000	380	20	186	17	92	15
112000	352	26	175	22	87	19
116000	332	30	164	27	83	23
120000	318	33	15	31	79	27

[a] Irradiation time: 2 h.
[b] Initial concentration: RY17, 1×10^{-3} M; RR2, 1.04×10^{-3} M; RB4, 4×10^{-4} M. Initial COD (mg/l): RY17, 476; RR2, 225; RB4, 108. Amount of TiO_2 (mg/100 ml): RY17, 200; RR2, 300; RB4, 250.

depends on the substrate nature and pH [35]. In the present case, it can be presumed that the main reaction is presented by the hydroxyl radical attack, which can be favoured by the high concentration of the hydroxyl radicals at around neutral pH. An additional explanation for the pH effects can be related with changes in the specification of the dye. That is, protonation or deprotonation of the dye can change its adsorption characteristics and redox activity.
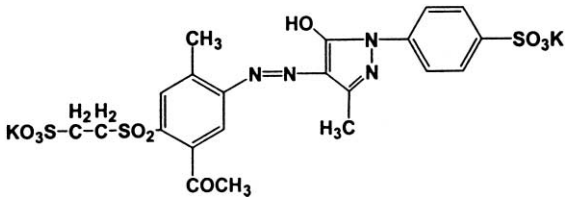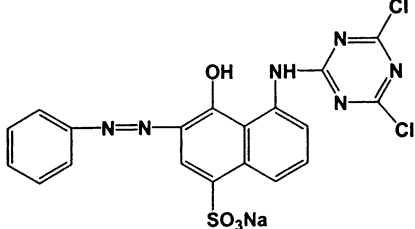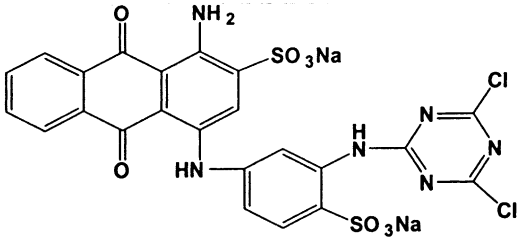
3.5. Effect of solar light intensity

The percentage degradation of all the three dyes increased with increasing solar light intensity (Table 4). Under the higher intensity of light irradiation, the enhancement was considerably higher because that the electron–hole formation is predominant and, hence, electron–hole recombination is negligible. However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the percentage degradation of the dyes [36].

3.6. Comparison of photocatalytic degradation of three dyes

The rate of COD removal efficiency of RR17 was found to be higher than the other two RR2 and RB4 dyes. (Table 2, see initial and final COD values of all three dyes). This possible explanation for this behaviour is as follows.

The three dyes have well-defined absorption in both UV as well as the visible region of the spectrum (Table 5). In that respect the dyes are similar. The important structural difference among the three molecules is that in case of RY17 and RR2 there is diazo group (N=N), which is not present in RB4. The diazo group N=N is susceptible to photodegradation [37]. That makes the first two dyes to degrade easily. Further –CH_2–OS_2– linkage in RY17 is also labile in the reaction environment [38]. In RB4, the presence of the anthraquinone structure and the absence of N=N makes it resistant to photodegradation. These basic structural differences explain the observed order of their degradation, i.e. RY17 > RR2 > RB4.

Table 5
Commercial dyes used for the experiment with their chemical structure and absorption maxima

Dyes (commercial name)	Chemical structure	λ_{max} (nm)
Reactive Yellow 17		426, 251
Reactive Red 2		512, 237
Reactive Blue 4		596, 253

3.7. Comparison of photocatalytic activity of commercial catalysts

From Table 6, it is clearly indicated that TiO_2 (Degussa P25) and ZnO are found to be the more active in the degradation of the three dyes using 8 h solar irradiation. Maximum 88% degradation in RY17 is observed with TiO_2 (Degussa P25) and 73% degradation over ZnO catalyst. TiO_2 (Merck) and CdS are less active compared to TiO_2 (Degussa P25) and ZnO, but ZrO_2 and WO_3 have not shown any significant photodegradation of these dyes. The same trend is observed even with UV irradiation (Table 7). The difference in the activity of catalysts is explained as follows. This is due to the fact that TiO_2 anatase and rutile form (70:30, anatase:rutile) appears to be the most photoactive catalyst. It is biologically and chemically inert. It is stable with respect to photocorrosion and chemical corrosion [39,40]. However, TiO_2 (Merck, surface area = $4.86\,m^2/g$) has the surface area 10 times less than that of TiO_2 Degussa P25 (surface area = $50.46\,m^2/g$) and, hence, its photocatalytic activity is less compared to Degussa P25 grade. ZnO is unstable with respect to incongruous dissolution [41] to yield $Zn(OH)_2$ on the ZnO particle surfaces and, thus, leading to catalyst inactivation. Moreover ZnO and CdS suffers from photocorrosion induced by self-oxidation. CdS (band gap = 2.3 eV) and ZnO (band gap = 3.2 eV) can

Table 6
Photocatalytic degradation of three dyes with solar light source[a,b]

Name of the catalyst	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
TiO_2 (Degussa P25)	56	88	18	92	15	82
ZnO	128	73	35	85	47	42
TiO_2 (Merck)	319	33	109	52	59	27
CdS	410	14	145	36	52	36
ZrO_2	438	8	210	7	72	11
WO_3	439	8	225	0	74	9

[a] Irradiation time: 8 h.
[b] Initial concentration: RY17, 1×10^{-3} M; RR2, 1.04×10^{-3} M; RB4, 3×10^{-4} M. Initial COD (mg/l): RY17, 476; RR2, 225, RB4, 81. Amount of catalyst (mg/100 ml): RY17, 200; RR2, 400; RB4, 200.

react with the photogenerated holes giving following reactions:

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \tfrac{1}{2}O_2 \tag{2}$$

$$CdS + 2h^+ \rightarrow Cd^{2+} + S \tag{3}$$

These competing reactions lead to decrease in photocatalytic activity. The occasional release of metal ions (Cd^{2+}) into the aqueous medium [42,43] may cause heavy metal pollution. In addition CdS is unsuitable as it readily undergoes photoanionic corrosion [12]. Thus, the use of CdS, though able to degrade organic contaminants in wastewater, it will lead to heavy metal pollution of water. The band gap in WO_3 (band gap = 2.76 eV) is less than TiO_2 and ZnO. Though ZrO_2 is stable and non-photocorrosive photocatalyst, its band gap is around 4 eV. Hence, it is less active compared to other photocatalysts. From the above

Table 7
Photocatalytic degradation of three dyes with UV light source[a,b]

Name of the catalyst	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
TiO_2 (Degussa P25)	25	90	4.6	90	6	85
ZnO	144	40	23	49	29	29
TiO_2 (Merck)	182	24	41	9	37	10
CdS	179	25	41	9	37	10
ZrO_2	210	12.5	42	7	39	5
WO_3	216	10	38	16	37	10

[a] Irradiation time (min): RY17, 300; RR2, 60, RB4, 180.
[b] Initial concentration: RY17, 5×10^{-4} M; RR2, 2.08×10^{-4} M; RB4, 1.5×10^{-4} M. Initial COD (mg/l): RY17, 240; RR2, 45, RB4, 41. Amount of catalyst (mg/100 ml): RY17, 100; RR2, 500; RB4, 50.

studies, it is concluded that TiO_2 (Degussa P25) is proved to be more a suitable bench mark catalyst for degradation of textile dyes.

3.8. Effect of solar/UV irradiation on the photocatalytic activity

The photocatalytic degradation of RY17 (5×10^{-4} M, 100 mg TiO_2/100 ml), RR2 (2.08×10^{-4} M, 100 mg TiO_2/100 ml) and RB4 (3×10^{-4} M, 100 mg TiO_2/100 ml) dyes using TiO_2 as photocatalyst and solar/UV irradiation as light source has been carried out and the results are presented in Figs. 1–3, respectively. From Fig. 1, it could be seen that complete degradation is achieved within 6 h UV irradiation whereas complete degradation requires more than 10 h in solar irradiation of RY17 dye. Similar observations are made in the case of RR2 and RB4 and the results are shown in Figs. 2 and 3. The difference in the rate of degradation is attributed to difference in the input energy. The energy of UV irradiation is large compared to band gap energy of the catalysts. Hence, the problem of electron–hole recombination is not fully but largely avoided with UV source.

But in sunlight only 5% of the total radiation possess the optimum energy [44] for the band gap excitation of electrons. Hence, the percentage degradation is found to be less in solar radiation of textile dyes. Although sunlight has only 5% of optimum energy for photocatalytic excitation and ultimately degradation of textile dyes, it could be safe and cost effective source. UV source is not only hazardous but also expensive because of large input of electric power to generate UV irradiation. In tropical countries intense sunlight is available throughout the years and, hence, it could be effectively used for photocatalytic degradation of pollutants in wastewater. In case of large surface demanding photocatalytic degradation,
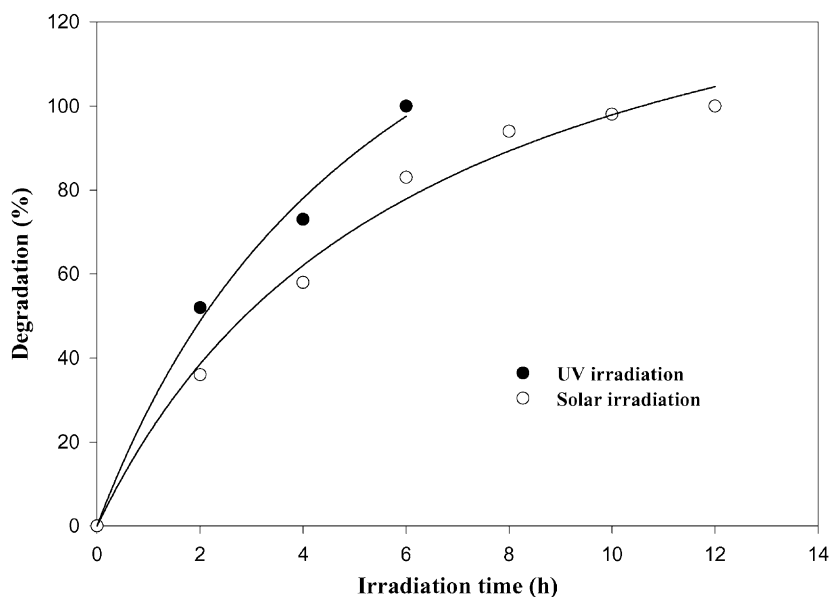

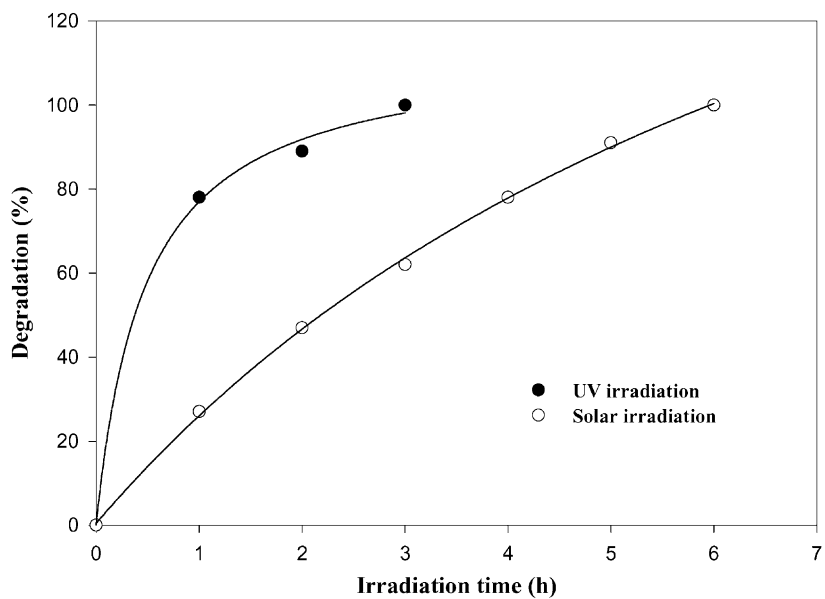Fig. 1. Effect of solar/UV light source on the degradation of RY17.

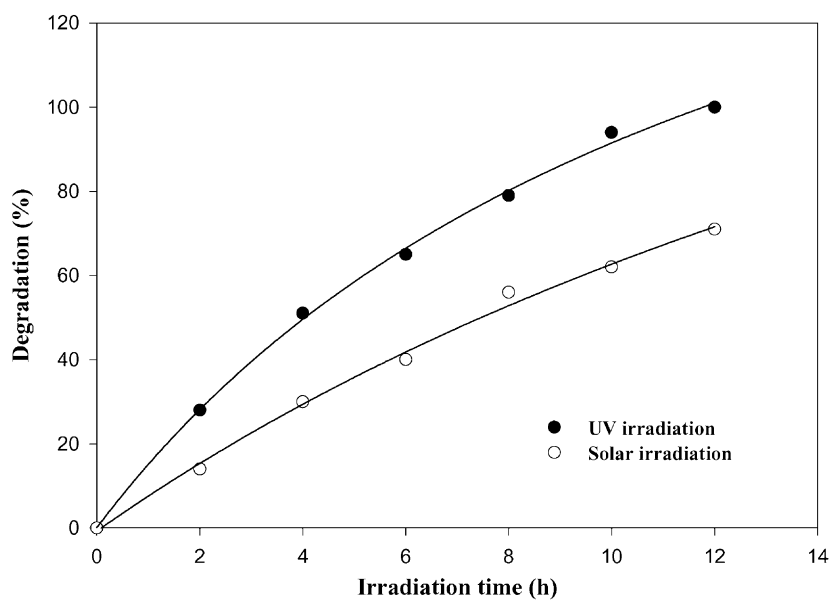Fig. 2. Effect of solar/UV light source on the degradation of RR2.

Fig. 3. Effect of solar/UV light source on the degradation of RB4.

Table 8
Photocatalytic degradation of dyes with TiO_2 as coating method[a]

Irradiation time (h)	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
1	40.0	31	38.0	16	76.0	6
2	29.0	50	32.0	29	72.0	11
4	22.0	62	21.0	53	60.0	26
6	16.6	71	18.0	60	53.0	35
8	9.5	84	15.6	65	48.0	41
10	4.0	93	12.0	73	40.0	51
12	0.0	100	7.5	83	32.4	60
14			2.6	94	24.0	70
18			0.0	100	14.0	83
20					3.0	96
24					0.0	100

[a] Initial concentration: RY17, 1.2×10^{-4} M; RR2, 2.08×10^{-4} M; RB4, 3×10^{-4} M. Initial COD (mg/l): RY17, 57.6; RR2, 45, RB4, 81. Ratio of TiO_2:cement (mg): RY17, 200; RR2, 200; RB4, 250.

sunlight would be the ultimate source. Moreover there is no material deterioration in case that sunlight is used as a radiation source. But UV light source may effect the catalyst decomposition [43].

3.9. Effect of coating method in the degradation of dyes

The experimental results are summarised in Table 8. It is clear that complete degradation of RY17 dye of concentration 1.2×10^{-4} M has been achieved in 12 h solar irradiation using TiO_2. RR2 and RB4 dyes (2.08×10^{-4} and 3×10^{-4} M) are also completely degraded in 18 and 24 h, respectively. Similarly, experiments were conducted with ZnO coated reactor and the results are presented in Table 9. Complete degradation of RY17 has occurred within 12 h (1.3×10^{-4} M) exposure in sunlight whereas RR2 and RB4 (3.12×10^{-4} and 3×10^{-4} M) have taken 14 and 18 h of exposure for complete degradation. The optimised concentration of dyes used (Tables 8 and 9) is less in comparison to slurry studies. The thin-film coating studies of TiO_2 and ZnO 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.

The reason for the use of low concentration of 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, TiO_2/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 minimised in this method. The photocatalyst

Table 9
Photocatalytic degradation of dyes with ZnO as coating method[a]

Irradiation time (h)	Name of the dye					
	RY17		RR2		RB4	
	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)	Final COD (mg/l)	Degradation (%)
1	43.0	32	52.8	22	74	9
2	40.0	37	43.1	37	68	16
4	30.0	53	33.0	52	56	31
6	18.0	72	20.4	70	48	41
8	5.8	91	10.0	85	39	52
10	3.2	95	5.4	92	32	61
12	0.0	100	3.2	95	25	69
14			0.0	100	20	75
18					0.0	100

[a] Initial concentration: RY17, 1.3×10^{-4} M; RR2, 3.12×10^{-4} M; RB4, 3×10^{-4} M. Initial COD (mg/l): RY17, 63; RR2, 68, RB4, 81. Ratio of ZnO:cement (mg): RY17, 250; RR2, 250; RB4, 350.

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.

4. Conclusions

Photocatalytic degradation of all the three textile dyes using TiO_2 (Degussa P25) photocatalyst depends on the amount of catalyst, concentration of dye, pH and solar light intensity. The degradation efficiency of the three dyes follows: RY17 > RR2 > RB4, respectively. Among the catalysts, TiO_2 (Degussa P25) is found to be an effective one because of its multiphase purity, large band gap and non-corrosive nature. Further the same catalyst can be used for a number of cycles which will reduce the cost of operation. Though the UV irradiation can bring better efficiency in the degradation of textile dyes, solar energy will emerge as an alternative cost effective light source because of its abundance and non-hazardous nature. Thin-film coating of photocatalyst may resolve the problems of leaching and separation. Hence, this technique may be a viable one for treatment of large volume of textile wastewater of low concentration.

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