Solar photocatalytic degradation of azo dye Reactive Black 5 in aqueous suspension of TiO_2

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ABSTRACT

Photocatalytic degradation of pollutants under solar light irradiation is an economically viable
process and a very promising clean wastewater treatment technology. The aim of this study is to
evaluate photocatalytic degradation of Reactive Black 5 (RB5) under natural sunlight irradiation with
TiO_2 as photocatalyst. The effects of initial concentration of RB5, dosage of TiO_2, with/without solar
irradiation, with/without air sparging and pH solution were examined. The decolorization rate
improved with a higher dosage of TiO_2, with sunlight irradiation and air sparging, and under acidic
solution. The photocatalytic process not only decolorized the RB5 but also mineralized the
intermediate products completely.

Key words | azo dye, photocatalytic degradation, Reactive Black 5, solar irradiation, TiO_2

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INTRODUCTION

The textile dyeing and finishing industry produces large
volumes of discharge effluent, and is considered as one of
the major industrial polluters (Correia *et al.* 1994). Among
the different dyes and pigments available, azo dyes consti-
tute over 50% of all textile dyes used in the industry
(Tang & An 1995). They pose serious environmental pro-
blems because of their colour, low biochemical oxygen
demand and high chemical oxygen demand. Various chemi-
cal and physical processes, such as chemical precipitation
and separation, electrocoagulation and elimination by
adsorption on activated carbon, etc., are currently used for
treating textile wastewater (Alinsafi *et al.* 2005; Daneshvar
et al. 2007a, b). These methods are ineffective since they
merely transfer dyes from water to solid; hence, further treat-
ment is necessary for the ultimate solution (Tanaka *et al.*
2000). Furthermore, dyes are mostly non-biodegradable
and resistant to destruction by conventional wastewater
treatments (Pagga & Brown 1986). Treatment of the spent
dye bath effluent is difficult and ineffective with biological
(activated sludge) processes (Peralta-Zamora *et al.* 1999;
Arslan *et al.* 2000) and results in approximately 15% of the

unfixed dyes being discharged into the environment
(Houas *et al.* 2001). This creates an aesthetic pollution pro-
blem and is a major perturbance to aquatic life. Thus,
conventional wastewater treatment facilities are unable to
meet effluent colour standards for discharge.

Recent studies indicated that toxic and refractory
organic compounds, including dyes in wastewater, can be
destroyed by the most advanced oxidation processes
(AOPs) (Tanaka *et al.* 2000; Gozmen *et al.* 2003; Kusvuran
et al. 2004). The photocatalytic degradation process (UV/
TiO_2) as one of the AOPs is receiving increasing attention
because of the low cost and relatively high chemical stability
of the catalyst and the possibility of using sunlight as the
source of irradiation. The process is initiated upon UV
irradiation of a semiconductor with the formation of high
energy electron/hole pairs by exciting an electron from the
valence band (VB) to the conduction band (CB) (Alinsafi
et al. 2005; Fujishima & Zhang 2006; Yates & Thompson
2006; Daneshvar *et al.* 2007b):

$$TiO_2 + hv \ (\lambda < 390 \, nm) \rightarrow e^-_{CB} + h^+_{VB}$$

The highly oxidative h^+_{VB} ($E^0 = +2.7$ V) may directly react with the surface sorbed organic molecules or indirectly oxidize the organic compounds via formation of $^\bullet$OH radicals (Silva & Faria 2003; Konstantinou & Albanis 2004). The purpose of this study was to investigate degradation of RB5 with a solar photocatalytic process and determine the effects of different parameters such as catalyst loading, concentration of dye, pH, with/without solar irradiation and with/without air sparging on the degradation efficiencies.

METHODS

Reactive Black 5 (RB5) with the molecular formula $C_{26}H_{21}N_5\ Na_4O_{19}S_6$ was supplied by Sigma Aldrich. The molecular structure is shown in Figure 1. Commercially available TiO_2 powders, which is known to possess very high photocatalytic activity, was selected for the study of mineralization of RB5. AEROXIDE TiO_2 P-25 from Evonik Industries was provided by Jebsen and Jessen. All chemicals were of analytical grade and used without further purification. Deionized water was used throughout this study.

Solar photocatalytic experiments were performed in a bench scale system consisting of a stirrer and a 500 mL beaker. The photocatalytic degradation of RB5 in aqueous solution was investigated under various conditions. Stock solution of synthetic wastewater was prepared by dissolving 1 g of RB5 with 1,000 mL deionized water using a 1 L volumetric flask. In each experiment an appropriate amount of RB5 from the stock solution was diluted to 300 mL with deionized water.
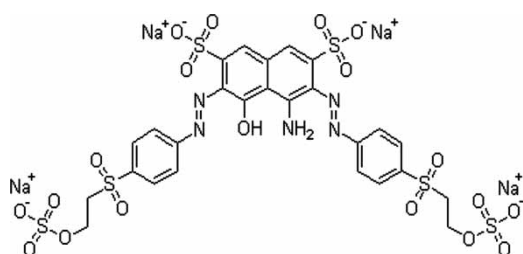

Figure 1 │ Molecular structure of Reactive Black 5.

Different concentrations of RB5, 20, 40 and 60 mg/L, were prepared and the solutions were placed on the stirrer, 0.2 g of TiO_2 was added into the RB5 solutions and the experiment was conducted under solar irradiation. During solar irradiation, the degradation experiment was maintained to ensure that the TiO_2 was in homogeneous suspension under magnetic stirring, to promote the adsorption on the surface of TiO_2 and sunlight absorption. Samples were collected at various time intervals and then filtered with a 0.45 μm membrane filter to remove the TiO_2 particles and the obtained filtrate was taken for RB5 concentration analysis using a UV–Vis spectrophotometer (Hitachi U-2800, Japan). The maximum absorbance wavelength (λ_{max}) of RB5 was found at 597 nm. The concentration of RB5 in the water sample can be determined by measuring the absorption intensity at λ_{max} 597 nm. The efficiency of decolorization was calculated as follows:

$$\text{Decolorization efficiency (\%)} = (1 - C_t/C_0) \times 100\%$$

where C_t is RB5 concentration at reaction time t (min) and C_0 is initial RB5 concentration.

Besides concentration, the effects of various parameters such as the amount of TiO_2, with and without aeration, pH, and with and without sunlight irradiation was evaluated on photocatalytic degradation of RB5 solution. When one of the effects of the parameter was evaluated on photocatalytic degradation of RB5, the others parameter would be made constant. In order to study the effect of solar irradiation on decolorization of RB5, two sets of experiments were run simultaneously, one set was exposed to sunlight and the other one was performed in the laboratory. In this study, the concentration of RB5 and the amount of TiO_2 used was 20 mg/L and 0.2 g, respectively. To evaluate the effect of air sparging on decolorization of RB5, air diffuser was used to supply aeration into 20 mg/L of RB5 solution with 0.2 g of TiO_2 as photocatalyst. The effect of pH on photocatalytic degradation of RB5 solution was also investigated in this study. The concentration of RB5 and amount of TiO_2 used was 20 mg/L and 0.2 g, respectively. An adjustment of pH from 3 to 11 in RB5 solution was conducted using H_2SO_4 and NaOH solutions.

RESULTS AND DISCUSSION

Effect of sunlight on photocatalytic degradation of RB5

The result for decolorization of RB5 under sunlight irradiation and using TiO_2 as photocatalyst is shown in Figure 2. Reactive Black 5 was decolorized after 90 min of irradiation by sunlight. Reactive Black 5 is actually stable to direct photolysis. The decolorization of RB5 was due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bond. In photocatalytic oxidation, TiO_2 has to be irradiated and excited in near-UV energy to induce change separation. The conduction band electrons (e^-) and valence band holes (h^+) are generated when aqueous TiO_2 suspension is irradiated with light energy greater than its band gap energy. The photogenerated electrons could reduce dye and cause decolorization of dye. The photogenerated holes can oxidize organic molecule to react with OH^- or H_2O oxidizing them into $^{\bullet}OH$ radicals (Konstantinou & Albanis 2004; Akpan & Hameed 2009). The resulting $^{\bullet}OH$ radical, being a very strong oxidizing agent, can oxidize RB5 resulting in decolorization and mineralization of the dye. Without sunlight, RB5 concentration slightly reduced. This was due to adsorption of RB5 onto the surface of TiO_2.

The time dependent UV–Vis spectrum of RB5 solution during photocatalytic degradation is shown in Figure 3. In this study, the concentration of RB5 solution and amount
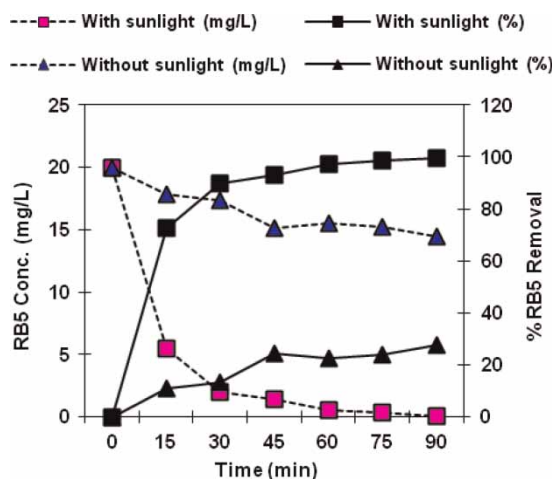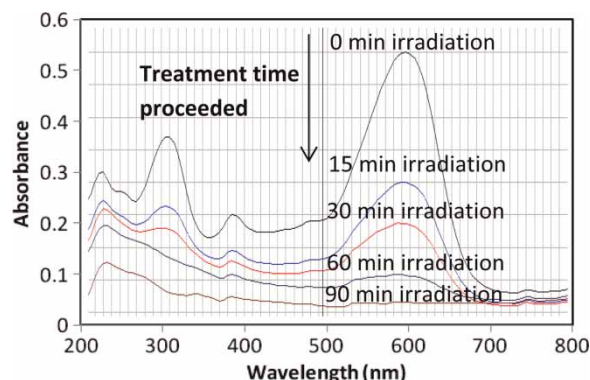
Figure 3 | Time dependent UV–Vis spectrum of RB5.

of TiO_2 used was 20 mg/L and 0.2 g, respectively. The water samples were collected at 0, 15, 30, 60 and 90 min for RB5 concentration determination. The UV–Vis spectrum of RB5 exhibits two main absorption peaks – one in the UV region (310 nm) and another in the visible region (597 nm). The UV peak is characteristic of two adjacent rings, whereas the visible peak is associated with a long conjugated system that is internally linked by two azo groups. As treatment time proceeded, the intensity of visible peak at 597 nm and UV peak at 310 nm declined rapidly. Absorption peaks in UV and visible region finally disappeared under photocatalytic reaction, indicating complete degradation of RB5. Initially, $^{\bullet}OH$ radicals attack the azo groups and open the –N=N– bonds, which are more easily destroyed than the aromatic structures. The higher decayed rate of visible peak was attributed to preferential hydroxylation of the azo-linkages during photocatalytic degradation process, which leads to rapid disappearance of chromophores in the dye structure (Muruganandham et al. 2006; Yu et al. 2010).

Effect of TiO_2 dosage on photocatalytic degradation of RB5

The amount of catalyst is one of the main factors that can strongly influence the dye degradation rate. The effect of TiO_2 on the initial rate of photocatalytic degradation of RB5 is presented in Figure 4. The concentration of RB5 decreased rapidly at 0.6 g catalyst loading. RB5 degradation was nearly complete at 45 min while at 0.2 g of TiO_2, decolorization of RB5 took approximately 60 min. The optical
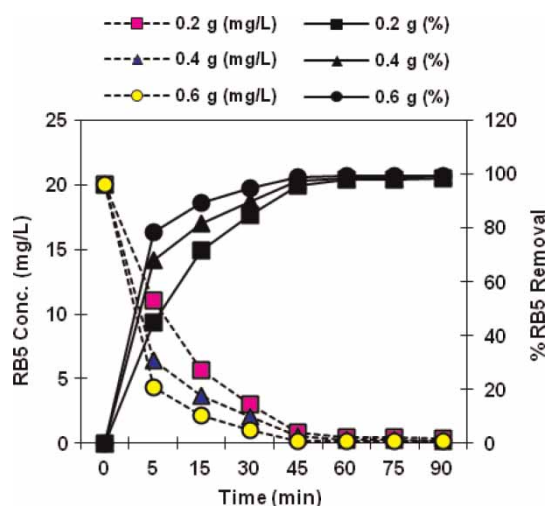
Figure 2 | Effect of sunlight on photocatalytic degradation of RB5.

Figure 4 │ Effect of TiO_2 dosage on photocatalytic degradation of RB5.

Figure 5 │ Effect of initial RB5 concentrations on photocatalytic degradation.

properties of photocatalyst were the main cause for the differences, indeed, the total active surface area increased with increasing catalyst dosage due to the penetration of UV light into the suspension, which in turn increases the number of $^{\bullet}OH$ radicals. As the amount of TiO_2 increases, the number of available adsorption and catalytic sites also increases (Muruganandham *et al.* 2006), hence the degradation efficiency of RB5 improved.

Effect of the initial RB5 concentration on photocatalytic degradation

The initial RB5 concentrations employed in this study were 20, 40 and 60 mg/L with 0.2 g of TiO_2 as catalyst. As shown in Figure 5, the degree of decolorization increased as the initial concentration of RB5 decreased. Nearly complete decolorization was observed within 45 min for 20 mg/L RB5 and approximately 75 min in the case of 40 mg/L RB5. The time required for complete decolorization of RB5 solutions increased with increasing initial RB5 concentration. The decrease of decolorization rate as the RB5 concentration increased was due to the generation of $^{\bullet}OH$ radicals on the TiO_2 surface reducing since the active sites were covered by RB5 through adsorption and its degradation products, aromatic amines, in concentrated solutions. At high dye concentration a significant amount of solar light may be absorbed by the dye molecules
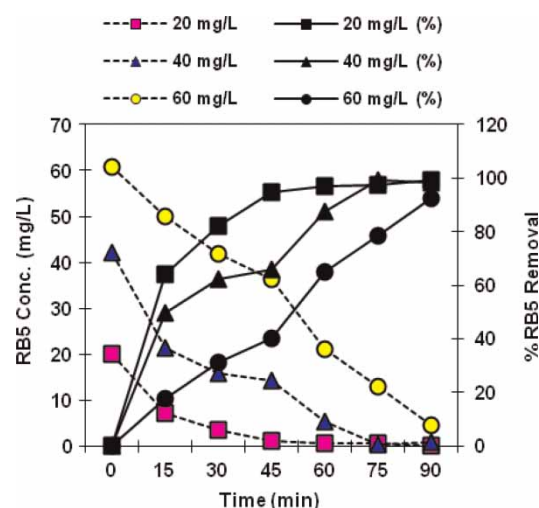
rather than the catalyst and this may also reduce the catalytic efficiency (Mills *et al.* 1993). As the concentration of RB5 in solution increased, the photons were intercepted before they could reach the TiO_2 surface, hence the absorption of photons by the catalyst decreased and resulted in slower production of $^{\bullet}OH$ radicals (Davis *et al.* 1994; Grzechulska & Morawski 2002; So *et al.* 2002; Rauf & Salman Ashraf 2009). Consequently the degradation of RB5 deteriorated.

Effect of air sparging on photocatalytic degradation of RB5

By air sparging, oxygen molecules are introduced into the photocatalytic system and the presence of excess oxygen molecules is expected to influence photocatalytic efficiency on the degradation of RB5. As shown in Figure 6, the photocatalytic system with air sparging enhanced the decolorization rate of RB5. In the heterogeneous photocatalytic system of UV/TiO_2, oxygen molecules act as an electron acceptor. Adding oxygen molecules increased the rate of decolorization by various means, such as prevention of electron–hole recombination via capturing conduction band electrons, increased formation of $^{\bullet}OH$ radicals and production of other species that oxidize intermediate compounds (Yu *et al.* 2010).
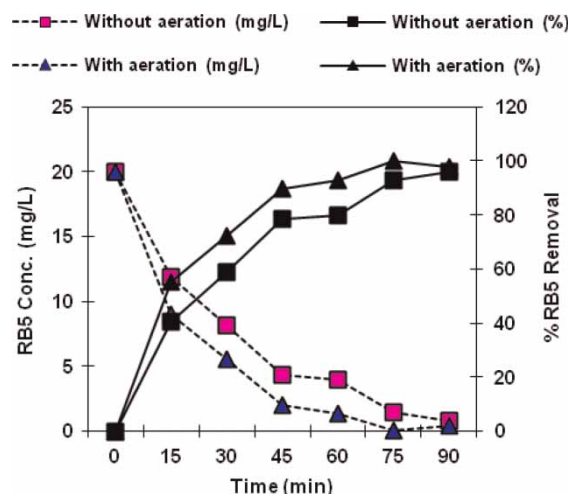
Figure 6 | Effect of air sparging on photocatalytic degradation of RB5.

Effect of pH on photocatalytic degradation of RB5

The efficiency of photocatalytic processes strongly depends upon pH solution. All photocatalytic experiments described so far were performed at ambient pH 9.8 due to the addition of NaOH during the dyeing process. In this study, additional photocatalytic experiments were conducted at pH values of 3, 7 and 11 at a TiO_2 concentration of 0.67 g/L and the results are shown in Figure 7.

In the presence of sunlight, TiO_2 absorbs UV light and generates $^\bullet OH$ radicals. The $^\bullet OH$ radicals formed on the illuminated TiO_2 surface attack the adsorbed azo dye RB5 or
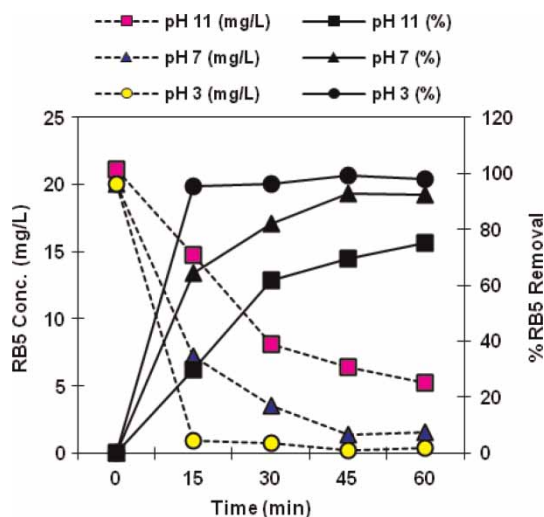
those close to the catalyst surface, thus resulting in their mineralization. Thus, the adsorption of RB5 onto TiO_2 surface is a factor for photocatalytic degradation of RB5. The point of zero charge (P_{zc}) of P-25 TiO_2 is known to occur at pH ≈ 6.8, at which the surface of the particles is electrically neutral (Zhao *et al.* 1993). Below the P_{zc}, the surface of TiO_2 is positively charged and above the P_{zc} it is negatively charged. The change of TiO_2 surface potential may occur by changes in pH solution. At pH 3 the TiO_2 surface becomes positively charged since the P_{zc} for TiO_2 is 6.8. Reactive Black 5 is an acid dye and can be represented as $Dye^- Na^+$. Therefore, the amount of RB5 adsorbed on the TiO_2 surface increased as the pH reduced to 3, which in turn enhanced the photocatalytic degradation process. When the pH of the solution is changed from 3 to 11, the positive charge formation on TiO_2 surface was decreased. Hence, adsorption of RB5 onto the TiO_2 surface was decreased and consequently reduced the photodegradation rate (Kusvuran *et al.* 2005).

CONCLUSIONS

The photocatalytic degradation of RB5 in aqueous suspension of TiO_2 was carried out under sunlight irradiation and various conditions. The initial RB5 concentrations, dosage of TiO_2, indoor/outdoor, pH solution and with/without air sparging have strong influences on the degradation of RB5 by photocatalytic processes. Decolorization rate increased significantly in the presence of sunlight, with air sparging, higher dosage of TiO_2 and in acidic solution. UV–Vis spectrum analysis shows the photocatalytic process not only caused the decolorization of RB5, but the intermediate products generated also mineralized completely.

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Figure 7 | Effect of pH on photocatalytic degradation of RB5.

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