

TiO₂ mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation

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Abstract

Photocatalytic degradation of an aqueous solution of azo dye (Reactive Red 198) used in textile industries by UV irradiation was investigated. The effect of initial dye concentration, TiO₂ loading, pH and H₂O₂ on degradation rate was ascertained and optimized conditions for maximum degradation were determined. The kinetics of photocatalytic degradation was found to follow a pseudo-first order according to Langmuir–Hinshelwood model. The degradation experiment under optimized reaction conditions was investigated under sunlight.
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1. Introduction

Considerable amount of water is used for dyeing and finishing of fabrics in the textile industries. Wastewaters generated from the textile industry contain large amount of azo dyes which owing to their non-biodegradability, toxicity and carcinogenic nature constitute a major threat to the ecosystem [1]. The reactive dyes are commercially available important class of textile dyes for which losses through processing operations are significant and the treatment is problematic. During the washing process reactive dyes exhausted are about 50% in their hydrolysed and unfixed form [2,3].

Several physical, chemical and biological methods are presently available for the treatment of textile wastewater. Biological treatment is cost-effective but it has been reported that most of the reactive dyes are non-biodegradable owing to their carcinogenic nature. Physical methods such as adsorption, coagulation, ion-exchange, etc. have limited applicability because of their high operational costs. Moreover, these methods do not result in dye degradation but merely transfer the dye material from one phase to another. Chlorination

and ozonation also lead to degradation by chemical reaction. However, discharging chlorinated organic compounds into the environment causes serious problems. Ozonation is a much cleaner process but due to its instability, its on-site preparation is required which involves significant capital costs.

Several studies on photoassisted catalytic degradation of various photostable dyes have been reported in literature [4–6]. The photocatalysed degradation of various organic systems employing irradiation in presence of TiO₂ can result in complete oxidation to carbon dioxide, water or mineral acids [7]. The initial step in the advanced oxidation processes generates powerful oxidizing agent, hydroxyl radicals which completely destroy the pollutants in wastewater. Heterogeneous photocatalysis through illumination of UV light on a semiconductor surface is an attractive advanced oxidation process. The semiconductor TiO₂ has a wide band gap of 3.2 eV and can be successfully used as a photocatalyst for the treatment of dye pollutants [8–10]. An attempt has been made to study the photocatalytic degradation of textile dye, Reactive Red 198 using TiO₂ in the form of slurries employing UV irradiation. Further degradation of the dye under sunlight in a shallow pond slurry reactor and recyclisation of catalyst has been studied. The results of the photocatalytic degradation of Reactive Red 198 have been presented here.

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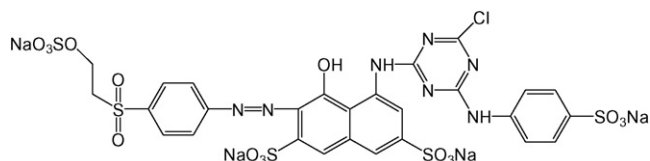


Fig. 1. Structure of Reactive Red 198.

2. Experimental procedure

2.1. Materials and equipments

Commercially available Reactive Red dye 198 (RR dye 198) was obtained from Nahar Fabrics, Derabassi, India and was used as such without any purification and its structure is given in Fig. 1. The photocatalyst used in all the experiments was anatase form of titanium dioxide powder (Degussa P25 TiO₂, procured from Degussa Company, Germany having a BET surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ with average particle size of 30 nm). Stock solutions of the dye containing the desired concentration were prepared in double distilled water. NaOH, HCl, H₂O₂ (30% (v/v) solution) were obtained from S.D. Fine Chemicals Limited, India. Samples after photocatalytic treatment were filtered through Millipore filter (0.45 μm) membrane. The pH of the solution was measured using ELICO, India LI 120 pH meter and concentration of Reactive Red 198 was determined by Hitachi U-2001 UV–vis spectrophotometer. Semi-automatic autoclave (EQUITRON, India) was used for the digestion of samples in COD determination. UV intensity of sunlight was measured by Eppley radiometer (model no. 33013).

2.2. Photoreactor

An immersion well photochemical reactor of 0.8 L capacity made of Pyrex glass equipped with a water-circulating jacket maintaining a temperature of 25 °C and opening for supply of oxygen as shown in Fig. 2 was used. A 125 W medium pressure mercury lamp was placed in the centre of the photocatalytic reactor as the UV light source. The slurry composed of dye solution and catalyst placed in the reactor was placed on a magnetic stirrer and stirred magnetically. The samples were withdrawn from the reactor vessel periodically for the analysis of decolourisation and degradation.

3. Method

3.1. Adsorption experiments

The adsorption tests were performed using 200 mL aqueous solution of dye in a 0.8 L reactor at different initial concentrations and pH of the solution put in contact with 0.3 g L^{-1} of TiO₂ for 2 h and kept in dark at 25 °C. The solution was filtered through 0.45 μm filter and concentration of the unabsorbed dye was measured to find the extent of adsorption as a function of initial concentration at different pH.

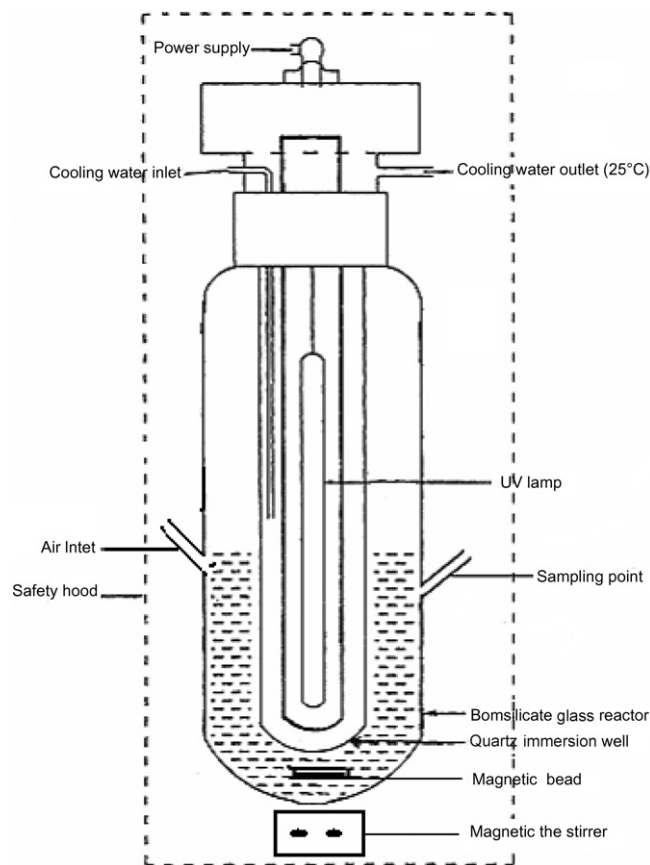


Fig. 2. The schematic representation of the immersion well type photoreactor employed.

3.2. Irradiation experiments

Stock solutions of dye of different concentrations were prepared in double distilled water with a natural pH of 4.6. 200 mL suspension of dye solution and TiO₂ were stirred in the photoreactor in dark and bubbled with molecular oxygen for 30 min till equilibrium was attained so that the loss of compound due to adsorption can be taken into account. All experiments were carried out at a constant temperature of 25 °C. The suspension was subsequently subjected to UV irradiation for the degradation of dye in solution. 5 mL aliquots of dye suspension were withdrawn over regular intervals of time, filtered and the filtrate was analyzed for determining the concentration of dye at $\lambda_{\text{max}} = 515 \text{ nm}$ using Hitachi U-2001 UV–vis spectrophotometer. The filter was washed every time to ensure that no residual dye remained on the microfilter.

The reaction kinetics was studied by varying different parameters like initial concentration of dye, catalyst loading, initial pH of the solution and amount of H₂O₂. Irradiation experiments under sunlight were done using shallow pond reactor [11]. All experiments were carried out in triplicate for reproducibility of the results. The photocatalytic experiment was repeated four times with the recovered TiO₂ to check the recyclability of the catalyst. The catalyst recovered through filtration was activated at 100 °C before using.

4. Kinetic studies

4.1. Kinetics of adsorption

The equilibrium constants for adsorption were determined by fitting the experimental data to the Langmuir Eq. (1) to describe the adsorption of the dye on the homogenous surface of TiO₂:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

where q_m is the maximum amount of dye adsorbed forming a complete monolayer, b the equilibrium parameter, C_e the concentration of dye in aqueous solution, and q_e is the concentration of dye on the solid.

4.2. Kinetics of irradiation experiments

The photocatalytic decolourisation and degradation of RR dye 198 containing TiO₂ obeys pseudo-first-order kinetics. At low initial dye concentration the rate expression is given by

$$\frac{-d[C]}{dt} = k'[C] \quad (2)$$

where k' is the pseudo-first-order rate constant. The dye is adsorbed onto the TiO₂ surface and the adsorption–desorption equilibrium is reached in 30 min. After adsorption the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (2) (with the limit of $C = C_0$ at $t = 0$ with C_0 being the equilibrium concentration of the bulk solution):

$$\ln \left[\frac{C_0}{C} \right] = kt \quad (3)$$

where C_0 is the equilibrium concentration of dye and C is the concentration at time ' t '.

The influence of initial concentration of the solute on the degradation rate of RR dye 198 can be described by a pseudo-first-order kinetics, which is given in terms of the Langmuir–Hinshelwood model Eq. (4), modified for heterogeneous catalytic reactions:

$$r_0 = -\frac{dC}{dt} = \frac{k_v K_e C_0}{1 + K_e C_0} \quad (4)$$

where k_v reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions. K_e represents the equilibrium constant for adsorption of dye on to illuminated TiO₂. In Eq. (4) k_v represents the apparent rate constant because it is also dependent on the source of visible light and the radiation field inside a photocatalytic reactor.

The kinetics of photodegradation as a function of pH are also described using Langmuir–Hinshelwood model Eq. (4).

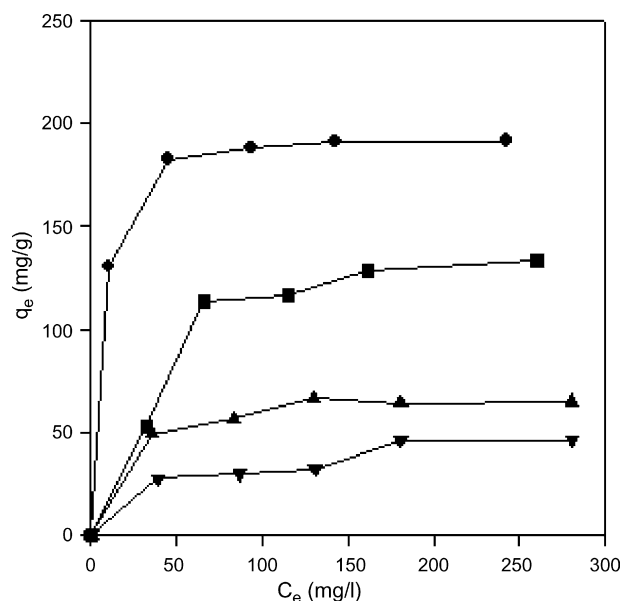


Fig. 3. Adsorption isotherms of RR dye on TiO₂ surface at different initial pH: (♦) pH 3.5, (■) pH 4.6, (▲) pH 7, and (▼) pH 9.

5. Results and discussion

5.1. Adsorption of RR dye 198 on TiO₂ in dark

A significant amount of RR dye 198 is adsorbed on the TiO₂ surface, as evidenced by the difference in the UV/vis spectra obtained before and after addition of TiO₂ in the solution and is shown in Fig. 3. This can be explained, since at the normal pH (pH 4.6), the photocatalyst surface is positively charged (the zero point of charge of TiO₂ suspensions is pH_{zpc} 6.25) and attractive forces between the Ti-(OH₂)⁺ surface groups and the dye molecules are operable [12,13]. However, in the basic medium the surface of TiO₂ acquires negative charge therefore repelling the anionic RR dye 198 and hence decreasing the amount of adsorption.

Langmuir equilibrium constants ($K_a = q_m b$) are shown in Table 1. The L-shaped isotherms were obtained in all the cases which mean that there is no strong competition between the solvent and the adsorbate for the adsorbent sites. The results are in accordance with those reported in literature [11].

5.2. Photodegradation of Reactive Red dye 198

As the photocatalytic mechanism suggests, both TiO₂ and a light source are necessary for the photooxidation reaction to

Table 1
Langmuir equilibrium constants for the adsorption of RR dye 198 on TiO₂ in dark

pH	K_a (g L ⁻¹)
3.5	10.55
4.6	1.51
7.0	1.00
9.0	0.50

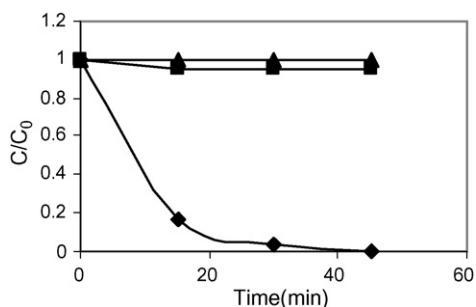


Fig. 4. Photocatalytic degradation of RR dye 198. (▲) only UV, (■) only TiO₂ (0.3 g L⁻¹), (◆) with TiO₂ (0.3 g L⁻¹), and UV light.

occur. A control experiment was conducted on the irradiation of RR dye 198 (100 mg L⁻¹) under only UV light, in the presence of TiO₂ (0.3 g L⁻¹) with and without UV irradiation over a period of 45 min. No degradation was observed in the presence of UV light only. In the presence of TiO₂, but without irradiation, slight loss was observed due to the adsorption of the dye on to the surface of TiO₂. However, on irradiating the dye with TiO₂ in aqueous dispersion about 99% of the dye was degraded within 45 min of irradiation as shown in Fig. 4.

The degradation, as exemplified by the RR dye 198 photodegradation data, can be approximated as first-order kinetics. Fig. 5 shows the linear fit between the ln(C₀/C) and irradiation time that supports this conclusion.

5.3. Effect of catalyst loading

The effect of photocatalyst concentration on the degradation rate of RR dye 198 has been investigated by employing different concentrations of TiO₂ with UV light varying from 0.05 to 0.5 g L⁻¹. It is observed that the initial rate increases with the increase in catalyst concentration, becomes maximum and remains almost constant thereafter as shown in Table 2. The optimum catalyst concentration for the degradation of RR dye 198 is 0.3 g L⁻¹. The number of photons absorbed and the number of dye molecules adsorbed are increased with the increase in catalyst concentration thereby enhancing the rate of degradation. Above a certain level the number of substrate molecules are not sufficient to fill the surface active sites of TiO₂. Hence further addition of catalyst does not lead to the enhancement of the degradation rate. The degradation rate also decreases due to the aggregation of TiO₂ particles at higher concentrations caus-

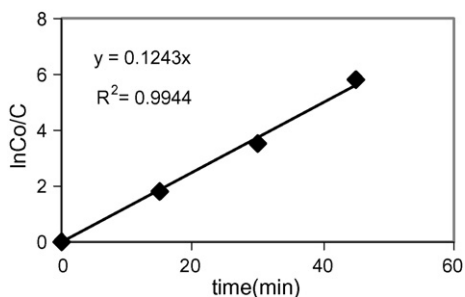


Fig. 5. Kinetics of photodegradation of RR 198: C₀ = 100 mg L⁻¹, pH 4.6, [TiO₂] = 0.3 g L⁻¹.

Table 2

Effect of TiO₂ loading on the degradation rate during the photocatalytic oxidation (C₀ = 100 g L⁻¹, pH 4.6)

[TiO ₂] (g L ⁻¹)	r ₀ (mg L ⁻¹ min ⁻¹)
0.05	2.4013
0.10	3.5034
0.15	4.3794
0.20	4.6534
0.25	4.8958
0.30	5.4026
0.35	5.3710
0.40	5.3329
0.50	5.2498

ing decrease in the number of surface active sites and also due to the increase in opacity and light scattering of TiO₂ particles at high concentration through the sample. Our results are in good agreement with those reported in literatures [11,14,15].

Galindo et al. [16] reported an empirical relationship between the initial decolourisation rate and TiO₂ concentration, r_{0α}[TiO₂]ⁿ[dye], where n is an exponent less than 1 for the dye studied [17]. In the present work, the dependence of TiO₂ concentration on the initial decolourisation rate follows a similar relationship (r_{0α}[TiO₂]^{0.45}), when catalyst concentration is less than 0.3 g L⁻¹ as calculated from Fig. 6.

5.4. Effect of initial substrate concentration

The effect of initial concentration of dye solution on the degradation rate of RR dye 198 has been investigated by varying the dye concentrations from 50 to 200 mg L⁻¹ in the presence of 0.3 g L⁻¹ TiO₂ under UV light as shown in Fig. 7. The photodegradation rate is observed to decrease with increasing initial concentration and our results are in accordance with those reported in the literatures [11,14,18]. As the concentration increases, the concentration of unadsorbed dye in the solution increases leading to lesser penetration of light through the solution on to the surface of TiO₂ thereby decreasing the concentration of OH radical which is the most reactive species formed on the surface and hence decreasing the rate of degradation.

The influence of the initial concentration of the solute on the degradation rate of most of the organic compounds can be described by a pseudo-first-order kinetics in terms of Langmuir–Hinshelwood equation (Eq. (4)) modified to accom-

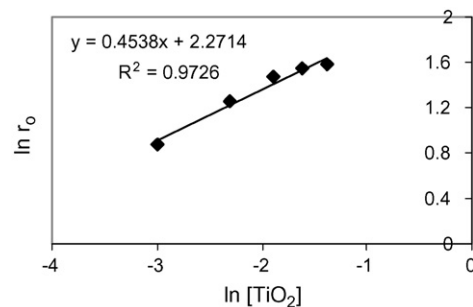


Fig. 6. Relationship between ln r₀ and the amount of TiO₂: pH 4.6, C₀ = 100 mg L⁻¹.

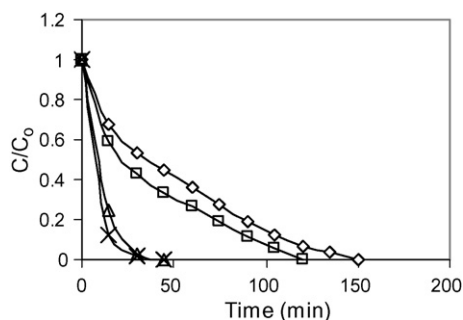


Fig. 7. Kinetics of photodegradation of RR dye 198 at different initial concentrations: $x=50$ ppm, (Δ) 100 ppm, (\square) 150 ppm, (\diamond) 200 ppm, pH 4.6, $[\text{TiO}_2]=0.3 \text{ g L}^{-1}$.

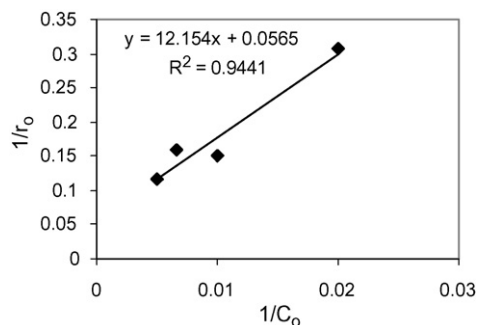


Fig. 8. Representation of Langmuir–Hinshelwood equation: pH 3.5, $[\text{TiO}_2]=0.3 \text{ g L}^{-1}$.

moderate reactions occurring at a solid–liquid interface. A linear expression can be obtained by plotting the reciprocal initial rate against the reciprocal initial concentration as shown in Fig. 8.

5.5. Effect of initial pH of the solution

Employing Degussa P25 as photocatalyst the degradation of RR dye 198 in the aqueous suspensions of 0.3 g L^{-1} TiO_2 was studied in the pH range between 3 and 11 as shown in Fig. 9. The pH of the solution plays an important role in the generation of OH radical which helps in the degradation process and thus is one of the important parameters to be studied.

The degradation rate is higher in acidic media and decreases with the increase in pH. In case of Degussa P25, the zero point charge of TiO_2 is at pH 6.25. Therefore, in acidic pH, the surface

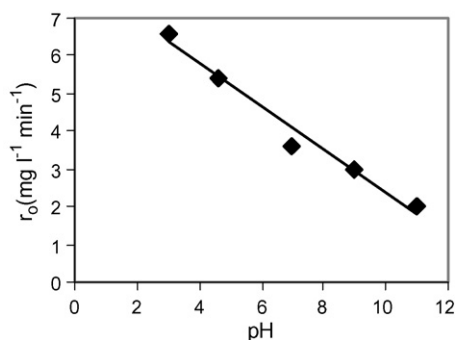


Fig. 9. Effect of pH on initial rate of degradation of RR dye: $[\text{TiO}_2]=0.3 \text{ g L}^{-1}$, $C_0=100 \text{ mg L}^{-1}$.

Table 3

Langmuir–Hinshelwood constants for the photodegradation of RR dye 198 at different pH values

pH	K_e (L mg^{-1})	k_v (min^{-1})
3.5	0.004649	17.69912
4.6	0.007372	11.16071
7.0	0.007110	6.747638
9.0	0.011186	3.402518

of TiO_2 acquires a positive charge thereby attracting the anionic RR dye 198, leading to greater adsorption and hence increasing the degradation rate in the acidic media. However, the reverse effect is observed in the basic medium where the TiO_2 surface is negatively charged which repels the dye thereby decreasing the degradation rate.

These results are seen by the k_v and K_e values of the Langmuir–Hinshelwood Eq. (4) and are given in Table 3.

5.6. Effect of H_2O_2

Fig. 10 shows the change in degradation rate by varying the amount of H_2O_2 concentration at pH 4.6 and optimum catalyst loading of 0.3 g L^{-1} . The role of added H_2O_2 is different depending on its concentration [19]. At a low concentration of H_2O_2 , it increases the formation rate of hydroxyl radical by acting as an electron donor, by reduction of H_2O_2 at the conduction band and via self decomposition by illumination. However, at a high concentration, H_2O_2 adsorbed on the TiO_2 particle surface could effectively scavenge not only the TiO_2 surface-formed hydroxyl radicals but also the photogenerated hole, which can inhibit the major pathway for generation of hydroxyl radicals [20]. The optimum H_2O_2 concentration for the degradation of RR 198 was found to be 5 mL L^{-1} of the dye solution.

5.7. Photodegradation by solar irradiation

After determining the optimum conditions for the degradation of dye under artificial UV light in the lab under laboratory conditions, the degradation of this dye was also studied under sunlight in a shallow pond slurry reactor. Previously we have demonstrated the efficient degradation of 3,4-dichlorophenol in a low cost non-concentration shallow pond reactor [11]. The dye solution was kept under sunlight and its decolourisation

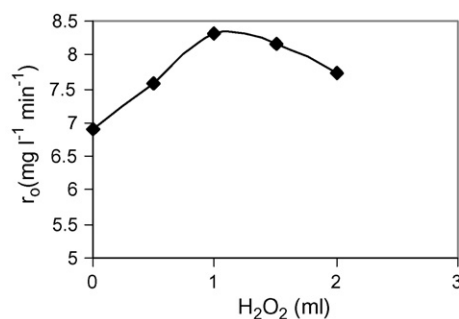


Fig. 10. Effect of H_2O_2 concentration on the initial rate at: $C_0=100 \text{ mg L}^{-1}$, pH 4.6, $[\text{TiO}_2]=0.3 \text{ g L}^{-1}$.

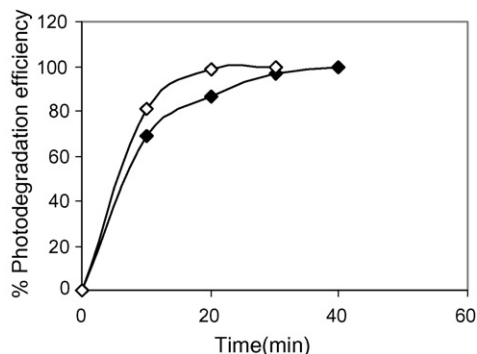


Fig. 11. Photocatalytic degradation of RR 198 in presence of: sunlight (◇) and under artificial UV light (◆).

was observed. The dye solution was irradiated under similar conditions as in the lab with artificial UV light. A 200 mL of 100 mg L^{-1} dye solution at its natural pH of 4.6 with 0.3 g L^{-1} of TiO_2 dispersed in it and reactor with A/V ratio of $1.14 \text{ cm}^2 \text{ mL}^{-1}$ was kept under sunlight with an average intensity of 29 W m^{-2} in the month of May. It was observed that degradation of dye under sunlight with average intensity of 29 W m^{-2} was 98% in 20 min as compared to 86% under artificial UV irradiation in the same duration of time and similar conditions as shown in Fig. 11.

5.8. Reuse of TiO_2

The catalyst's lifetime is an important parameter of the photocatalytic process, due to the fact that its use for longer period of time leads to a significant cost reduction of the treatment. For this reason, the catalyst was recycled four times as shown in Fig. 12 which shows a drop in efficiency from 98% to 40%. This is likely due to fouling of the catalyst and loss due to filtration.

5.9. Mineralization of RR dye 198

The mineralization of RR dye 198 is reported by measuring the initial and final COD of the illuminated solution under optimized conditions with initial concentration of 100 mg L^{-1} , pH 4.6, and catalyst loading of 0.3 g L^{-1} under artificial UV light. The COD value decreased from 104 to 5 mg L^{-1} after

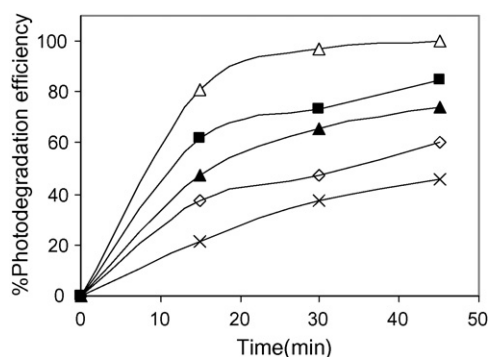


Fig. 12. Recyclability of TiO_2 : (△) original, (■) recycled 1st time, (▲) recycled 2nd time, (◇) recycled 3rd time, and (×) recycled 4th time.

3 h of irradiation which indicates mineralization to a significant extent. 95% mineralization was observed.

6. Conclusion

Heterogeneous photocatalytic oxidation process using UV light and oxygen could be efficiently applied for the degradation of non-biodegradable azo RR dye 198. It is observed that adsorption plays a major role in the photodegradation of the model compound and the photodegradation kinetics follow the Langmuir–Hinshelwood model. The results clearly delineate the important role of the selection of the optimum reaction conditions in achieving the highest level of degradation efficiency for RR 198. The rate of photodegradation was found to be maximum in the acidic medium with optimum TiO_2 concentration of 0.3 g L^{-1} at low dye concentrations with good recyclisation of catalyst. The experiments under sunlight show that higher photodegradation efficiency can be achieved under the same optimized conditions. Thus this can be used as an efficient technology for solar photocatalytic degradation of the coloured wastewater discharged from the textile industry which is under Indian climatic conditions.

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References

- [1] H. Zolinger, Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, VCH Publishers, New York, 1991.
- [2] I.A. Alaton, I.A. Balcioglu, D.W. Bahnemann, Advanced oxidation of a reactive dyebath effluent: comparison of O_3 , $\text{H}_2\text{O}_2/\text{UV-C}$ and $\text{TiO}_2/\text{UV-A}$ processes, Water Res. 36 (2002) 1143–1154.
- [3] U. Pagga, D. Brown, The degradation of dyestuffs. Part II. Behaviour of dyestuffs in aerobic biodegradation tests, Chemosphere 15 (1986) 479–491.
- [4] C. Nasr, K. Vinodgopal, L. Fisher, S. Hotchandani, A.K. Chattopadhyay, P.V. Kamat, Environmental photochemistry on semiconductor surfaces: visible light induced degradation of a textile diazo dye, naphthol blue black, on titanium dioxide nanoparticles, J. Phys. Chem. 100 (1996) 8436–8442.
- [5] C. Hachem, F. Bocquillon, O. Zahraa, M. Bouchy, Decolorization of textile industry wastewater by the photocatalytic degradation process, Dyes Pigments 49 (2001) 117–125.
- [6] M. Muneer, R. Philips, S. Das, Photocatalytic degradation of waste water pollutants. Titanium dioxide-mediated oxidation of a textile dye, Acid Blue, Res. Chem. Intermediat. 23 (1997) 233–246.
- [7] D.F. Ollis, E. Pelizzetti, N. Serpone, Destruction of water contaminants, Environ. Sci. Technol. 25 (1991) 1523–1529.
- [8] I. Poullos, I. Aetopoulou, Photocatalytic decomposition of commercial azo dye reactive orange 16, Environ. Technol. 20 (1999) 479–488.
- [9] G.A. Epling, C. Lin, Photoassisted bleaching of dyes utilizing TiO_2 and visible light, Chemosphere 46 (2002) 561–570.
- [10] W.Z. Tang, Z. Zhang, H. An, M.O. Quintana, D.F. Torres, Photoassisted bleaching of dyes utilizing TiO_2 and visible light, Environ. Technol. 18 (1997) 1–12.
- [11] A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai, V. Singh, Photocatalytic degradation of direct yellow 12 dye using UV/ TiO_2 in a shallow pond slurry reactor, Dyes Pigments 68 (2006) 53–60.
- [12] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.

- [13] F. Kiriakidou, D.I. Kondarides, X.E. Verykios, The effect of operational parameters and TiO₂ doping on the photocatalytic degradation of azo dyes, *Catal. Today* 54 (1999) 119–130.
- [14] D. Chen, A.K. Ray, Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension, *Water Res.* 32 (1998) 3223–3234.
- [15] A. Mills, S. Morris, Photomineralization of 4-chlorophenol sensitised by titanium dioxide: a study of the initial kinetics of carbon dioxide photo-generation, *J. Photochem. Photobiol. A: Chem.* 71 (1993) 75–83.
- [16] C. Galindo, P. Jacques, A. Kalt, Photooxidation of the phenylazonaphthol AO20 on TiO₂: kinetic and mechanistic investigations, *Chemosphere* 45 (2001) 997–1005.
- [17] T. Sauer, G.C. Neto, H.J. Jose, R.F.P.M. Moreira, Kinetics of photocatalytic degradation of reactive dyes in a TiO₂ slurry reactor, *J. Photochem. Photobiol. A: Chem.* 149 (2002) 147–154.
- [18] B. Neppolian, M.V. Shankar, V. Murugesan, Semiconductor assisted photodegradation of textile dye, *J. Sci. Ind. Res.* 61 (2002) 224–230.
- [19] M.Y. Cheng, I.C. Yu, P.K. Wang, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, *Chemosphere* 46 (2002) 905–912.
- [20] A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai, V. Singh, Photocatalytic degradation of 3,4-dichlorophenol using TiO₂ in a shallow pond slurry reactor, *Ind. J. Chem. Technol.* 12 (2005) 75.