

Kinetics of the decoloration of reactive dyes over visible light-irradiated TiO₂ semiconductor photocatalyst

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Abstract

Photocatalytic decoloration kinetics of triazine (Reactive Red 11, Reactive Red 2, and Reactive Orange 84) and vinylsulfone type (Reactive Orange 16 and Reactive Black 5) of reactive dyes have been studied spectrophotometrically by following the decrease in dye concentration with time. At ambient conditions, over 90–95% decoloration of above dyes have been observed upon prolonged illumination (15 h) of the reacting system with a 150 W xenon lamp. It was found that the decoloration reaction followed first-order kinetics. The values of observed rate constants were found to be dependent of the structure of dyes at low dye concentration, but independent at higher concentration. It also reports for the first time the decoloration of two different dyes together in a binary dye mixture using visible light-irradiated TiO₂ photocatalyst. Rate of decoloration of two different dyes together in a binary dye mixture using visible light-irradiated TiO₂ photocatalyst is governed by the adsorptivity of the particular dye onto the surface of the TiO₂ photocatalyst.

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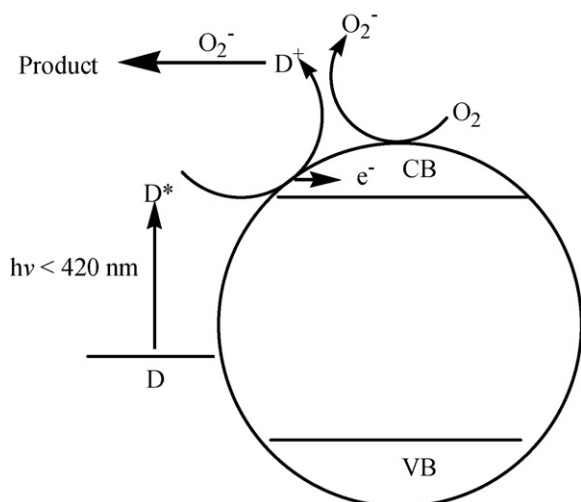
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1. Introduction

Textile dyes are potentially toxic because of their low removal rate [1,2] and if untreated would cause long-term health concerns [3]. Estimates indicate that approximately 15–20% of the synthetic textile dyes used are lost in wastewater streams during manufacturing or processing operations [4]. Therefore, textile dyes and other commercial colorants had emerged as a focus of environmental remediation efforts [5]. Among dyestuffs, reactive azo dyes constitute a significant portion of dye pollutants and probably have the least desirable consequences in terms of the surrounding ecosystem [1b]. Conventional methods [6] are available for treatment of textile wastewater, but most of the processes are either not very effective or environmentally compatible. In this regard, TiO₂ semiconductor photocatalytic system because of its many desirable properties, appear to be the most attractive means [7–10] for environmental purification

than the other conventional chemical oxidation methods. The only drawback of TiO₂ semiconductor is that it absorbs a small portion of solar spectrum in the UV region (band gap energy of anatase TiO₂ is 3.2 eV and 3.0 eV for rutile TiO₂). Therefore, modification of TiO₂ photocatalysts for pollutant degradation using visible light is a demanding area of research. Dye sensitization seems to be one of the viable methods for dealing with this issue [10]. The sensitized photocatalytic process has some possible advantage over direct photocatalysis. It extends the range of excitation energies of the semiconductor into visible region, making a more complete use of solar energy and could promote removal of colored pollutants. However, durability of such dye-sensitizer adsorbed TiO₂ photocatalytic system suffers a setback due to self-degradation of surface adsorbed sensitizer molecules. By deliberately avoiding, a regenerative step by directly oxidizing one-electron deficient dye molecule (D⁺, Scheme 1) has an advantage in treating textile wastewater with visible light. Because of the above reasons dye degradation over light-irradiated TiO₂ semiconductor photocatalyst has been the subject of continued interest [11–17]. Recently, we have started a research program on the visible

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Scheme 1. Self-sensitized degradation of colored contaminant on a TiO_2 semiconductor surface.

light assisted degradation of organic pollutants in wastewater using TiO_2 semiconductor. We have explored [18–20] the application of dye-sensitizer adsorbed TiO_2 in the degradation of colorless organics using visible light. In our very recent studies we have shown [21] dye-sensitized photocatalytic degradation of a non-emissive dye over visible light illuminated TiO_2 photocatalyst. In the present investigation, we have examined the degradation kinetics of a number of commercially available reactive dyes, viz. Reactive Red 11, Reactive Red 2, Reactive Orange 84, Reactive Orange 16 and Reactive Black 5 in aqueous suspensions of TiO_2 under visible light. We wish to report herein the results of our studies of photocatalytic decoloration of above dyes over visible light illuminated TiO_2 semiconductor. Since, textile effluent usually contains mixture of dyes, we have also extended our studies to photocatalytic decoloration of colored solution containing two dyes. A working mechanism in agreement with the kinetic data is proposed.

2. Experimental

2.1. Materials and methods

The dyes Reactive Red 11, Reactive Red 2, Reactive Orange 84, Reactive Orange 16 and Reactive Black 5 were procured from local commercial source and used as-received. The anatase grade Degussa P25 titanium dioxide (TiO_2) with particle size of 20 nm and BET surface area $50 \text{ m}^2 \text{ g}^{-1}$ (according to the company's specification) was used in the present studies. All other chemicals used in the present study were of A.R. grade and doubly distilled water was used throughout the experiment. Spectral (UV–vis) measurements were carried out with a PerkinElmer (Model Lambda 35) spectrophotometer. Spectroelectrochemical studies were performed using a CH Electrochemical Instruments (CHI-660B) attached with online Ocean Optics Inc., USA spectrophotometer (USB 4000) with TP-3000 plastic transmission dipprobe (10 mm path). Cyclic voltammetric experiments were

conducted in a glass cell equipped with a platinum working electrode, platinum-wire auxiliary electrode and standard calomel electrode (SCE) as reference electrode.

2.2. Adsorption studies

The adsorption studies were performed using aqueous solutions of dyes. For this purpose dye solutions (50 ml) of different concentrations were magnetically stirred in presence of 100 mg of TiO_2 photocatalyst in dark for 4 h at 25°C . Thereafter, the suspensions were allowed to settle for 30 min, centrifuged for 15 min (12000 rpm) and filtered (using $0.1 \mu\text{m}$ membrane filter). The dye concentration (C_e) in the supernatant liquid was measured spectrophotometrically. The amount of dye adsorbed (q_e) onto the surface of TiO_2 photocatalyst was estimated by subtracting the value of equilibrium dye concentration (C_e) from initial dye concentration (C_0).

2.3. Photodegradation of dyes

Photocatalytic experiments were performed in a similar manner as described in earlier reports [20,21]. The pre-aerated reaction mixture taken in a flat-surfaced glass reactor was illuminated with a 150 W xenon lamp (Oriol Illuminator 7340) under continuous magnetic stirring. A filter solution containing sodium nitrite, copper sulfate and ammonium hydroxide was used as a UV-filter [22] to eliminate light $<420 \text{ nm}$. At a chosen interval of irradiation time aliquots of reaction mixture were withdrawn, centrifuged and filtered by using a membrane filter ($0.1 \mu\text{m}$) and the extent of dye decoloration was estimated spectrophotometrically at the absorption maximum (λ_{max}) of the concerned dye (Table 1). Chemical oxygen demand (COD) measurements were carried out with titrimetric method [23]. The colorless solution (5 ml) that obtained at the end of the photolysis was shaken with 10 ml of dichloromethane, and the organic layer was subjected to gas chromatography–mass spectra (GC–MS) studies on a GC–MS–MS equipment (Thermo Electron Corporation) equipped with PolarisQ mass detector. However, results were inconclusive in regard to the identification of any particular intermediate due to complicated mass spectra. Sulfate, nitrate and ammonium ions were analyzed using Mettler Delta Ion meter (Model MA 350) using corresponding ion-selective electrodes.

3. Results and discussion

Spectral data and structural representations of the dyes selected for the present work are shown in Table 1. Cyclic voltammetric behavior of the dyes in KCl medium was examined in the potential range -0.4 V to 0.8 V . No well-defined oxidation waves are seen in the cyclic voltammograms under the specified conditions. A reversible reduction wave observed at $E_{1/2} = -0.15 \text{ V}$ (vs. SCE) in case of RB 5 may be attributed to the reduction of quinone to hydroquinone moiety [24]. The results of cyclic voltammetric studies did not allow us to identify the redox properties of the chromophoric group in the selected dyes. Controlled potential electrolysis of dye solution (10 ppm at

Table 1
Structural representation of some selected reactive dyes

CI name of the dyes	Molecular structure of the dyes
Reactive Red 11 (RR 11, $\lambda_{\max} = 545$ nm)	
Reactive Red 2 (RR 2, $\lambda_{\max} = 540$ nm)	
Reactive Orange 84 (RO 84, $\lambda_{\max} = 496$ nm)	
Reactive Orange 16 (RO 16, $\lambda_{\max} = 495$ nm)	
Reactive Black 5 (RB 5, $\lambda_{\max} = 599$ nm)	

pH 5.0) was carried out at 0.8 V, and analysis of the electrolyzed dye solution using online diode array spectrometer (USB 4000) revealed negligible decoloration of dyes (2–3%) after 4 h. The results of the above electrochemical studies suggest that the ground state oxidation potential of the chromophore groups in the selected dyes is more than 0.8 V (vs. SCE).

Preliminary photocatalytic experiments revealed that in the absence of TiO_2 there was no noticeable change in dye concentration after prolonged irradiation (4 h) of solution of each dye compound under investigation. The adsorption of the enlisted reactive dyes on TiO_2 in dark was evaluated. The results of adsorption studies are typically represented in Fig. 1a. The

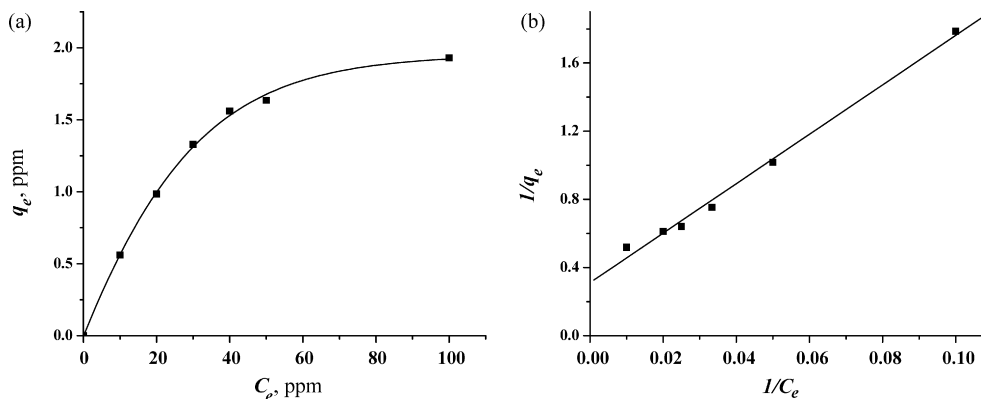


Fig. 1. Plot of (a) C_e vs. q_e and (b) $1/C_e$ vs. $1/q_e$ for adsorption of Reactive Red 11. $\text{TiO}_2 = 100$ mg, pH 5.0.

Table 2
Adsorption parameters^a and kinetic data for photocatalyzed dye decoloration^b

Dyes	q_m (ppm)	b (ppm ⁻¹)	K_a ^c	k_{obs} ($\times 10^3$ min ⁻¹) ^d	Decoloration (%) ^{b,d}
Reactive Red 11	3.1303	0.0234	0.073	2.42	93
Reactive Red 2	3.1812	0.0202	0.077	2.63	93
Reactive Orange 84	3.0571	0.0165	0.058	2.13	91
Reactive Orange 16	3.6192	0.02211	0.08	2.72	94
Reactive Black 5	3.961	0.0173	0.093	2.85	95

^a Experimental conditions as depicted in Fig. 1.

^b 11 h photolysis at pH 5.0, initial concentration of each dye was 50 ppm.

^c $K_a = q_m b$.

^d Based on initial dye concentration (50 ppm).

experimental data were fitted to the Langmuir equation (Eq. (1)), which is as follows

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

where q_m is the maximum amount of dye adsorbed forming a complete monolayer, b is the equilibrium parameter, C_e is the equilibrium concentration of dye and q_e is the amount of dye adsorbed on the surface of TiO₂ photocatalyst. Plot of $1/q_e$ versus $1/C_e$ (Fig. 1b) was linear in each case. Adsorption parameters estimated from the slope and intercept of the plots are summarized in Table 2. The values of Langmuir equilibrium constant ($K_a = q_m b$) for adsorption of dye onto TiO₂ surface at dark are summarized in Table 2.

Prolonged illumination (10–12 h) of air-equilibrated aqueous dye solutions containing TiO₂ photocatalyst resulted in substantial decoloration (Table 2) of each dye under specified conditions. In each case sulfate, nitrate and ammonium ions together with formate and oxalate were identified as end products by analyzing the colorless solution obtained after 20 h of irradiation. In order to identify the intermediates formed in the photocatalytic reactions, we have taken partially decolorized solutions (50–60%) that undergone 4–5 h photolysis and extracted with dichloromethane for subjecting GC–MS analysis. Identification of the reaction intermediates was difficult due to complicated GC–MS spectra, however, GC–MS peaks and their multiple MS–MS fragmentation patterns confirmed the presence of naphthionic acid, 1-amino-2-naphthol, 2-naphthol, 1,2-naphthoquinone as intermediates in the photolysis of Reactive Black 5, Reactive Red 11, Reactive Red 2 and Reactive Orange 16. In case of Reactive Orange 84 sulfonated aminonaphthalenes, naphthalene sulfonic acids were also evidenced.

Time course of dye decoloration reaction was followed at the absorption maximum of the corresponding dye. In each case it exhibited first-order kinetics and, plot of A_t/A_0 versus time (where A_0 and A_t are initial absorbance and absorbance of the photolyzed solution at time t , respectively) displayed excellent single exponential fit as shown typically in Fig. 2 for decoloration of Reactive Red 11. The values of first-order rate constant (k_{obs}) are summarized in Table 2. In Fig. 3 plot of k_{obs} versus initial dye concentration of dye (close to the values of equilibrium concentration dye concentration, C_e) is shown. The values of q_m , the maximum limit of adsorption of dye (Table 2) lie in the range 3.1–3.96 ppm. The observed decrease in k_{obs}

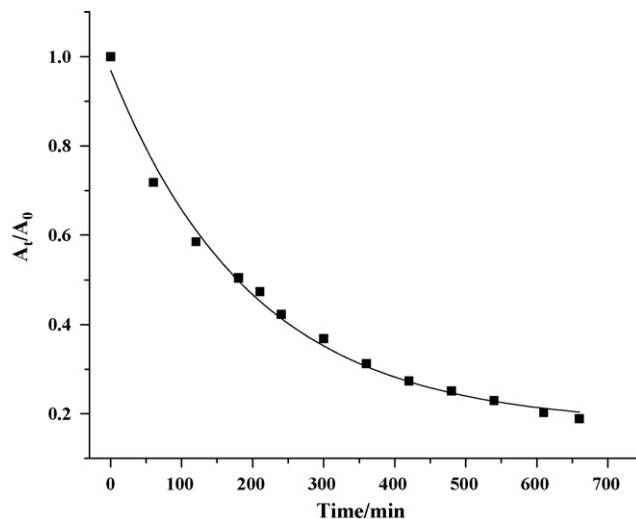


Fig. 2. First-order kinetic trace for the photocatalytic decoloration of Reactive Red 11 at pH 5.0. TiO₂ = 100 mg, initial dye concentration = 50 ppm.

values for dye decoloration with increasing initial dye concentration (Fig. 3), may be explained by the fact that at higher dye concentration the visible light photons ($\lambda > 420$ nm) cannot get significant access to the surface adsorbed dye molecules

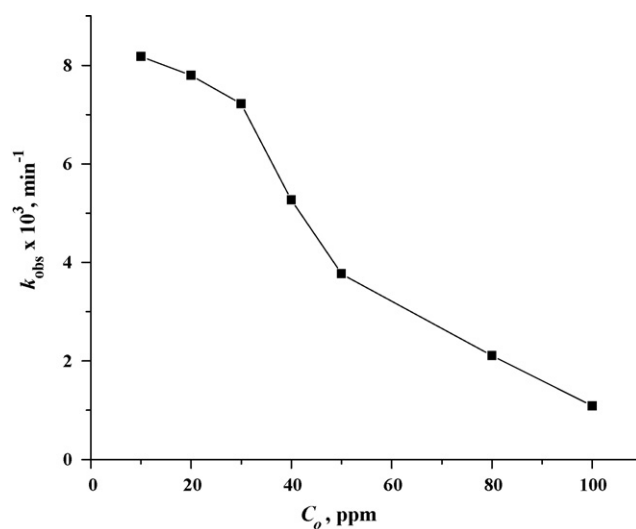
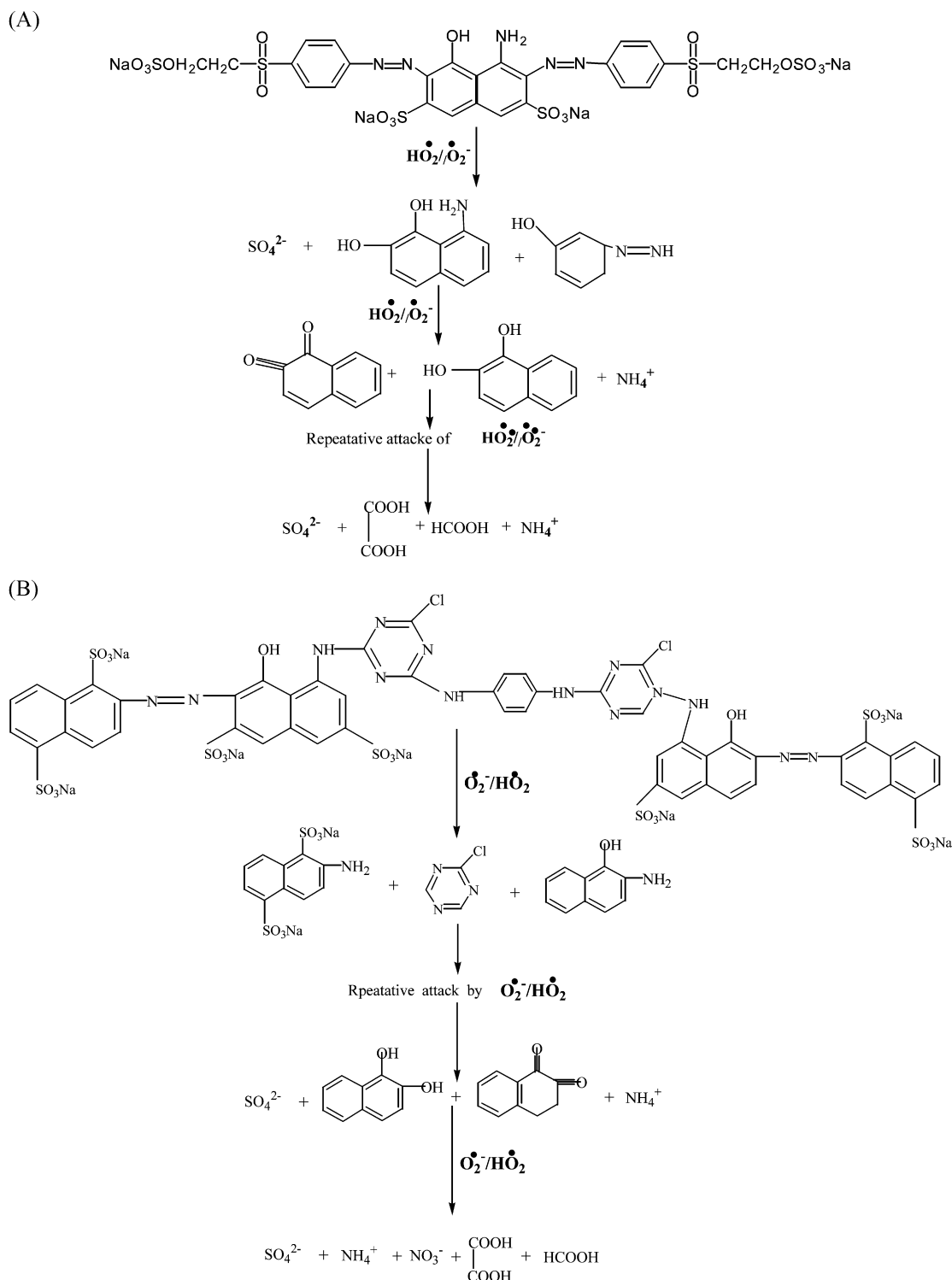


Fig. 3. Effect of initial dye concentration (C_0) on photocatalytic decoloration of Reactive Red 11 at pH 5.0. TiO₂ = 100 mg.

(forming monolayer). At high dye concentration, visible light absorbed excited dye molecules in the bulk cannot accomplish energy transfer to the surface adsorbed dye because of its deactivation due to self-collision. Therefore, visible light assisted photosensitization of the surface adsorbed dye molecules followed by subsequent charge injection to the conduction band of the TiO_2 photocatalyst is reduced substantially with increas-

ing dye concentration. The trend of the decrease in k_{obs} values appeared to be almost independent of dye structure as the values of q_m are not differed much for the dyes under investigation.

The rates of dye decoloration under the specified reaction conditions are not markedly changed for different dye molecules used in this investigation (Table 1). This suggests that at lower concentration range the rate-controlling step in the above decol-



Scheme 2. (A) Degradation of Reactive Black 5. (B) Degradation of Reactive Orange 84.

Table 3
Results of photocatalytic decoloration of aqueous mixture of two dyes^a

Dye	Adsorption (%) ^{b,c}			Photocatalytic decoloration (%) ^c		
	RO 84	RB 5	RO 16	RO 84	RB 5	RO 16
RO 84 (25 ppm)	3.63	NA	NA	47	NA	NA
RB 5 (25 ppm)	NA	5.83	NA	NA	66	NA
Binary dye mixture RO 84 (25 ppm) and RB 5 (25 ppm)	1.4	3.4	NA	14	63	NA
RO 16 (25 ppm)	NA	NA	4.87	NA	NA	59
RB 5 (25 ppm)	NA	5.83	NA	NA	63	NA
Binary dye mixture RO 16 (25 ppm) and RB 5 (25 ppm)	NA	3.4	2.4	NA	43	39

NA = not applicable.

^a 6 h photolysis, concentration of each dye was kept at 25 ppm.

^b Magnetically stirred for 4 h at dark; concentration of each dye in was kept at 25 ppm.

^c Based on initial dye concentration (25 ppm).

oration reactions is governed by the adsorption efficiency (q_m) of dye molecules onto the surface of the TiO₂ photocatalyst. In order to gain mechanistic insight we carried out photocatalytic decoloration studies taking a mixture of two dyes. It is worth mentioning here that textile effluent usually contains more than one dye. We have selected Reactive Orange and Reactive Black because their absorption maxima (λ_{max}) are appreciably separated affording their straightforward spectrophotometric monitoring of the decoloration of the dyes simultaneously. No change in the spectral pattern was observed after 5 h of stirring the aqueous mixture of both the dyes in dark or under prolonged illumination (5 h, without TiO₂). This indicated that the dyes did not interact with each other in dark, and neither in light. Results of adsorption studies with TiO₂ in dark reveal that in an aqueous mixture of Reactive Orange 84 and Reactive Black 5 (present at equal concentration of 25 ppm), adsorption of Reactive Black 5 was more onto the surface of TiO₂ photocatalyst than Reactive Orange 84 (Table 3). Photolysis of the mixture of Reactive Orange 84 and Reactive Black 5 in the presence of TiO₂ photocatalyst resulted in an appreciable decoloration of Reactive Black 5 (Table 3), whereas, decoloration of Reactive Orange 84 after 6 h was comparatively much lower. Based on the product analysis and considering superoxide is the oxidizing species formed in visible light assisted dye sensitization photocatalysis (Scheme 1), a following reaction pathways have been proposed in Scheme 2 for decoloration of the dye mixture containing Reactive Black 5 and Reactive Orange 84 under visible light illumination. In Scheme 2, the proposed triazenyl intermediate was not identified as it could have rapidly undergone oxidation by indiscriminate attack of O₂^{•-}/HO₂[•] radical species under specified conditions. In another case, dye mixture containing Reactive Black 5 and Reactive Orange 16 which is structurally smaller than Reactive Orange 84 (Table 1), adsorption of the later dye was quite comparable with that of the former (Table 3). Furthermore, the extent of decoloration for both Reactive Black 5 and Reactive Orange 16 was found to be similar under photocatalytic conditions (Table 3). The results of the above studies signify that the dye having greater adsorption undergoes decoloration preferentially over visible light illuminated TiO₂. The COD values of dye solution (50 ml) containing Reactive Black 5 (25 ppm) and Reactive Orange 16 (25 ppm) measured before and after 20 h of the photocatalysis were found to be 197 ppm and

98 ppm, respectively. Illumination of the practically colorless solution (that obtained after prolonged photolysis) with visible light did not show any further decrease of COD of the solution. This signifies that once the visible light absorbing chromophore of the dyes is decomposed due to oxidative attack of superoxide radical formed during photocatalytic decoloration process (*cf.* Scheme 1), it can no longer absorb visible light to initiate the photosensitization process. Therefore, further degradation of colorless intermediate(s) could not take place, consequently low COD removal was observed for visible light irradiation. However, a different mechanism involving band gap excitation of TiO₂ semiconductor followed by electron (e⁻)–hole (h⁺) pair formation would become operative when the TiO₂ is irradiated with UV–vis light [25]. Therefore, under UV irradiation, dye decoloration followed by degradation of colorless intermediates had also been observed. In case of prolonged (15 h) illumination with sunlight which contains both UV (4%), and visible light, photocatalytic degradation of the selected dyes was observed with COD removal (90–95%).

4. Conclusion

The results of the present study clearly demonstrate the capability of visible light/TiO₂ photocatalytic system to remove the aesthetic appearance of the selected triazine and vinylsulfone type of reactive dyes to a large extent either separately or in mixture. Efficacy photodegradation depend on the susceptibility of the dyes as well as the intermediates formed. The results of the present study further impart the significance of using sunlight (as 4% UV light is available in the solar spectrum) to treat textile wastewater through dye sensitization coupled with superoxide radical-mediated oxidative degradation process. Further studies with real textile effluents pertinent to this matter are in progress.

Acknowledgments

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