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Visible light induced photodegradation of organic pollutants on dye adsorbed TiO_2 surface

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Abstract

Visible light assisted degradation of aromatics, viz phenol, chlorophenol, 1,2-dichloroethane, trichloroethylene and surfactants, viz cetyl pyridinium chloride (CPC; cationic), sodium dodecylbenzene sulfonate (DBS; anionic) and neutral Triton-X 100 in air-equilibrated aqueous mixtures has been achieved on the surface of TiO_2 semiconductor modified with methylene blue (MB) and rhodamine B (RB). Under 5 h of irradiation with a 150 W xenon lamp, over 40–75% degradation of pollutants has been observed. The failure of pollutants to degrade on non-conducting Al_2O_3 surface essentially suggests the role of semiconducting TiO_2 photocatalyst in the photochemical process. A working mechanism involving excitation of surface adsorbed dye, followed by charge injection into the TiO_2 conduction band and formation of reactive $^{\bullet}O_2^-/^{\bullet}HO_2$ radicals is proposed for the degradation of organics to carbon dioxide.

Keywords: Photodegradation; Dye sensitization; TiO_2 semiconductor; Halocarbons; Surfactants; Visible light; Methylene blue; Rhodamine B

1. Introduction

Photosensitized degradation of colored contaminants in waste water on semiconductor surface is of current importance [1–10]. The visible light assisted degradation process involves the initial excitation of the surface adsorbed dye followed by the charge injection to the conduction band of the semiconductor. In all the cases referenced above, the colored compounds in presence of molecular oxygen (acting as an electron scavenging agent) undergoes oxidative degradation to colorless end product following steady state photolysis. Although semiconducting TiO_2 in presence of UV radiation has become the benchmark photocatalyst for degradation of myriad of a water bound pollutants as documented in the literature [11–22], the vital drawback of TiO_2 semiconductor is that it absorbs a small portion of solar spectrum in the UV region (band gap energy of TiO_2 is 3.0–3.2 eV). Hence, the photosensitized degradation process has the advantage that it harvests maximum solar energy by utilizing visible light for degradation of water bound organics.

Very recently we had explored [23,24] that the dye sensitization technique for degradation of colorants in visible light illuminated dye modified TiO_2 dispersion could also be workable for degradation of *colorless* water bound pollutants. Photodegradation of phenol, chlorophenol, 1,2-dichloroethane and trichloroethylene was achieved in visible light irradiated dye modified TiO_2–D (D: thionine, eosinY) particulate system [23,24]. In the present investigations we have examined the prospect of TiO_2 surface adsorbed methylene blue and rhodamine B towards decomposition of various water bound organic pollutants in presence visible light and air. The photoexcited state redox properties of methylene blue and rhodamine B (Fig. 1) are different. Photoexcited methylene blue, like thionine, accepts an electron to produce semi methylene blue dye species [25], whereas, surface adsorbed rhodamine B upon excitation injects electron to the conduction band of the semiconductor [26]. We wish to report herein the results of our studies of visible light assisted decomposition of various halocarbons, viz phenol, chlorophenol, 1,2-dichloroethane trichloroethylene and some common surfactants, viz cetyl pyridinium chloride (CPC; cationic), sodium dodecylbenzene sulfonate (DBS; anionic) and Triton-X 100 (non-ionic) using above dye adsorbed TiO_2 semiconductor particulate system.

2. Experimental

2.1. Materials and methods

Adsorption of dye samples on to the surface of TiO_2 semiconductor (obtained from Fluka) and characterization

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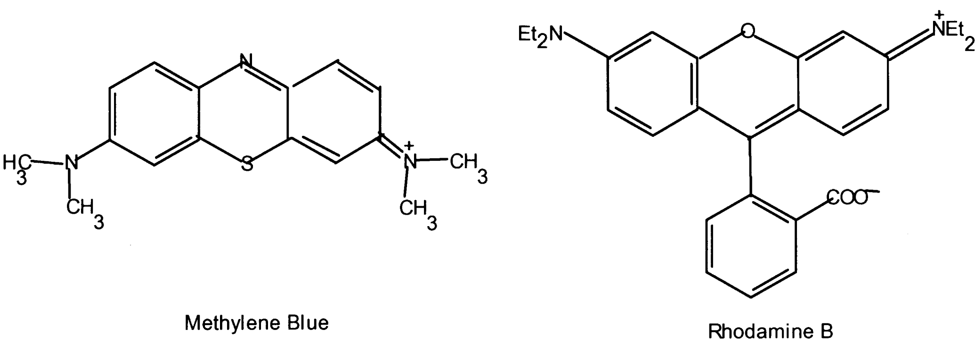

Fig. 1. Pictorial representation of the various dye species.

of surface adsorbed dyes were carried by following the procedure reported earlier [23,24]. In a typical experiment 50 ml of an aqueous solution of dye (usually 10^{-5} M at pH ∼5) containing TiO_2 (500 mg) was magnetically stirred for 4 h in dark. The concentration of adsorbed dye determined spectrophotometrically (by measuring the difference in absorbance of free dye and that in the supernatant liquid obtained after filtration) was found to be 583 and 530 μeq./g for methylene blue and rhodamine B, respectively. Spectra of the dyes adsorbed on TiO_2 surface was recorded in a qualitative manner by rubbing the solid sample on a piece of transparent paper and placing it into the optical path of built-in cell-holder of the spectrophotometer (another piece of the same paper was placed in the reference cell-holder). All other chemicals used were of AR grade and doubly-distilled water was used throughout the experiment. Spectral (UV-Vis) measurements were carried out with a GBC Cintra 10 spectrophotometer. Fluorescence measurements were performed in the Chemistry Department, Burdwan University using a Hitachi F-4010 spectrofluorometer.

2.2. Photodegradation of organic pollutants

In a typical photocatalysis experiment aqueous suspension (50 ml) containing 100 mg of surface modified photocatalyst designated as TiO_2–D and 0.1 mmol of pollutant (designated as *P* hereafter) were taken in a flat-surfaced glass-reactor. The pre-aerated reaction mixture was illuminated with a 150 W xenon lamp (Oriel Instruments) under continuous magnetic stirring. The distance between the lamp and the glass-reactor containing reaction mixture was set at 8 in. Oxygen was replenished by opening the photoreactor to the atmosphere when the reaction mixture was sampled after an appropriate interval of irradiation time. The pH of reacting system was adjusted at 5.0 (NaOH). After chosen interval of irradiation time the 2 ml aliquot of reaction mixture was subsequently centrifuged and filtered and the change in the concentration of pollutant in each degraded solution was monitored spectrophotometrically in UV region (at the respective absorption maxima of the pollutant). Depletion of 1,2-dichloroethane and trichloroethylene were followed gas chromatographically (GC) using a Carlo Erba GC 8000^{Top} series on a Tenax column fixed with a FID detector. Production of CO_2 was verified by the precipitation of $BaCO_3$ in the $Ba(OH)_2$ solution. The evolved CO_2 was flushed with oxygen through alkali (KOH) scrubber and estimated by titration against acid (HCl). Presence of Cl^- (ascertained by $AgNO_3$ test) at the end of the experiment indicated the dechlorination of halocarbons under investigation. The extent of chloride accumulation in the reacting system was determined titrimetrically with $AgNO_3$ solution using potassium chromate as an indicator.

3. Results and discussion

Aqueous solutions methylene blue exhibited absorption and emission spectra similar to that reported earlier ($\lambda_{\text{max}}^{\text{absorption}} = 665$ nm; and $\lambda_{\text{max}}^{\text{emission}} = 677$ nm) [25]. At pH 5.0 rhodamine B exists predominantly in its zwitterionic form [27]. Spectral features displayed by rhodamine B at pH 5.0 ($\lambda_{\text{max}}^{\text{absorption}} = 555$ nm; $\lambda_{\text{max}}^{\text{emission}} = 575$ nm) have been found to be in good agreement with the previously reported spectral data for zwitterionic rhodamine B [28]. Spectra of the dyes adsorbed on to the surface of the TiO_2 recorded in the solid state revealed no appreciable difference in the spectral features that has been noticed for free dyes in the aqueous solutions.

A series of blank experiments revealed that 12–15% of the initial concentration of various pollutants selected for this studies were found to be adsorbed on to the surface of the TiO_2 catalyst in the dark under experimental conditions. No appreciable photodegradation of these compounds was observed by illumination of unmodified TiO_2 with visible light. Dye molecules were found to be non-interacting with the pollutant molecules in dark as there was no change in the spectral pattern of dyes observed after 8 h of stirring the aqueous solution of dyes with pollutants in dark. However, prolonged illumination (8–10 h) of air-equilibrated aqueous dye solutions containing pollutants results in an appreciable decrease in absorbance of dye, as typically shown in Fig. 2. The observed spectral changes (Fig. 2a) is attributed to the reduction of photo excited methylene blue dye by the surfactant DBS. The spectral bleaching of methylene blue in

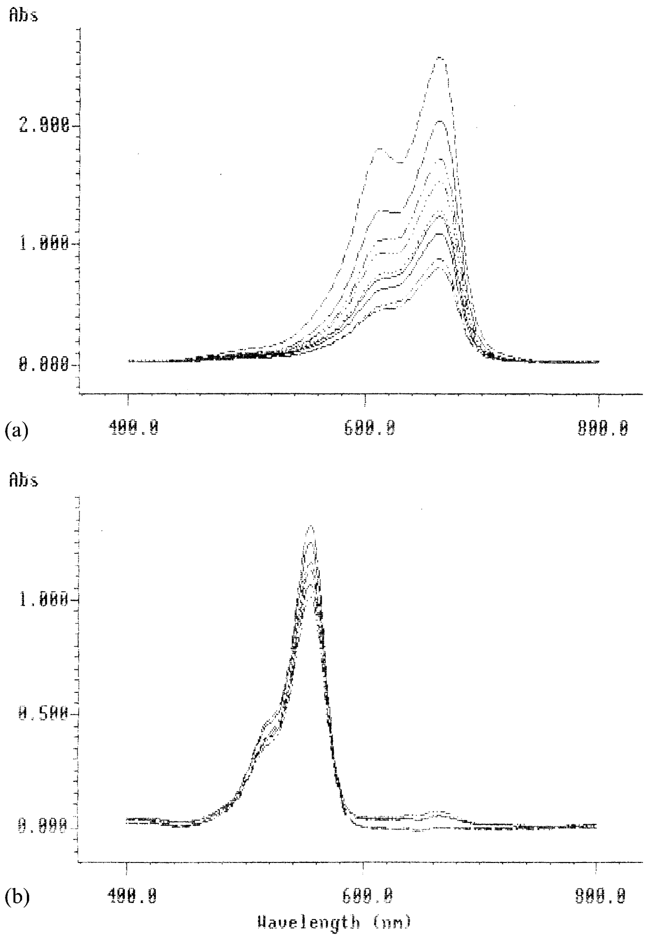

Fig. 2. Spectral changes that occurs during photolysis of aerated aqueous solution of (a) methylene blue (1×10^{-5} M) and DBS (1.55×10^{-4} M), and (b) rhodamine (1×10^{-5} M) and DBS (1.55×10^{-4} M) at pH 5.0.

presence of a reductant is not unexpected [25] as thiazines and oxazines dyes in their excited state are known to undergo one electron reduction followed by disproportion to produce their corresponding leuco-dyes which are almost featureless in 400–800 nm region [25]. For rhodamine B the collapse of spectral features (Fig. 2b) appeared to be unusual since, rhodamine B at the excited gives up electron [26]. However, reduction of photoexcited rhodamine B by electron donating DBS molecule leading to the formation of colourless product can not be ruled out. In one similar observation for eosinY (which behaves as an electron donor in the excited state) reported very recently [29] that free eosinY in presence of light accept one electron from TEOA to produce *trianion radical* which subsequently undergoes hydrogenation to form a stable species spectrum of which is almost featureless in 400–800 nm region. However, the same dye when adsorbed at TiO_2 reduces conduction band (CB) of TiO_2 upon excitation by giving up one electron. The one electron deficient eosinY adsorbed at TiO_2 subsequently gets its electron back from TEOA. It seems that the kinetic barrier for one electron transfer from eosinY to the conduction band of TiO_2 dropped substantially when eosinY is adsorbed at TiO_2 surface, whereas, TEOA though appears to be a stronger reductant as it reduces free eosinY in presence of light, could not transfer electron to the conduction band of TiO_2, but reduces one electron oxidized dye species. In view of above and considering the spectral changes observed in the present case (Fig. 2b) it appears that upon illumination rhodamine B undergoes reduction by the surfactant DBS to yield a stable colorless product.

Results of photodegradation of organic pollutants with dye modified TiO_2 are summarized in Table 1. Time course of photodegradation of 1,2-dichloroethane and DBS are shown in Fig. 3a and b, respectively. Fig. 4a and b display the concomitant CO_2 mineralization yield with time.

Table 1
Results of TiO_2–D catalyzed photodegradation of pollutants in water

P	P_{in} (mmol)	P_{ur} (mmol)[a]	Degradation of P (%)[b]	Photocatalyst	CO_2 (mmol)[c]	Cl^- (mmol)[d]
Phenol	1.0	0.33	67	TiO_2–rhodamine B	3.4	–
Chlorophenol	0.1	0.038	62		0.27	0.054
Trichloroethylene	1.0	0.28	72		0.98	1.86
1,2-Dichloroethane	1.0	0.24	76		1.02	0.98
CPC	0.1	0.050	50		0.90	–
DBS	0.04	0.0148	63		0.33	–
Triton X 100	0.1	0.039	61		1.37	–
Phenol	1.0	0.36	64	TiO_2–methylene blue	3.04	–
Chlorophenol	0.1	0.045	55		0.20	0.045
Trichloroethylene	1.0	0.37	63		0.89	1.03
1,2-Dichloroethane	1.0	0.34	66		0.92	0.90
CPC	0.1	0.058	42		0.68	–
DBS	0.04	0.0184	54		0.24	–
Triton X 100	0.1	0.055	45		0.95	–

[a] Concentration of unreacted pollutant (P_{ur}) after 5 h of reaction.
[b] Based on pollutant concentration taken i.e. ($P_{in} - P_{ur}/P_{in}$) × 100.
[c] Mineralized CO_2 estimated after 5 h of reaction.
[d] Organic chlorine recovered as Cl^- after 5 h of reaction.

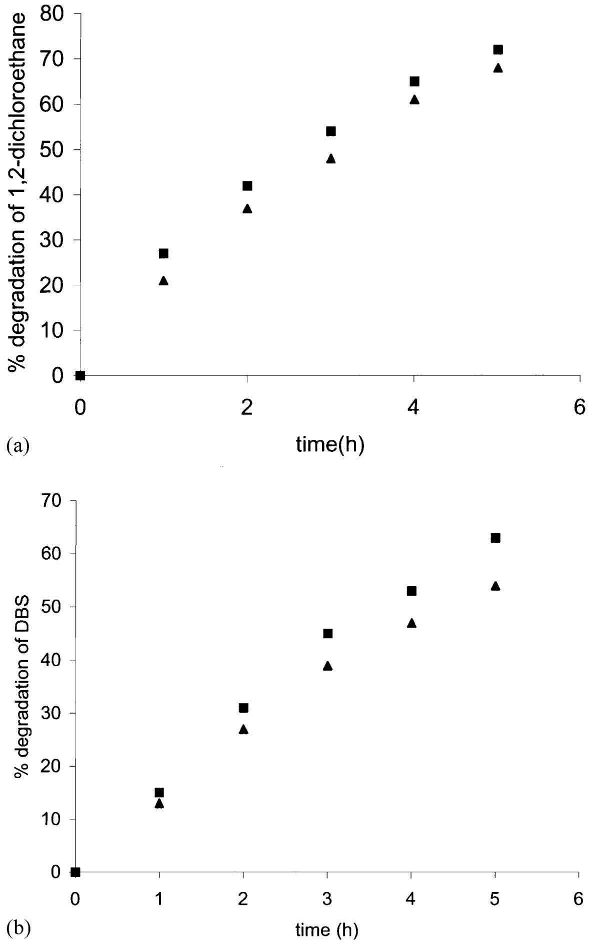

Fig. 3. Visible light induced decomposition of (a) 1,2-dichloroethane and (b) DBS with time in dye modified TiO_2 dispersion at pH 5.0; 1,2-dichloroethane = 1 mmol, DBS = 0.04 mmol, (▲) methylene blue, (■) rhodamine B.

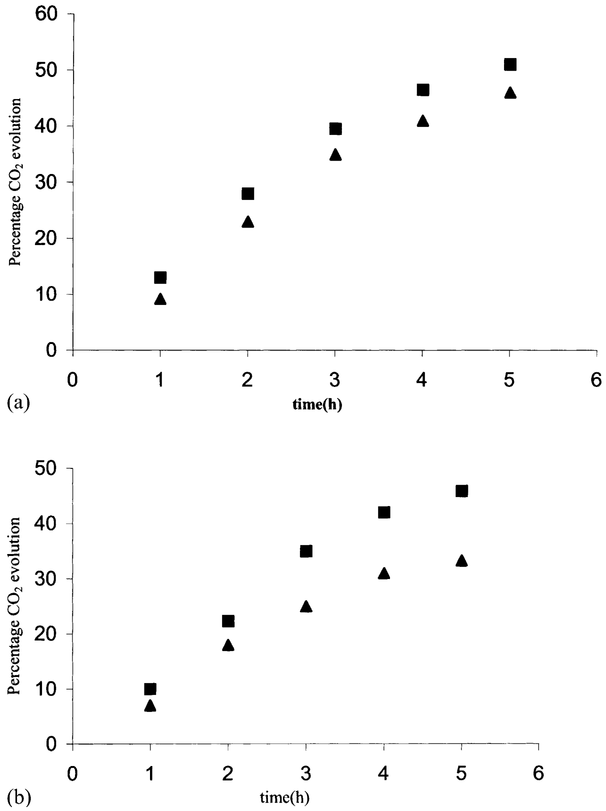

Fig. 4. Evolution of CO_2 with time in visible light induced decomposition of (a) 1,2-dichloroethane and (b) DBS with time in dye modified TiO_2 dispersion at pH 5.0; 1,2-dichloroethane = 1 mmol, DBS = 0.04 mmol, (▲) methylene blue, (■) rhodamine B.

The major reaction intermediate identified earlier [30,31] using GC–MASS and HPLC techniques in the photodegradation of chlorophenols is hydroquinone (HQ). However, in the present case formation of such intermediate(s) could not be evinced spectrophotometrically in the photodegradation of phenol and chlorophenol. However, in case of surfactants, formation of aldehyde intermediates at initial stage of photolysis (after 30 min) of was evidenced by spectrophotometric analysis (Nash method [32]) of the irradiated sample solution, however, continued irradiation ultimately resulted in the further decomposition of the intermediates to carbon dioxide. Failure of noticing any appreciable photodegradation of any above pollutants after prolonged (8 h) illumination either with dye adsorbed TiO_2–D system in absence of oxygen or with dye adsorbed onto non-conducting material alumina (Al_2O_3–D) in place of TiO_2–D provides good evidences that the above described photodegradation is a semiconducting TiO_2-mediated phenomenon and oxygen is essential for an effective photodegradation process.

Based on the above findings and considering the earlier reports on the excited state redox properties of methylene blue and rhodamine B adsorbed on the surface of TiO_2 semiconductor [25,26], the reduction of conduction band of the TiO_2 semiconductor through photoexcitation of methylene blue (MB) and rhodamine B (RB) can be represented in Schemes 1 and 2, respectively.

$$\mathrm{TiO_2\text{-}(MB)_s} \xrightarrow{h\nu} \mathrm{TiO_2\text{-}(MB^*)_s} \qquad (1)$$

$$\mathrm{TiO_2\text{-}(MB^*)_s} + P \longrightarrow \mathrm{TiO_2\text{-}(SMB^-)_s} + P^{+\bullet} \qquad (2)$$

$$\mathrm{TiO_2\text{-}(SMB^-)_s} \longrightarrow \mathrm{TiO_2\text{-}(MB)_s} + e^-_{CB} \qquad (3)$$

Scheme 1.

$$\mathrm{TiO_2\text{-}(RB)_s} \xrightarrow{h\nu} \mathrm{TiO_2\text{-}(RB^*)_s} \qquad (4)$$

$$\mathrm{TiO_2\text{-}(RB^*)_s} \longrightarrow \mathrm{TiO_2\text{-}(RB^+)_s} + e^-_{\mathrm{CB}} \qquad (5)$$

$$\mathrm{TiO_2\text{-}(RB^+)_s} + P \longrightarrow \mathrm{TiO_2\text{-}(RB)_s} + P^{+\bullet} \qquad (6)$$

($h\nu$ = visible light ; P = pollutant)

Scheme 2.

$$e^-_{\mathrm{CB}} + \mathrm{O_2} \longrightarrow {}^\bullet\mathrm{O_2}^- \qquad (7)$$

$$^\bullet\mathrm{O_2}^- + \mathrm{H^+} \longrightarrow {}^\bullet\mathrm{HO_2} \qquad (8)$$

Scheme 3.

Upon visible light irradiation surface adsorbed methylene blue (MB) gets excited (Eq. (1)) and undergoes one electron reduction by the pollutant molecules present in excess to produce semimethylene blue (SMB) species (Eq. (2)). This one electron rich semimethylene blue species subsequently transfer one electron to the conduction band of TiO_2 (Eq. (3)). Empty conduction band edge of TiO_2 (E_{CB} = 0.3 V versus NHE at pH 5.0) [33] seems to be thermodynamically capable of oxidizing surface adsorbed singly electron reduced methylene blue ($E_{MB/SMB} = 0.01$ V versus NHE) [25]. Since, the dye molecules are immobilized onto the surface of the TiO_2, disproportionation of semimethylene blue to leco-species [25] is prevented in the present situation. Reduction of conduction band by photoexcited rhodamine B as outlined in Eqs. (4)-(6) in Scheme 2 is based on earlier report on the electron transfer fluorosence quenching of rhodamine B adsorbed on to semiconductor surface [26]. Rhodamine B adsorbed at the surface of TiO_2 gives up one electron to the conduction band upon excitation as outlined in Eq. (5). Pollutants (P) under investigation serve here to reduce back the one electron deficient oxidized form of surface adsorbed rhodamine B (RB^+) to rhodamine B (Eq. (6)).

Generation of $^\bullet O_2^-/^\bullet HO_2$ species through scavenging of conduction band electrons by oxygen molecules is an essential requirement for an effective photocatalytic demineralization of water bound organics has been well established in the literature by various research groups [1–22]. Formation of these radical species are outlined in Scheme 3.

The presence of oxygen is profoundly related to the effective photodegradation of organics. In absence of oxygen the extent of photodegradation of any pollutants in the present studies was found to be negligible in the present case, which necessarily indicates that the rapid scavenging of the conduction band electron by the dioxygen is very important for an effective photodegradation process as the reduced oxygen species press forward the degradation of organics [34]. Repeated attacks of $^\bullet O_2^-/^\bullet HO_2$ radicals to pollutant species ($P/P^{+\bullet}$) in the reacting system essentially lead the degradation of organic molecules ultimately to carbon dioxide in a secondary autocatalytic dark reaction.

The vulnerability of surface adsorbed rhodamine B towards $^\bullet O_2^-/^\bullet HO_2$ radicals attack could not be ruled out in the present case because in absence of pollutant it suffers slow photodegradation as evident by the disappearance of the characteristic spectral features of rhodamine B in spectrum of the solid mass, obtained after filtration of the reaction mixture that undergone prolonged photolysis (10 h). However, in presence of pollutants instead of self-degradation of surface adsorbed sensitizer dyes, pollutants undergo decomposition as observed experimentally (Table 1). The results in Table 1 are explicable in term of the following that under specified reaction conditions the concentration of pollutants is highly in excess as compared to the concentration of surface adsorbed dyes. As a result interaction of pollutants molecules with $^\bullet O_2^-/^\bullet HO_2$ radicals would be kinetically more viable than with immobilized dye molecules.

The extent of degradation for surfactants (Table 1) have been found to in the following order DBS (anionic) > Triton X 100 (neutral) > CPC (cationic). A similar observation in this regard was reported earlier [35]. The comparatively low degradation of cationic CPC may be explained in terms of the Coulombic repulsion between cationic CPC and positively charged surface of the TiO_2 semiconductor particle (which becomes more acidic due proton liberation during photolysis) and as a result approach of the cationic CPC towards TiO_2 semiconductor particle surface is hindered and as a consequence electron transfer reaction between active sites and cationic molecules could not take place effectively.

4. Conclusion

The results of the present studies evidently demonstrate that in presence of visible light the surface adsorbed methylene blue and rhodamine B dyes can sensitize air-equilibrated TiO_2 semiconductor particulate system for generation of oxidizing and highly reactive $^{\bullet}O_2^-/^{\bullet}HO_2$ radical species. Repeated attack of these radical species on to organic pollutant molecules results in their ultimate decomposition to carbon dioxide.

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