Evidence of superoxide radical formation in the photodegradation of pesticide on the dye modified TiO_2 surface using visible light

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Abstract

Degradation of a pesticide (atrazine) in air-equilibrated aqueous mixture has been achieved on the surface of TiO_2 semiconductor modified with thionine and eosin Y by using visible light. Under 5 h of irradiation with a 150 W xenon lamp, appreciable degradation of atrazine has been observed. A working mechanism involving excitation of surface adsorbed dye, followed by charge injection into the TiO_2 conduction band and formation of reactive $O_2^{\bullet-}/HO_2^{\bullet}$ radicals is proposed for the degradation of the pesticide to carbon dioxide. Formation of $O_2^{\bullet-}$ radical has been evidenced by using a chemiluminescent probe, luminol.
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Keywords: Photodegradation; Thionine and eosin Y; TiO_2 semiconductor; Pesticide; Chemiluminescent probe; Luminol

1. Introduction

The large amount of pesticides used in agriculture cause contamination of the quality of environmental water [1]. The removal of these non-biodegradable organic chemicals is a crucial ecological problem. The triazines group of pesticide (atrazine, prometryn, metribuzine) is applied by spraying. Polluted water resulting from the rinsing of spray container (for pest treatment in a wide range of crops) contains significant level (10–100 ppm) of this group of pesticide. The conventional chemical or biological treatment are often slow or non-effective to eliminate these stubborn organics. Although advanced oxidation process with TiO_2 photocatalysts have been shown to be an effective alternative in this regard [2–8], the vital snag 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 3.2 eV). Hence, in order to harvest maximum solar energy, it is necessary to shift the absorption threshold towards visible region. Very recently, we have explored [9,10] that the dye sensitization, a technique reported for degradation of colorants in visible light illuminated dye modified TiO_2 dispersion [11–13], could also be workable for degradation of *colorless* water bound pollutants. We had shown in our earlier reports [9,10] that semiconductor grade TiO_2 surface modified with various dye (thionine, eosin Y, rhodamine B, methylene blue) effect degradation of phenols, halocarbons, surfactants in presence of visible light and air. In the present investigation, we have selected atrazine (Fig. 1) to examine the efficacy of our photocatalytic system towards pesticide degradation. Formation of superoxide radical ($O_2^{\bullet-}$) by rapid scavenging of the conduction band electron by the dioxygen had been hypothesized in our earlier studies [9,10]. The $O_2^{\bullet-}/HO_2^{\bullet}$ radical species repeatedly attacks to the pollutant molecules in the reacting system and essentially leads the degradation of organic molecules ultimately to carbon dioxide in a secondary autocatalytic dark reaction. In the present paper, we afford the experimental evidence in favor of the formation of the superoxide radical ($O_2^{\bullet-}$) using a chemiluminescent probe, luminol. The use of luminol as a chemiluminescent probe in monitoring superoxide radical ($O_2^{\bullet-}$) in TiO_2 photocatalysis has recently been reported by Nosaka et al. [14]. We wish to report herein the results of our studies of visible light assisted decomposition of pesticide catalyzed by suspended dye modified TiO_2 semiconductor particulate system. Photocatalysts used in the present investigation are thionine and eosin Y modified TiO_2 semiconductor particles [9].

2. Experimental

2.1. Material

Semiconductor grade TiO_2 (obtained from Fluka) was used for the present investigation. Atrazine (Sigma) was used

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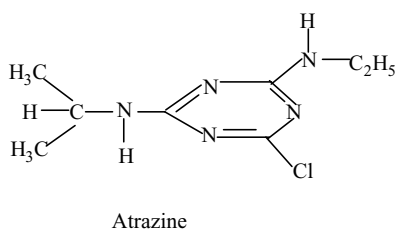*E-mail address:* dchat57@hotmail.com (D. Chatterjee).

Atrazine

Fig. 1. Pictorial representation of atrazine.

as received. All other chemicals used were of AR grade and multi-distilled water obtained from Monodest 3000E quartz multi-distillations apparatus was used throughout the experiment.

2.2. Method

Surface modification of semiconductor grade TiO_2 and characterization of surface modified dyes thionine and eosin Y were carried by adopting the procedure reported elsewhere [9]. The dye uptake estimated spectrophotometrically by measuring the free dye and in the supernatant liquid obtained after filtration was found to be 543 μeq./g for thionine and 521 μeq./g for eosin Y. Spectral (UV-Vis) measurements were carried out with a GBC Cintra 10 spectrophotometer. Fluorescence measurements were carried out in the Chemistry Department, Burdwan University, by using a Hitachi F-4010 spectrofluorometer.

2.3. Photocatalysis studies

Photocatalytic experiments were performed in a flat-surfaced glass reactor as described elsewhere [9,10]. The pre-aerated reaction mixture (50 ml) containing 100 mg of surface modified photocatalyst designated as TiO_2-D (D = thionine, eosin Y) and 0.0686 mmol of atrazine (designated as 'P' hereafter) was irradiated with a 150 W xenon lamp (Oriel Instruments) under continuous magnetic stirring. In our earlier reports [9,10], we had established that photodegradation of organics over dye modified TiO_2 catalyst is indeed visible light assisted phenomena. In the present case also we have used a filter solution containing sodium nitrite, copper sulfate and ammonium hydroxide as UV filter [15] to carry out photodegradation of atrazine and found no appreciable difference in the results of photodegradation with or without UV filter. This suggests that the UV light generated by the 150 W xenon lamp source is not effective to carry out the photodegradation of organics under specified conditions.

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 aliquot of reaction mixture was withdrawn and filtered by using a membrane filter (0.1 μm) and the change in the concentration of pollutant

in each degraded solution was monitored spectrophotometricaly at 224 nm (λ_{max} of atrazine). The chemical oxygen demand of (COD) of the photodegraded solution was determined by usual procedure (digesting 10 ml of sample using $K_2Cr_2O_7/H_2SO_4$ and subsequent titration) [16]. 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).

2.4. Detection of superoxide ($O_2^{\bullet-}$) radial

Experimentation on the detection of superoxide was carried out in a following manner maintaining the protocol reported earlier [14]. An alkaline solution (0.2 ml) of luminol (1.58 mM) was added to pre-aerated reaction mixture containing 15 mg of dye modified TiO_2 in 3.5 ml NaOH solution (0.01 M). The reaction mixture was irradiated with 50 W tungsten lamp for 15 min. The reaction mixture was filtered with a membrane filter (0.1 μm) fitted at the tip of a syringe and the filtrate was immediately subjected to spectral (emission) measurement using a Hitachi F-4010 spectrofluorometer.

3. Results and discussion

Spectral properties of thionine and eosin Y adsorbed on the surface of TiO_2 photocatalyst had been discussed in the earlier reports [9,17,18]. Preliminary experiments revealed that atrazine is adsorbed (about 10% of its initial concentration) in dark on the surface of the TiO_2 in the dark under specified conditions. As observed in the earlier studies [9,10], the TiO_2 photocatalyst, not customized with dye, could not effect the degradation of atrazine appreciably by illumination with visible light. Necessity of semiconducting nature of TiO_2 in effective photodegradation of atrazine was ascertained by the fact that dye adsorbed on non-semiconducting material alumina could not result in any appreciable degradation of atrazine after prolonged (8 h) illumination. The thionine and eosin Y dyes were found non-interacting with atrazine in the dark. However, prolonged illumination of the aqueous solution containing both free dye and atrazine caused a substantial loss of spectral features of the dyes and eventually the resulting solutions become colorless with concomitant attenuation of atrazine concentration. The loss of spectral features of the dyes as described above is associated with the reduction reaction of photo excited dyes. For thionine, the observed spectral bleaching is attributable to the one electron reduction of thionine, as thiazines and oxazines groups of dyes are known to undergo one electron reduction in their excited state followed by disproportion to produce their corresponding leuco-dyes which are almost featureless in 400–800 nm region [17]. Whereas, the formation of a reduced and hydrogenated species of eosin Y which is colorless, as reported by

Table 1
Results of TiO_2-D catalyzed photodegradation of atrazine in aerated aqueous solution

TiO_2-D	P_{in} (mmol)	P_{ur}[a] (mmol)	Degradation of P[b] (%)	CO_2[c] (mmol)
D = thionine	0.0686	0.0315	54	0.196
D = eosin Y	0.0686	0.026	62	0.24

[a] Concentration of unreacted pollutant (P_{ur}) after 5 h of reaction.
[b] Based on pollutant concentration taken, i.e. $(P_{in} - P_{ur}/P_{in}) \times 100$.
[c] Mineralized CO_2 estimated after 5 h of reaction.

Arakawa and coworkers [18] in case of free eosin Y/TEOA system, seems to be the reason for having the colorless photolyzed solution of the eosin Y containing atrazine in the present case. It may be noted here, that photolysis of free dyes with other pollutants also exhibited the similar spectral changes [9,10] as noticed in the present case.

Results of photodegradation of atrazine with dye modified TiO_2 are summarized in Table 1. We had followed the degradation of atrazine spectrophotometrically by monitoring the decrease in absorbance at 224 nm. As the photodegradation of atrazine evolved CO_2 alongwith some unidentified intermediate(s) containing fewer carbon atoms than atrazine, the COD decreased with irradiation time. The variation of COD with irradiation time is shown in Fig. 2a, whereas Fig. 2b displays the concomitant CO_2 mineralization yield with irradiation time. Since, we are limited to spectrophotometric methods with regard to product identification and the absorbances of fleeting or comparatively stable intermediate (cyanuric acid) lie in the region 200–208 nm [19], we could not identify any particular intermediate spectrophotometrically. However, decrease in atrazine concentration in the photolyzed solution together with concomitant decrease in COD and formation of CO_2 undeniably substantiate the degradation of atrazine under specified conditions.

In absence of oxygen photodegradation of the atrazine was found to be negligible. This further emphasizes the essential role of oxygen for effective photodegradation of organics [20].

On the basis of the above experimental results and considering the earlier reports [9,10] on the visible assisted degradation of organics on dye modified TiO_2 semiconductor, a
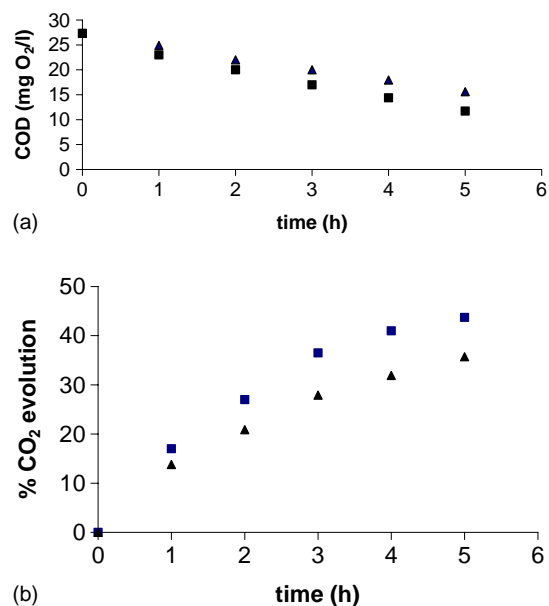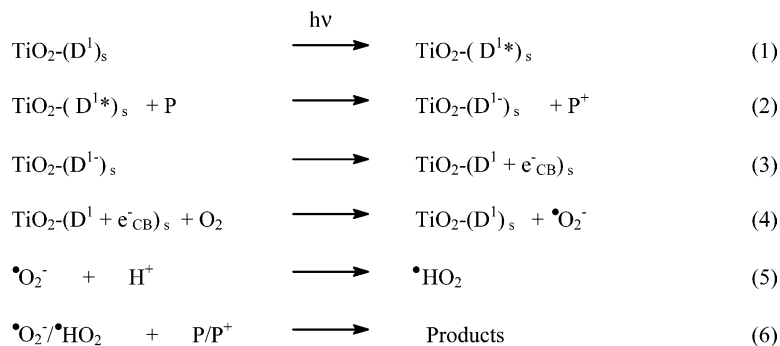

Fig. 2. (a) Decrease in COD with irradiation time in photocatalytic decomposition of atrazine in dye fixed TiO_2 system at pH = 5.0, atrazine = 0.0686 mmol: (▲) thionine; (■) eosin Y. (b) Evolution of CO_2 with irradiation time in photocatalytic decomposition of atrazine in dye fixed TiO_2 system at pH = 5.0, atrazine = 0.0686 mmol: (▲) thionine; (■) eosin Y.
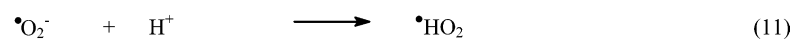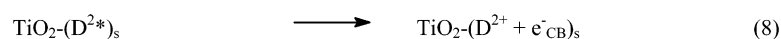
mechanism is suggested for photocatalyzed degradation of atrazine (Schemes 1 and 2).

The results of the previous work [9] clearly demonstrated that the surface adsorbed thionine or eosin Y dyes though differ in their excited state redox behaviors, can sensitize TiO_2 semiconductor by effecting charge injection to the conduction band for degradation of various organic pollutants. It had been presumed that the oxygen present in the reacting system interacts with the electron of the conduction band of TiO_2 semiconductor to produce $O_2^{\bullet-}/HO_2^{\bullet}$ species which essentially promote degradation organic molecules in a secondary autocatalytic dark reaction. In the present work, we have used chemiluminescent probe, luminol to detect the superoxide radical ($O_2^{\bullet-}$) in the reacting

$$TiO_2\text{-}(D^1)_s \xrightarrow{h\nu} TiO_2\text{-}(D^{1*})_s \tag{1}$$

$$TiO_2\text{-}(D^{1*})_s + P \longrightarrow TiO_2\text{-}(D^{1-})_s + P^+ \tag{2}$$

$$TiO_2\text{-}(D^{1-})_s \longrightarrow TiO_2\text{-}(D^1 + e^-_{CB})_s \tag{3}$$

$$TiO_2\text{-}(D^1 + e^-_{CB})_s + O_2 \longrightarrow TiO_2\text{-}(D^1)_s + {}^{\bullet}O_2^- \tag{4}$$

$${}^{\bullet}O_2^- + H^+ \longrightarrow {}^{\bullet}HO_2 \tag{5}$$

$${}^{\bullet}O_2^-/{}^{\bullet}HO_2 + P/P^+ \longrightarrow Products \tag{6}$$

($h\nu$ = visible light ; D^1 = thionine ; P = atrazine)

Scheme 1.

$$\text{TiO}_2\text{-}(\text{D}^2)_s \xrightarrow{\ h\nu\ } \text{TiO}_2\text{-}(\text{D}^{2*})_s \tag{7}$$

$$\text{TiO}_2\text{-}(\text{D}^{2*})_s \longrightarrow \text{TiO}_2\text{-}(\text{D}^{2+} + e^-_{CB})_s \tag{8}$$

$$\text{TiO}_2\text{-}(\text{D}^{2+} + e^-_{CB})_s + P \longrightarrow \text{TiO}_2\text{-}(\text{D}^2 + e^-_{CB})_s + P^+ \tag{9}$$

$$\text{TiO}_2\text{-}(\text{D}^2 + e^-_{CB})_s + O_2 \longrightarrow \text{TiO}_2\text{-}(\text{D}^2)_s + {}^\bullet O_2^- \tag{10}$$

$${}^\bullet O_2^- + H^+ \longrightarrow {}^\bullet HO_2 \tag{11}$$

$${}^\bullet O_2^-/{}^\bullet HO_2 + P/P^+ \longrightarrow \text{Products} \tag{12}$$

$$(h\nu = \text{visible light}; D^2 = \text{eosin Y}; P = \text{atrazine})$$

Scheme 2.

system. The results of luminescence studies are displayed in Fig. 3. It had been reported [14] that the interaction of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) with superoxide radical ($O_2^{\bullet-}$) produces a light-emitting species 3-aminophthalate (AP), which upon excitation by 387 nm light shows a emission maximum at 420 nm. Photolysis of reaction mixture containing thionine and eosin Y adsorbed TiO_2 and luminol produces AP as evidenced by the emission spectra shown in Fig. 3a and b, respectively. The emission maxima noticed in both the cases is 417 nm which
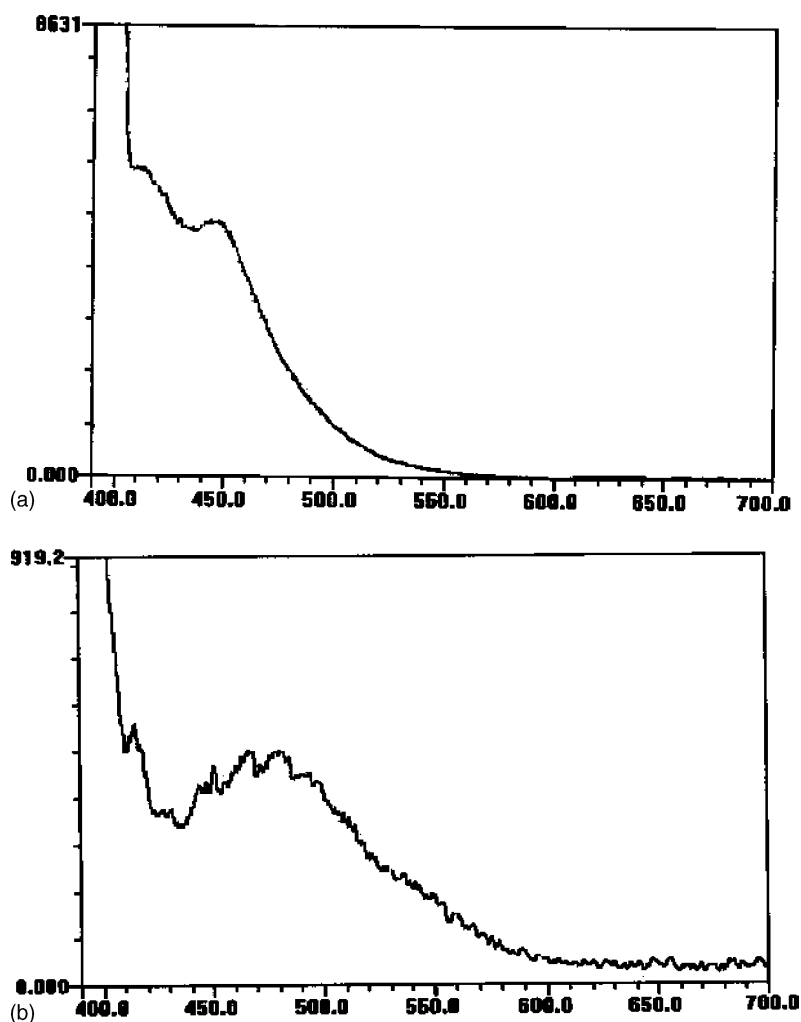

Fig. 3. Emission spectra of photolyzed solution of luminol: (a) photocatalyst used is thionine adsorbed TiO_2; (b) photocatalyst used is eosin Y adsorbed TiO_2. Excitation wavelength = 387 nm.

is in very good agreement to characteristic emission maximum (420 nm) of AP [14]. In absence of luminol no peak at 417 nm was observed in the luminescence spectrum. Formation of AP from luminol/luminol radical thus confirms the existence of superoxide radical ($O_2^{\bullet-}$) in the present reacting system (Scheme 2).

As reported earlier [9,10] in case of degradation of other organic pollutants the vulnerability of surface adsorbed dyes (thionine/eosin Y) towards $O_2^{\bullet-}$/$HO_2^{\bullet}$ radicals attack could not be discarded in the present case also because in absence of atrazine it suffers slow photodegradation as evident by the disappearance of the characteristic spectral features of surface adsorbed dyes (thionine/eosin Y) in spectrum of the solid mass, obtained after filtration of the reaction mixture that undergone prolonged photolysis (10 h). However, in presence of atrazine instead of self-degradation of surface adsorbed sensitizer dyes (thionine/eosin Y), it effects decomposition of atrazine 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 $O_2^{\bullet-}$/$HO_2^{\bullet}$ radicals in the reacting system would be kinetically more viable than with immobilized dye molecules.

4. Conclusion

The results of the present work evidently demonstrate that dye modified TiO_2 semiconductor particulate system is not only effective in degrading various organic pollutants like phenols, halocarbons, surfactants [9,10] in presence of visible light, but also efficiently decomposes pesticide under similar experimental conditions. Involvement of $O_2^{\bullet-}$/$HO_2^{\bullet}$ radical species in the present photodegradation process has been experimentally evidenced by chemiluminescence studies.

Acknowledgements

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