

Photoassisted degradation of dye pollutants in aqueous TiO₂ dispersions under irradiation by visible light

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Abstract

The photoassisted degradation of two dye compounds, erythrosine and rhodamine B, has been investigated in an aqueous TiO₂ dispersion under irradiation by visible light. The compounds can be easily decomposed photochemically by visible light, which provides possibly a new approach for the treatment of dye pollutants in wastewater.

Keywords: Photodegradation; Dye; Titanium dioxide

1. Introduction

In recent years, the photocatalytic purification of water by irradiated titanium dioxide particles has proven to be a very effective process, which leads to the complete mineralization of organic substrates [1–7]. The photocatalyst used, titanium dioxide (anatase), is however a wide bandgap semiconductor ($E_g = 3.2$ eV), and thus only the light with wavelengths below 400 nm can be absorbed by TiO₂ particles to generate e^-/h^+ pairs [8] which are prerequisite for the photodegradation process. It is known that < 5% of the solar energy reaching the surface of the earth is ultraviolet light, which is too little to achieve significant photodegradation in

short time. Artificial light sources (such as mercury lamp or Xe-lamp) need high electrical power; they are also expensive and unstable. All these factors place some limitations on the application of TiO₂ in the treatment of wastewaters.

The sensitization process for photographic science and photoelectrochemistry has been extensively reported [9–15]. A dye molecule in its excited state generated upon irradiation with visible light can inject an electron into the conduction band of semiconductor particles. Watanabe et al. [9,10] gave a photochemical evidence for the electron transfer mechanism of the sensitization process in which a dye molecule (rhodamine B) underwent a *N*-deethylation reaction when CdS particles were suspended in the aerated dye solution. Dye pollutants from

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the textile industry and photographic industry are a principal source of environmental contamination [16,17]. In China, above 1.6×10^9 m³ of dye-containing wastewater per year drains into environmental water system without treatment. The photodegradation of several dye compounds in aqueous TiO₂ suspensions with ultraviolet irradiation has been reported [18–20]. It is expected that these colored compounds can also be degraded in the presence of TiO₂ particles with visible irradiation because of their absorption spectra in the visible region. The mechanism of the photoassisted degradation under visible light illumination will be different from that taking place under UV light illumination, the former is to excite the dye compounds directly and the latter is to generate an e⁻/h⁺ pairs as a result of irradiating the TiO₂ particle with ultraviolet light which then initiates the degradation of organic compounds. Research into the photoassisted degradation with visible light should elucidate a new mechanism of photodegradation (to some extent) and should prove useful for application of photochemical technology to the treatment of dye polluted wastewaters.

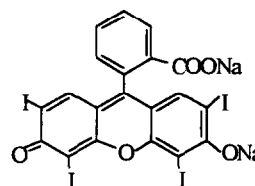
Kamat et al. have reported on the photodegradation of dyes preadsorbed on the surface of TiO₂ particles with visible light [21,22], in which the photoreaction system was almost water-free and only the molecules that were in direct contact with the TiO₂ surface (the molecules at monolayer or submonolayer coverage) underwent photodegradation.

In this paper, the photochemical decomposition of two dye compounds, erythrosine (Er) and rhodamine B (Rh), was investigated in an aqueous TiO₂ dispersion under irradiation by visible light. Although in some cases they may not be the major pollutants, they can be adsorbed strongly on the surface of TiO₂ particles and inject an electron into the conduction band of TiO₂ from their respective excited states [9,10]. This study was undertaken to obtain valuable information on the photodegradation with semiconductor particles under illumination

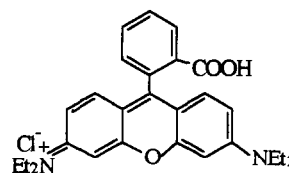
in the visible region. For comparison, the photodegradation behavior of rhodamine B in the presence of SiO₂ insulator particles was also examined.

2. Experimental details

Samples of erythrosine and rhodamine B (purchased from Beijing Chemical; see formula below) were of analytic grade and were used without further purification. Titanium dioxide was kindly supplied by Degussa. (P-25, mainly anatase, surface area of 55 m²/g). The water used was deionized and doubly distilled throughout.



Erythrosine Disodium Salt



Rhodamine B

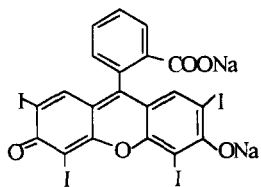
An aqueous suspension of a dye (2.0×10^{-5} M, 50 ml) and TiO₂ (25 mg) was contained in a 70 ml Pyrex glass vessel and was stirred overnight in the dark to permit the adsorption/desorption equilibrium to be reached. Subsequently, the dispersion was irradiated under air-equilibrated conditions. The light source was a 500 W halogen lamp (made by the Insti-

tute of Electric Light Source of Beijing) equipped with a light cut-off filter to completely remove wavelengths below 470 nm to guarantee illumination with visible light. A 3 ml aliquot was taken at various intervals; it was filtered through a Millipore membrane filter (pore size 0.2 μm) prior to analysis. Variations in the concentration of dyes in each degraded solution were monitored by UV–Vis spectroscopy (Shimadzu 1600A, absorption at λ_{max} , 526 nm for erythrosine and at 554 nm for rhodamine B). Iodide ion concentrations were determined by Ion Chromatography (Shimadzu LC-10AS). The CO_2 evolution was assayed by Gas Chromatography (Shimadzu GC-7AG) using TCD detection [4]. Before irradiation, the vessel (66.5 ml) containing 50 ml of TiO_2 dispersion was closed with a septum and was purged with pure oxygen gas for 30 min enabled excess oxygen to exist.

3. Results and discussion

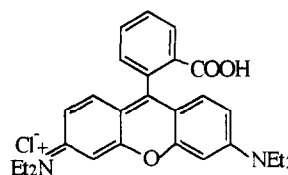
3.1. The degradation of anionic erythrosine dye

Variations in the absorption spectra of erythrosine during its photocatalyzed degradation was recorded at various irradiation times with visible light (Fig. 1). The absorption peaks of erythrosine decreased with increasing the irradiation time and the absorption bands disappeared after irradiation for 2 h, which indicated the degradation of erythrosine. A new peak appeared at $\lambda_{\text{max}} = 215.5 \text{ nm}$ which increased with irradiation time. We attribute this peak to I^- ion



Erythrosine Disodium Salt

Fig. 1. Absorption spectra of erythrosine in the photocatalytic degradation under irradiation with visible light.



Rhodamine B

Fig. 2. The photodegradation of erythrosine ($2.0 \times 10^{-5} \text{ mol/l}$, 50 ml) in an aqueous TiO_2 (25 mg) suspension with visible light, (a) Er/ TiO_2 + light, (b) Er + light, (c) Er/ TiO_2 in dark, (d) I^- ion formation.

formed in the degradation of erythrosine as evidenced by measurements both with the ion chromatography and by comparison with the absorption spectra of standard KI aqueous solutions.

The temporal changes in the concentrations of erythrosine (curve a) and I^- ions (curve d) in the photodegradation process are illustrated in Fig. 2. The difference in the concentration before irradiation in the presence and absence of TiO_2 particles is caused by the adsorption of erythrosine on the TiO_2 surface (about 10%). In the presence of TiO_2 particles, erythrosine underwent a rapid degradation under irradiation by visible light; concomitantly, I^- ions were generated gradually. The degradation of erythrosine and formation of I^- ions follow apparent first-order kinetics with rate constants, $k_d = 3.6 \times 10^{-2} \text{ min}^{-1}$ ($t_{1/2} = 19 \text{ min}$) and $k_f = 2.3 \times 10^{-2} \text{ min}^{-1}$, respectively. Identical results for changes in the concentration of I^- ions formed were obtained from ionic chromatographic measurements and from calculations based on the intensities of the I^- absorption of Fig. 1. After 4 h of irradiation, the degradation yield of erythrosine to I^- ions was about 65%. Further irradiation led to a slight increase in the concentration of I^- ions but could not reach a stoichiometric conversion possibly owing to the adsorption of the formed I^- ions on the TiO_2 surface as evidenced by a control experiment.

The oxidation potentials of the dyes examined and the band edges of the TiO_2 semiconductor (anatase, at neutral condition) are illus-

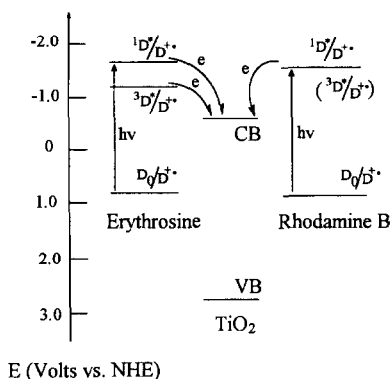
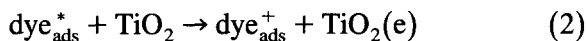


Fig. 3. Energy diagram describing the oxidation potentials of dyes and the band-edge potentials of the conduction and valence bands of TiO_2 semiconductor at neutral conditions.

trated in Fig. 3. An erythrosine molecule in its excited state can inject an electron into the conduction band of TiO_2 [21], subsequent to which it undergoes chemical changes if the cation radical formed does not regenerate in a time less than a time needed for its decomposition (Eqs. (1)–(3)).



In an aqueous dispersion system composed of dye and TiO_2 particles, the dye molecules in the solution can diffuse to and adsorb on the TiO_2 surface, and then may undergo photodegradations until all the molecules in solution are decomposed.

For comparison, an aqueous erythrosine solution was also irradiated in the absence of TiO_2 particles under otherwise identical conditions. Curve b in Fig. 2 shows a relative slower degradation process compared to that in the presence of TiO_2 particles. The erythrosine concentration versus irradiation time decreased linearly, from which we refer a zero-order process likely implicating singlet oxygen which reacts with ground-state molecules of erythrosine to initiate its degradation [23,24].

By contrast, no degradation occurred when an erythrosine– TiO_2 aqueous dispersion was

stirred without irradiation (curve c, Fig. 2). It is also evident from Fig. 3 that the energy level of the erythrosine ground state is below the conduction band of TiO_2 and hence the dye molecules cannot inject electrons into the conduction band without irradiation, or in fact into a surface state within the bandgap even in the dark.

3.2. The degradation of cationic rhodamine B dye

The photoassisted degradation of the cationic dye rhodamine B (Rh), a dye often used as a tunable laser dye because of its stable photochemical property [25], was carried out as a function of irradiation time with visible light in the presence and absence of TiO_2 particles. The results are depicted in Fig. 4. After an induction time (1 h), rhodamine B degraded by an apparent zero-order kinetics in the presence of TiO_2 particles (curve a in Fig. 4), however, the degradation rate was slower compared to the decomposition of the anionic erythrosine dye. No degradation occurred in the absence of TiO_2 particles (curve d). For comparison, no changes occurred when the suspension was stirred in the dark (curve b in Fig. 4), a result similar to the one for the erythrosine system. An excited rho-

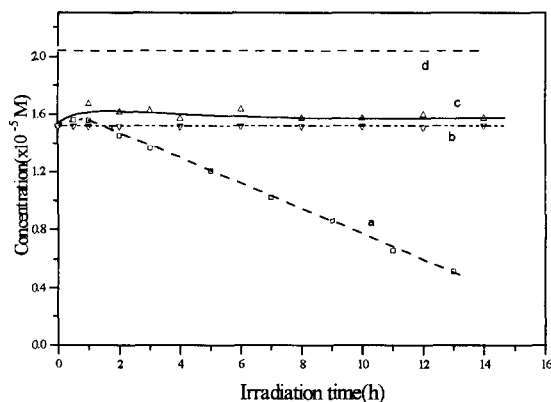


Fig. 4. The photodegradation of rhodamine B (2×10^{-5} mol/l, 50 ml) in an aqueous TiO_2 (25 mg) suspension with visible light, (a) Rh/ TiO_2 + light, (b) Rh/ TiO_2 in dark, (c) Rh/ SiO_2 + light, (d) Rh + light.

damine B molecule can also inject electrons into the conduction band of TiO₂ particles (Fig. 3), and then initiates its degradation. In a dispersion in which the insulator material SiO₂ particles was used instead of TiO₂ as a reference support in this experiment, no degradation was occurred even after 13 h of irradiation (curve c).

It is interesting to note that the absorption bands of both erythrosine and rhodamine B dyes decreased and finally disappeared during the degradation, and that no new absorption bands appeared both in the visible and ultraviolet regions, especially the bands pertaining to aromatic moieties and other similar intermediates (except the new peak of I⁻ ions in erythrosine degradation). This is different from the photocatalyzed degradation of many organic compounds in the presence of TiO₂ under irradiation by ultraviolet light, in which intermediates can easily be detected by absorption spectra [4,26].

Table 1 presents the CO₂ evolution from the TiO₂-suspended and TiO₂-free aqueous solution of dyes after irradiation for 24 h. An initial concentration of 1×10^{-4} mol/l was employed for each dye solution so as to lower the CO₂ measurement error. Under our experimental conditions, the mineralization yields of dyes into CO₂ were 28.1% and 19.3% for erythrosine and rhodamine B, respectively, after irradiation for 24 h. Further irradiation led to an increase in the formation of CO₂. Only 8.0% of conversion of erythrosine into CO₂ was observed in a TiO₂-free system after the same irradiation time and no CO₂ evolution was detected from the free TiO₂ system of rhodamine B. A control experiment showed that no CO₂ was evolved if

the dispersion was purged with pure nitrogen gas instead of oxygen gas. Determination of intermediates, role of reduced oxygen, as well as further studies on the mechanism of the photoassisted degradation of dyes in aqueous TiO₂ dispersion using visible light are in progress.

In summary, the erythrosine and rhodamine B dyes can be degraded in an aqueous TiO₂ dispersion under irradiation by visible light. This provides yet another approach to the treatment of dye polluted waters.

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Table 1
Conversion of dyes into CO₂ (%)^a

	Erythrosine		Rhodamine B	
	TiO ₂ -free	with TiO ₂	TiO ₂ -free	with TiO ₂
Before irradiation	0	0	0	0
Irradiation for 24 h	8.0	28.1	0	19.3

^a Initial dye concentration: 1×10^{-4} mol/l, TiO₂: 2 g/l.

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