



Photocatalytic degradation of the dye sulforhodamine-B: A comparative study of different light sources

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Abstract

The photocatalytic degradation of dye pollutant sulforhodamine-B (SRB) in aqueous titanium dioxide (TiO₂) dispersions was examined under three lighting regimes: UV light (330 nm < λ < 380 nm), sunlight, and visible light (λ > 450 nm), all investigated at pH=2.5. Total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) assays show that the degradation rate of SRB is much higher when irradiated with UV and sunlight compared with visible light. The temporal concentration changes of SRB illustrated a first-order reaction and the rate constant, k , is 0.197 min⁻¹, 0.152 min⁻¹, 0.027 min⁻¹, respectively, under the three lighting conditions. The final mineralized products were amine compounds identified by infrared spectrophotometry. When irradiated with visible light, the photocatalytic degradation rate could be improved by lowering the H₂O₂ concentration and inhibited by increasing the H₂O₂ concentration, but results contrary to the above were obtained when UV light was used for irradiation.

Key words: TiO₂; photocatalytic degradation; sulforhodamine-B (SRB)

Introduction

Titanium dioxide (TiO₂) has been intensively investigated as a photocatalyst since Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes in 1972 (Honda and Fujishima, 1972). Recently, the application of TiO₂ as a photocatalyst has mainly focused on the elimination of toxic and hazardous organic substances and metal ions (Ohko *et al.*, 2001; Fox and Dulay, 1993) in wastewater, drinking water, and air in view of environmental protection (Hoffmann *et al.*, 1995; Fujishima *et al.*, 2000; Legrini *et al.*, 1993). There are certain distinct advantages such as chemical stability, low toxicity, and low cost, when TiO₂ is used as a photocatalyst (Herrmann *et al.*, 1993). However, the band gap of 3.2 eV for TiO₂ anatase limits its photoresponse in the ultraviolet region (λ < 387 nm), which severely limits its application in photochemical oxidation technology. Use of the photocatalytic process to degrade organic dye pollutants with visible light has important industrial implications because it can use the relatively inexpensive solar light. Some studies showed that the electron transfer between dyes and semiconductor particles can take place under visible and UV illumination and that some dyes can be degraded to smaller organic substances and ultimately mineralized completely to water, carbon dioxide, and other inorganic

ions (Linsebigler *et al.*, 1995; Vinodgopal *et al.*, 1996; Zhao *et al.*, 1998). However, the experimental results reported in these investigations are limited to irradiation by visible and UV light and do not include the effect of sunlight (Liu and Zhao, 2000; Chen *et al.*, 2001; Horikoshi *et al.*, 2002). Research on the effect of different lighting regimes on TiO₂-induced photocatalytic degradation of organic dyes has helped determine how light activates a catalyst and how an appropriate light source should be selected to degrade various pollutants. In this article, the photocatalytic degradation of the dye sulforhodamine-B (SRB) in aqueous TiO₂ dispersions was examined at pH 2.5 under three lighting regimes: UV light (330 nm < λ < 380 nm), sunlight, and visible irradiation (λ > 450 nm). Total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}) assays show that the degradation rate of SRB is much higher when irradiated with UV and sunlight compared with visible light. The reaction rate kinetics of SRB degradation is first-order with a rate constant, k , of 0.197 min⁻¹, 0.152 min⁻¹, 0.027 min⁻¹, respectively, for UV light, sunlight, and visible light. The final mineralized products were amine compounds.

1 Experimental

1.1 Materials

TiO₂ powders (ca. 80% anatase, 20% rutile; BET surface area, ca. 50 m²/g) were supplied by Degussa. Horseradish peroxidase (POD) was purchased from

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Lizhudongfeng Biologic Technique, and N,N-diethyl-phenylenediamine (DPD) reagent was purchased from Merck. The dye sulforhodamine-B (structure is given in Fig.1) was of spec-pure grade (Across), and the other chemicals were of analytical reagent grade. Deionized and double-distilled water was used throughout the experiments. The pH of the solution was adjusted using either dilute HClO₄ or NaOH.

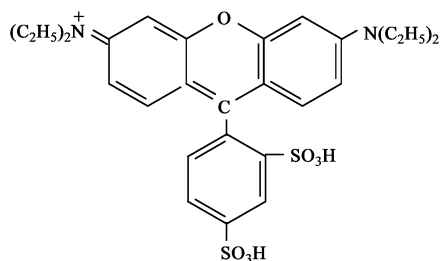


Fig. 1 Molecular structure of sulforhodamine-B (SRB) in acid.

1.2 Instruments

UV-visible spectroscopy (Model 3010, Hitachi), TOC/TN analysis (Multi N/C 2100, Jena), and infrared spectroscopy (Nicolet) were used to monitor the degradation process. A Luminometer-ST (Beijing Photoelectric) was used to measure light intensity. A centrifuge (Beijing Medicine and Application) was used to separate the TiO₂ powders from suspensions.

1.3 Photoreactor and light source

A photoreaction device for visible light was constructed. The source of visible light was a 500-W halogen lamp (Electrical Equipment and Illumination Company) positioned inside a double-quartz cylindrical Pyrex vessel surrounded by a circulating water jacket to cool the lamp. A cutoff filter was also placed outside the Pyrex jacket to eliminate radiation below 450 nm to ensure that only visible light was used for the irradiation of the dispersion. The intensity of visible light was 70.6×10^3 I_x. The UV light source was a 100-W mercury lamp, the intensity of which was 103×10^3 I_x. When sunlight was the light source, irradiation occurred between 12:00 am and 2:30 pm, and the intensity was $(80 \pm 5) \times 10^3$ I_x.

1.4 Experiment methods

An aqueous solution of SRB (2×10^{-5} mol/L, 50 ml) at pH 2.5 with suspended TiO₂ (1.0 g/L) was stirred in a 70-ml Pyrex vessel. Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibria of the dye on the surface of the TiO₂ particle. At given irradiation time intervals, samples (3 ml) were removed, centrifuged, and then filtered through a Millipore filter (0.22 μm). The filtrates were analyzed using UV-visible spectroscopy to examine the decomposition of SRB ($\lambda_{\text{max}} = 565$ nm). Assays of the chemical oxygen demand (COD_{Cr}) were carried out using the potassium dichromate titration method (Chinese National Standard, 1989). The COD_{Cr} of the

suspensions (50 ml of 4×10^{-5} mol/L SRB, TiO₂ loading 1.0 g/L) was measured directly without removal of the TiO₂ powders at various irradiation time intervals. Changes in the TOC of the suspensions (50 ml of 4×10^{-5} mol/L SRB, TiO₂ loading 1.0 g/L) were determined using a TOC analyzer after filtration at various irradiation time intervals. Samples for infrared (IR) spectroscopy were prepared using a method similar to that used for TOC.

The concentration of H₂O₂ at various reaction intervals was determined using the DPD method (Bader *et al.*, 1988).

2 Results and discussion

2.1 Photocatalytic degradation of SRB under visible light

The UV-Visible spectral changes of SRB (2.0×10^{-5} mol/L, 50 ml) in aqueous TiO₂ (1.0 g/L) dispersions are shown in Fig.2. The absorbance maximum at 565 nm is close to zero after irradiation for 120 min.

2.2 Degradation kinetics of SRB under irradiation with UV light, sunlight, and visible light

Fig.3 shows the comparison of degradation kinetics of SRB in aqueous solutions with and without TiO₂ under three types of irradiation and at different time intervals. In the dark, SRB is not decomposed and the degradation rate of SRB under all the three types of irradiation was faster in TiO₂ dispersions compared with dispersions without TiO₂. The observed decrease in the concentration of SRB in aqueous TiO₂ suspensions exposed to sunlight point to a photosensitized oxidation process (Kamat, 1993; Zhang *et al.*, 2002). Furthermore, the broken line in Fig.3 shows a blueshift in the SRB absorbance peak that indicates the occurrence of N-de-ethylation. Similar observations have been made earlier in SRB/TiO₂/UV or visible light systems (Liu *et al.*, 2000). Thus, N-de-ethylation occurs during the photosensitized oxidation of SRB under solar light or exposure to visible or UV irradiation. The relevant kinetic plots obtained under the above-described conditions are shown in Fig.4. Analysis of the results indicates that photocatalytic destruction of SRB in aqueous TiO₂ dispersions follows first-order kinetics for all the three types of irradi-

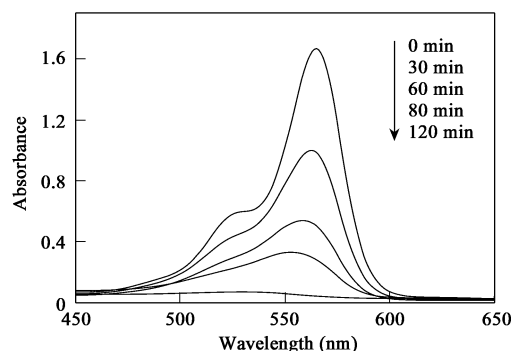


Fig. 2 UV-Visible spectral changes for the degradation of SRB under visible light. Irradiation for 0, 30, 60, 80, and 120 min. [SRB] = 2.0×10^{-5} mol/L, TiO₂ = 1.0 g/L, pH = 2.5.

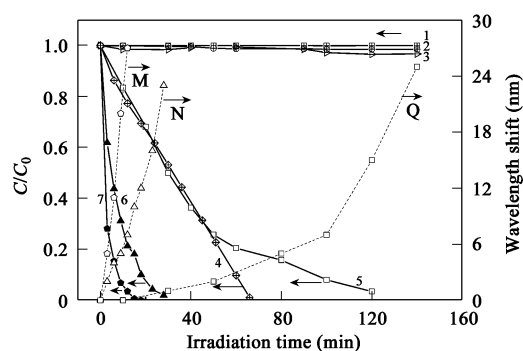


Fig. 3 Degradation of SRB under different light sources and the shift of maximum absorption. (1) SRB, dark; (2) SRB, visible light; (3) SRB, TiO₂, dark; (4) SRB, UV; (5) SRB, TiO₂, visible light; (6) SRB, TiO₂, sunlight; (7) SRB, TiO₂. The shift in maximum absorption is shown as broken lines under irradiation with three types of light sources: (M) UV; (Q) visible light; (N) sunlight.

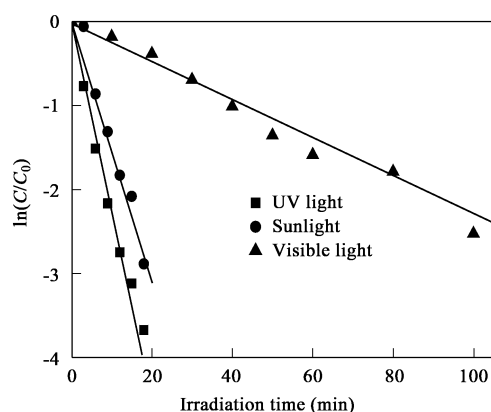


Fig. 4 First-order kinetic plots. The conditions are similar to those in Fig. 3. [SRB] = 2.0×10^{-5} mol/L, TiO₂ = 1.0 g/L, pH = 2.5.

ation. For UV, solar, and visible light irradiation, the rate constants are 0.197 min^{-1} , 0.152 min^{-1} , and 0.027 min^{-1} , respectively. The results also indicate that the reaction rate is much higher when the dispersions are exposed to UV or solar irradiation compared with visible light.

Figs. 3 and 4 show that SRB can be photocatalytically decomposed in aqueous TiO₂ dispersion illuminated by visible, solar, or UV light radiation. The decomposition data are consistent with the first-order kinetics. Details on the light intensity, rate constant, and the correlation coefficient (R^2) are shown in Table 1.

Table 1 Degradation rate of SRB (2×10^{-5} mol/L) dispersions under the three lighting regimes

Light source	Intensity $\times 10^3$ (I_x)	Rate constant (min^{-1})	Correlation coefficient (R^2)
UV light	103	0.197	0.99238
Solar light	80 ± 5	0.152	0.98911
Visible light	70.6	0.027	0.99205

2.3 Measurement of TOC and COD_{Cr}

Changes in the COD_{Cr} and TOC values reflect the degree of degradation or mineralization of an organic

substrate during the irradiation period. Fig. 5 shows the changes in COD_{Cr} and TOC during the degradation of SRB under three types of irradiation. The results show that the mineralization of SRB occurs during the decomposition of the chromophore of SRB. Interestingly, the change in COD and TOC values under all the three types of irradiation is very similar to the degradation kinetics: UV and solar light are more efficient in degrading SRB compared with visible light.

To verify the degree of mineralization, COD_{Cr} and TOC reductions are summarized in Table 2. COD_{Cr} values for the irradiated SRB/TiO₂ suspensions finally decrease by 95.0%, 93.4%, and 82.0% for UV, solar, and visible light, respectively. TOC removal is 66.2%, 65.3%, and 43.7% under the three types of irradiation.

Table 2 COD_{Cr} and TOC removals in SRB dispersions under irradiation with three types of light sources

Light source	Irradiation time (min)	TOC removal (%)	Mineralization extent (%)
UV light	75	66.2	95.0
Solar light	200	65.3	93.4
Visible light	360	43.7	82.0

[SRB] = 2×10^{-5} mol/L; pH = 2.5; TiO₂ = 1.0 g/L.

2.4 Detection of H₂O₂ generated during the photodegradation process

The H₂O₂ produced during the photodegradation of the dye/TiO₂ dispersions at various reaction intervals was determined using the DPD method and is shown in Fig. 6. The

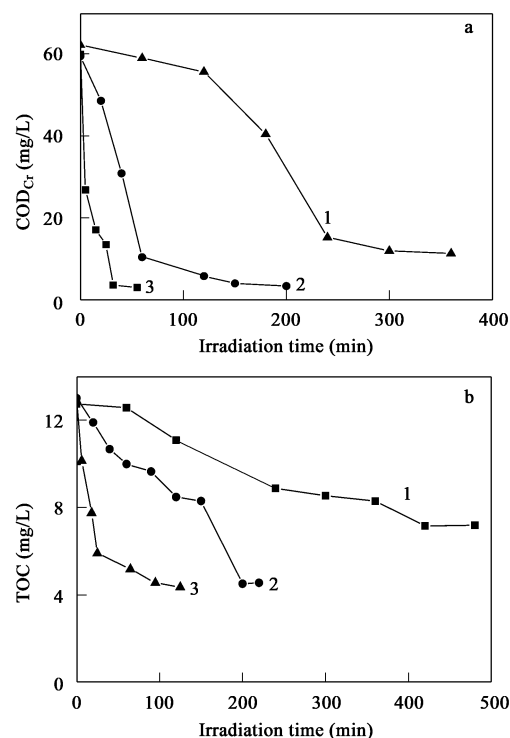


Fig. 5 Changes of COD_{Cr} (a) and TOC (b) during degradation of SRB under irradiation with three light sources. (1) visible light; (2) sunlight; (3) UV. [SRB] = 2.0×10^{-5} mol/L; TiO₂ = 1.0 g/L; pH = 2.5.

dyes were first excited using visible light. Subsequently, the excited state inject electron into the conduction band of TiO_2 . The injected electron captures the oxygen molecules (O_2) that are adsorbed on the surface of TiO_2 and forms the oxidative species $\text{O}_2^{\cdot-}$ and then forms H_2O_2 (Wu *et al.*, 1999). The maximal concentration of H_2O_2 was 6.3×10^{-6} mol/L after 60 min of irradiation. The concentration of H_2O_2 gradually decreased and then reached equilibrium (5.4×10^{-6} mol/L).

2.5 Effect of the addition of H_2O_2 during the degradation process

Investigations were carried out on the effect of addition of H_2O_2 during the degradation process under irradiation with UV and visible light. The formation mechanisms of H_2O_2 were different in the dye/ TiO_2 dispersions under irradiation with UV and visible light (Hirakawa and Nosaka, 2002). Under UV illumination, H_2O_2 could be produced not only by the oxidation of H_2O by the positive holes and adsorption of OH^\cdot on the TiO_2 but also by the further oxidation of $\text{O}_2^{\cdot-}$. The consumption of H_2O_2 was mainly facilitated by the electron reduction and the oxidation of positive holes (Kormann *et al.*, 1988; Hoffmann *et al.*, 1994). However, during the process of photocatalysis under visible light, H_2O_2 was produced mainly by the constant reduction of oxygen molecules adsorbed on the surface of TiO_2 and consumed mainly due to photolysis of the surface complexes, $\text{Ti}^{4+}/\text{H}_2\text{O}_2$ (Li *et al.*, 2001). The reaction rate is accelerated only when the consumption and formation of H_2O_2 reach equilibrium. Otherwise, the reaction rate decreases.

The effect of addition of H_2O_2 on the degradation of SRB was tested by increasing the H_2O_2 concentration from 2×10^{-6} mol/L to 5×10^{-2} mol/L (Fig.7). As we know, it is mainly the positive holes, but the $\cdot\text{OH}$ that participate in the oxidation of the dye irradiated by UV light. Because the small amount of H_2O_2 is easier to be adsorbed and oxidized by the positive holes on the surface of TiO_2 , competing with dye SRB for the oxidation reaction with the positive holes, it eventually decreases the degradation rate of SRB. The results indicate that the addition of high concentrations of H_2O_2 may increase direct photolysis under UV light due to the formation of $\cdot\text{OH}$ that is formed

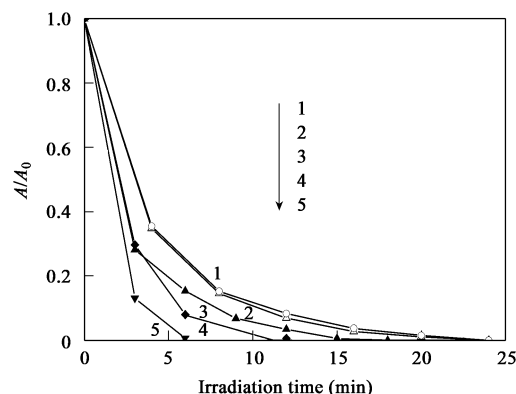


Fig. 7 Effect of addition of H_2O_2 during the degradation process under irradiation with UV light. (1) $[\text{H}_2\text{O}_2] = 2 \times 10^{-6}$ mol/L; (2) $[\text{H}_2\text{O}_2] = 2 \times 10^{-4}$ mol/L; (3) free H_2O_2 ; (4) $[\text{H}_2\text{O}_2] = 2 \times 10^{-2}$ mol/L; (5) $[\text{H}_2\text{O}_2] = 5 \times 10^{-2}$ mol/L.

by the rapid photolysis of H_2O_2 .

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In contrast, the photocatalyst could be activated at low concentration and inhibited at high concentration under irradiation with visible light when the concentration of H_2O_2 added was increased from 2×10^{-6} mol/L to 1.0 mol/L (Fig.8). The H_2O_2 molecule can easily adsorb on the surface of TiO_2 and form yellow surface complexes ($\equiv\text{Ti}^{\text{IV}}\text{-OOH}$), which show photoresponse to visible light and can be excited by visible light. The generation of $\cdot\text{OH}$ radicals is proof of the occurrence of electron transfer process between surface complexes and TiO_2 conduction band under visible light irradiation (Li *et al.*, 2001). When the concentration of H_2O_2 added is higher, the photodegradation rate of SRB is also high. The greater the amount of H_2O_2 adsorbed on the surface of TiO_2 , the easier will be transfer of the surface electron, which will result in the more rapid degradation of SRB. However, when the amount of H_2O_2 is too high, the H_2O_2 that could not be effectively photolyzed by the visible light is gradually adsorbed on the surface of TiO_2 and hinders the formation of molecular oxygen and surface complexes ($\equiv\text{Ti}^{\text{IV}}\text{-OOH}$), eventually decreasing the rate of degradation of SRB.

2.6 Infrared spectra analysis

The IR spectra shown in Fig.9 were used to identify the degradation products of SRB (2×10^{-5} mol/L) dispersions ($\text{pH} = 2.5$; $\text{TiO}_2 = 1.0$ g/L) under the three types of irradiation. The principal bands in the IR spectra of SRB

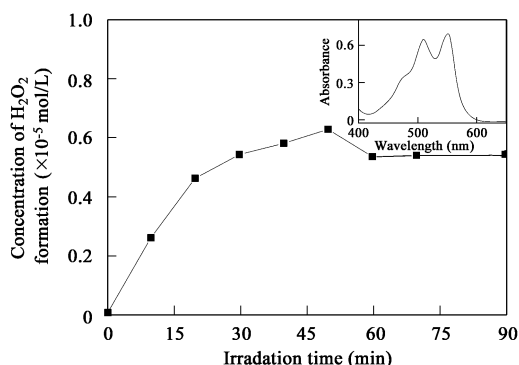


Fig. 6 The detection of H_2O_2 generated during the degradation of SRB under visible light. $[\text{SRB}] = 2 \times 10^{-5}$ mol/L, $\text{TiO}_2 = 1.0$ g/L, $\text{pH} = 2.5$; inset figure: the spectrophotometric DPD method is used ($\lambda = 551$ nm).

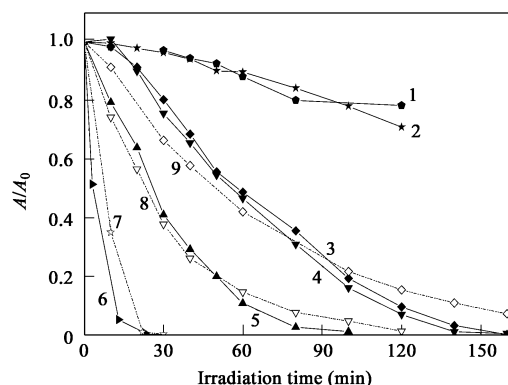


Fig. 8 Effect of additions H_2O_2 during the degradation process under visible light. (1) TiO_2 +dark+SRB+ H_2O_2 ; (2) SRB+ H_2O_2 +h ν ; (3) free H_2O_2 ; (4) $[\text{H}_2\text{O}_2]=2\times 10^{-6}$ mol/L; (5) $[\text{H}_2\text{O}_2]=2\times 10^{-4}$ mol/L; (6) $[\text{H}_2\text{O}_2]=2\times 10^{-2}$ mol/L; (7) $[\text{H}_2\text{O}_2]=5\times 10^{-2}$ mol/L; (8) $[\text{H}_2\text{O}_2]=2\times 10^{-1}$ mol/L; (9) $[\text{H}_2\text{O}_2]=1.0$ mol/L.

are available in previously published reports; the bands at 1590, 1558, 1530, 1510, 1490, and 1470 cm^{-1} corresponded to aromatic ring vibrations, whereas the 1344 cm^{-1} band corresponded to aryl-C bond vibrations (Mchedlov *et al.*, 1995). The bands at 1120–1145 cm^{-1} and 628–625 cm^{-1} are caused by vibrations in the $-\text{SO}_3^{2-}$ group, the band at 1649 cm^{-1} is attributed to vibrations of the carbon-nitrogen, and the band at 1530–1558 cm^{-1} is caused by heterocyclic vibrations. During photooxidation, the band of vibrations characteristic of the carbon-nitrogen band (1649 cm^{-1}), the aryl-C bond (1344 cm^{-1}), the aromatic ring, and heterocyclic vibrations (1470–1590 cm^{-1}), all decreased with irradiation time and eventually disappeared (Fig.9a). The IR results confirm that the large conjugated chromophore structure of SRB is destroyed under all three types of irradiation. The infrared spectra of the mineralized products that are ultimately formed under three types of irradiation are shown in Fig.9b. The absorption bands produced by amines appeared at 2500, 1600, and 1400 cm^{-1} , and a strong new IR band appeared at 1150 cm^{-1} , attributable to C–N vibrations. These results indicate that the final mineralized products were amine compounds. The differences between our results and those found in

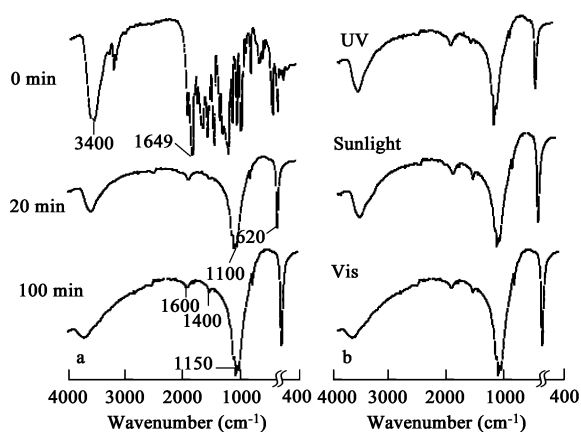


Fig. 9 Analysis of infrared spectra. (a) Temporal variations in the IR spectra of SRB under UV irradiation; (b) the IR spectra of the ultimate product under irradiation with three types of light sources.

previously published reports likely due to the use of HClO_4 instead of HCl to adjust the pH. This research needs to be investigated further.

2.7 Photodegradation mechanism for dyes irradiated by sunlight

The scheme shown in Fig.10 illustrates a possible mechanism of the degradation of dye illuminated by sunlight. The oxidation potential of the SRB dye's excited state to the cationic radical ($E(\text{D}^*/\text{D}^+)$) is -1.30 V vs. NHE (Liu *et al.*, 2000), lies above the conduction band edge of TiO_2 ($E_{\text{cb}}=-0.5$ V vs. NHE), the potentials for reduction of oxygen to superoxide ion ($E(\text{O}_2/\text{O}_2^-) = -0.15$ V vs. NHE), and for the reduction of H_2O_2 to hydroxyl radical ($E(\text{H}_2\text{O}_2/\cdot\text{OH}) = 0.3$ V vs. NHE) lie below the conduction band edge (Jaeger and Bard, 1979; He *et al.*, 1998). There is no doubt that electron injection from the dye to the conduction band of TiO_2 yields cationic radicals, a process that is determined by the nature of HOMO orbits of the excited state. Therefore, the photogenerated electrons in the excited dye have sufficient energy to produce the superoxide ion and hydroxyl radicals under solar irradiation.

The dye SRB adsorbed on TiO_2 is mainly oxidized by a photogenerated hole localized at the surface of the irradiated TiO_2 by sunlight including UV light, thereby accelerating the transformation of dye cationic radicals to cationic radicals that are easily attacked by hydroxyl radicals (Shkrob and Sauer, 2004). So the photocatalyst shows good photoactivity under solar irradiation.

3 Conclusions

Research was carried out to compare the degradation of sulforhodamine-B in aqueous TiO_2 dispersions under three types of irradiation. TOC and COD_{Cr} assays were used to monitor the degradation rate. The final mineralized products were amine compounds analyzed by IR spectra. This investigation showed that the photocatalyst showed good photoactivity when sunlight was used as the source

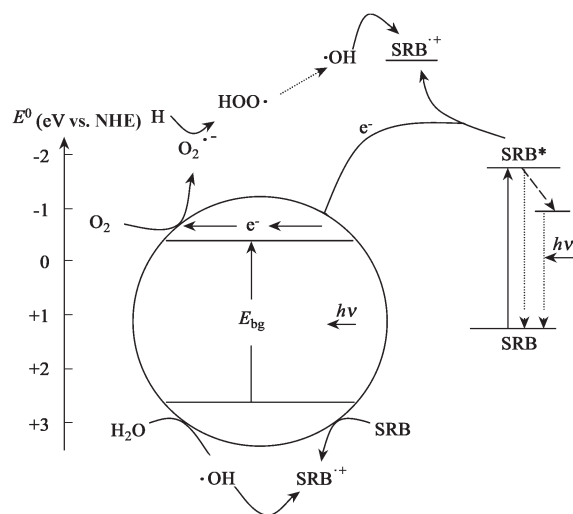


Fig. 10 Possible mechanism for the degradation of dye illuminated by solar radiation.

of irradiation. It was found that, when visible light was used for irradiation, the photocatalytic degradation could be improved by the addition of low concentrations of H_2O_2 and inhibited by high concentrations, but results contrary to the above were obtained when UV light was used for irradiation. The photodegradation mechanism of SRB irradiated by solar radiation was also investigated and a plausible mechanism has been suggested.

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