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The photocatalytic oxidation of phenylmercaptotetrazole in TiO_2 dispersions

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Abstract

Phenylmercaptotetrazole (PMT) undergoes photocatalytic oxidation in aerated TiO_2 dispersions on irradiation with UV light ($\lambda > 330$ nm). The kinetic process of photodegradation of PMT was monitored by following the changes in the absorption spectrum and total organic carbon (TOC) on irradiation. From a comparison with the degradation of phenyltetrazole (PTZ) and mercaptotetrazole (MTZ), a mechanism involving the formation of CO_2, SO_4^{2-}, NO_3^- and NH_4^+ is proposed for the degradation of PMT. In addition, the influence of the reaction environment on the photodegradation of PMT is discussed. © 1997 Elsevier Science S.A.

Keywords: Phenylmercaptotetrazole; Photocatalysis; Photodegradation; TiO_2

1. Introduction

In recent years, photocatalysis using metal oxide semiconductors has been studied extensively with regard to the partial or total mineralization of organic compounds and the reduction of inorganic compounds [1–5]. In this field, TiO_2 has often been used because of its high efficiency and photostability. It has been established that the photocatalysed reaction is initiated by the photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the catalyst (Eq. (1)). The photogenerated electrons possess a reducing power equivalent to the conduction band energy, and the holes possess an oxidizing power equivalent to the valence band energy. For example, in the case of TiO_2 at pH 7, $E_{CB}(e^-) = -0.84$ V (normal hydrogen electrode (NHE)) and $E_{VB}(h^+) = 2.39$ V (NHE) [6]. This means that e^- and h^+ are strong reducing and oxidizing species respectively. The bulk photoelectrons and photoholes can recombine with each other to produce thermal energy, or can migrate rapidly to the surface and react with adsorbates. The high oxidative potential of the holes in the catalyst permits the direct oxidation of organic matter (OM) to give reactive intermediates (Eq. (2)). Holes can also react with surface hydroxyl groups to produce hydroxyl radicals (Eqs. (3) and (4)) [7]. Hydroxyl radicals are extremely strong, non-selective, oxidants ($E^0 = +3.06$ V) [8], which lead to partial or complete mineralization of organic chemicals.

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$OM + TiO_2(h^+) \rightarrow OM^{\bullet +} + TiO_2 \quad (2)$$

$$H_2O + TiO_2(h^+) \rightarrow {}^{\bullet}OH + H^+ + TiO_2 \quad (3)$$

$$OH^- + TiO_2(h^+) \rightarrow {}^{\bullet}OH + TiO_2 \quad (4)$$

$$O_2 + TiO_2(e^-) \rightarrow O_2^{\bullet -} + TiO_2 \quad (5)$$

The trapped electrons are removed by a suitable electron acceptor. In most cases, $O_2(g)$ is the normal electron scavenger (Eq. (5)). The production of superoxide anion has been confirmed by Hidaka et al. [9] using electron spin resonance experiments. In addition to acting as a scavenger, the presence of O_2 leads to an increase in upward band bending, and therefore suppresses the electron–hole recombination process resulting in more efficient photoactivity [10].

Phenylmercaptotetrazole (PMT) is a toxic organic material in waste solutions from photographic development. Its chemical and electrochemical properties are very stable [11]. The photodegradation of PMT in TiO_2–H_2O has been investigated due to its environmental consequences. Phenyltetrazole (PTZ) and mercaptotetrazole (MTZ) were also studied so as to probe the mechanism of photodegradation of PMT. The reaction and intermediates were monitored by following

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the changes in the absorption spectrum and total organic carbon (TOC) on irradiation.

2. Experimental section

2.1. Materials

PMT, PTZ and MTZ were of analytical grade (Aldrich). TiO_2 powder (commercial product of Beijing Chemical Factory), consisting of approximately 100% anatase, was used as photocatalyst. The average diameter of the TiO_2 particles was about 160 nm with a specific surface area of 10.9 $m^2\ g^{-1}$ [12].

All the other chemicals used in the experiments were analytical grade reagents. Doubly distilled deionized water was used for solution preparation.

2.2. Apparatus and measurements

All the photoreactions were carried out in a home-built photochemical reactor described previously [12]. TiO_2 powder (0.3 g) was dispersed in 150 ml of solution containing PMT at the desired concentration, and the pH of the system was adjusted using 0.1 mol l^{-1} NaOH or $HClO_4$. The mixture was stirred ultrasonically for about 15 min to obtain well-distributed TiO_2 powder. The dispersion was irradiated with a 300 W high-pressure mercury lamp ($\lambda > 330$ nm) with continuous stirring and O_2 bubbling (approximately 0.5 l min^{-1}); cooling was provided by cold water.

At the desired irradiation times, 5 ml dispersions were sampled and centrifuged immediately. The solutions were used for analysis. Absorption changes caused by irradiation were measured on a Hewlett-Packard 845A diode array UV–visible spectrophotometer. The TOC content of the samples was determined using a TOC-500 analyser (Shimadzu Company).

3. Results and discussion

3.1. Spectral changes of PMT in TiO_2 dispersions on UV irradiation

Fig. 1 shows the spectral changes of PMT (1×10^{-4} mol l^{-1}) in a TiO_2 dispersion with O_2 bubbling on illumination. The spectral absorption of PMT decreases successively on illumination. This indicates that the concentration of PMT in the TiO_2 dispersion decreases on irradiation. As shown in curve 0 in Fig. 1, PMT exhibits two peaks: one at 208 nm due to transition of the phenyl ring and one at about 250 nm (shoulder). As shown in Fig. 1, the absorption around 250 nm disappears very rapidly, whereas that at 208 nm decreases very slowly. In order to follow the degree of photodegradation of PMT, the absorption changes at 208 nm were chosen. Fig. 2 shows the corresponding changes in the relative absorption (A/A_0) during irradiation. A_0 and A are the initial absorption and the absorption at different irradiation times respectively. After irradiation for 60 min, A/A_0 decreases to about 0.2. This means that 80% of PMT has been degraded after irradiation for 60 min.

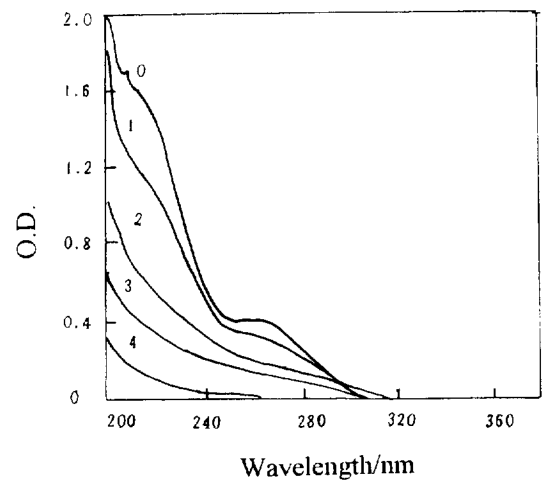


Fig. 1. Spectral evolution of PMT (1×10^{-4} mol l^{-1}) in an aqueous suspension of TiO_2 (2 g l^{-1}) during irradiation. The irradiation times from 0→4 were 0, 10, 30, 40 and 60 min respectively; pH 3.14.

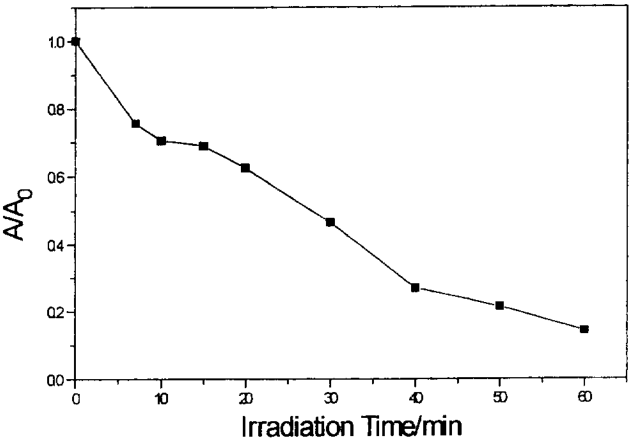


Fig. 2. Relative absorbance ($\lambda = 208$ nm) vs. time profiles for PMT in aqueous suspensions of TiO_2 during irradiation; pH 3.14.

The above results clearly show that PMT in aerated TiO_2 suspension can be photodegraded on irradiation. It should be noted that both O_2 and TiO_2 are necessary for the photodegradation of organic compounds. When O_2 bubbling is replaced by N_2, or when TiO_2 is absent, no spectral changes occur.

3.2. Mechanism of photodegradation of PMT

Fig. 3 shows the variation in TOC during the photodegradation of PMT (5×10^{-4} mol l^{-1}). TOC decreases to 13% of the initial amount after reaction for 5 h. In addition, after 5 h, SO_4^{2-}, NO_3^- and NH_4^+ can be determined by ion chromatography. Their concentrations are 4×10^{-4}, 3.4×10^{-6} and 3.4×10^{-5} mol l^{-1} respectively. Therefore the following evolution for the photodegradation of PMT is assumed

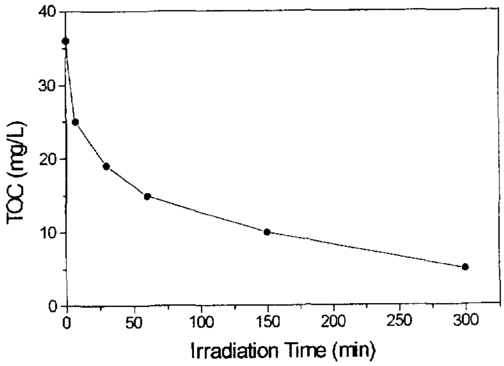


Fig. 3. Change in TOC vs. illumination time for PMT (5×10^{-4} mol l^{-1}) in an aqueous suspension of TiO_2; pH 3.07.

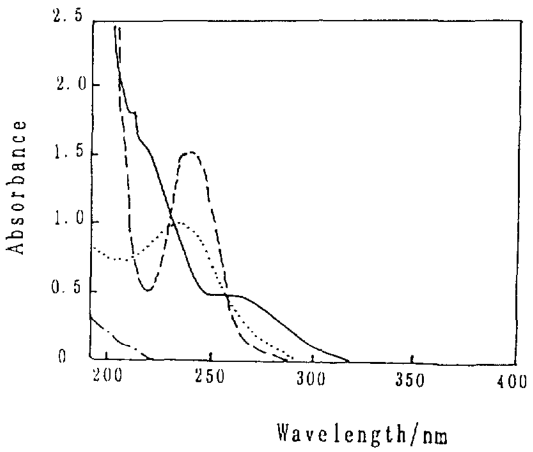


Fig. 4. Absorption spectra of PMT, PTZ, MTZ and TZ. Concentration, 1×10^{-4} mol l^{-1}. PMT (——); PTZ (– – –); MTZ (· · ·); TZ (– · –).

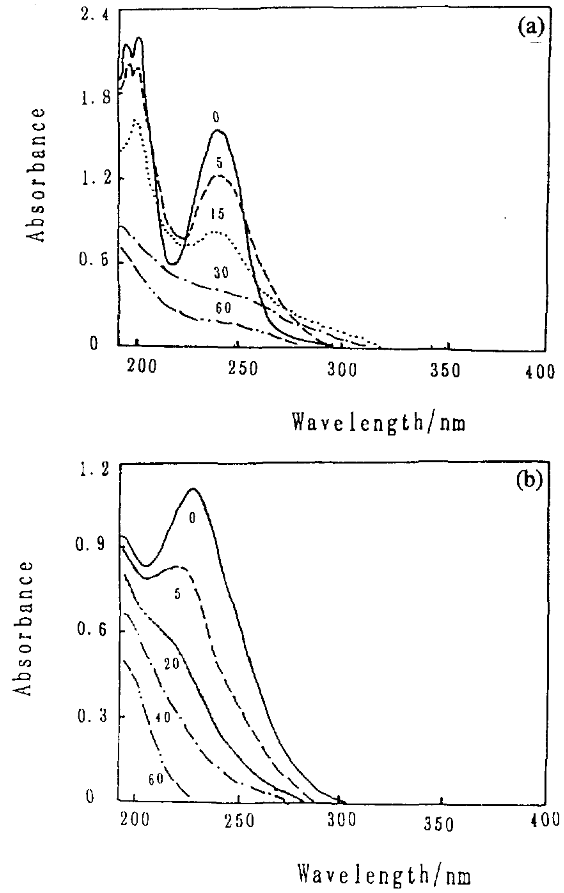


Fig. 5. Spectral evolution of 1×10^{-4} mol l^{-1} PTZ (a) and 1×10^{-4} mol l^{-1} MTZ (b) in an aqueous suspension of TiO_2 (2 g l^{-1}) during irradiation. The numbers represent the irradiation times (min); pH 3.14.

$$C \rightarrow CO_2 \qquad (6a)$$

$$S \rightarrow SO_4^{2-} \qquad (6b)$$

$$N \rightarrow NO_3^-, NH_4^+ \qquad (6c)$$

According to the stoichiometry of the reaction, the phenyl ring of PMT is nearly completely oxidized to CO_2, almost 80% of the mercapto group (–SH) is oxidized to SO_4^{2-}, but only 2% of the tetrazole ring is converted into NO_3^- and NH_4^+ after reaction for 5 h. Therefore, when PMT is photodegraded, the phenyl ring and mercapto group are easily oxidized and mineralized, but the tetrazole ring is relatively stable.

The PMT molecule consists of a phenyl ring, mercapto group and tetrazole ring. In order to study the photodegradation mechanism of PMT, the optical absorption spectra of tetrazole (TZ), PTZ and MTZ were measured, and the photodegradation processes of PTZ and MTZ were studied. As shown in Fig. 4, PTZ and MTZ exhibit absorption peaks at 235 nm and 225 nm respectively; TZ exhibits a very weak absorption in the range 190–220 nm. From Fig. 4, it can be concluded that the shoulder around 250 nm is related to the coordination of the phenyl and mercapto groups with the tetrazole ring. As shown in Figs. 5 and 6, both PTZ and MTZ are degraded via a first-order dynamic process. Clearly, the kinetic process of degradation of PTZ and MTZ is simpler than that of PMT. The shoulder which disappears very rapidly during the photodegradation of PMT (Fig. 1) implies that the phenyl and mercapto groups are broken down first during the photodegradation process. Moreover, from Fig. 6(b), it can be seen that the rate constant of PTZ is somewhat larger than that of MTZ. Therefore the oxidation of the phenyl group into CO_2 is easier than that of the mercapto group into SO_4^{2-}. This agrees well with the results of TOC and ion chromatography. It can also be seen from Figs. 1 and 5 that tetrazole is much more difficult to degrade compared with the phenyl and mercapto groups. From the viewpoint of the molecular structure, –SH can be oxidized easily because of its reduction properties. For the phenyl ring in PMT, the electron densities of the carbon atoms are not equal as in benzene, because of the n–π conjugation of the nitrogen atom with the phenyl ring, making the phenyl group more active than that in benzene. The carbon atom in the phenyl ring, which binds with the nitrogen atom, acquires more negative charge, and should be preferentially attacked by the oxidant. A possible mechanism for the degradation of PMT is given in Scheme 1. For adsorbed PMT molecules, the sulphur atom is in contact with TiO_2, and –SH can be attacked directly by

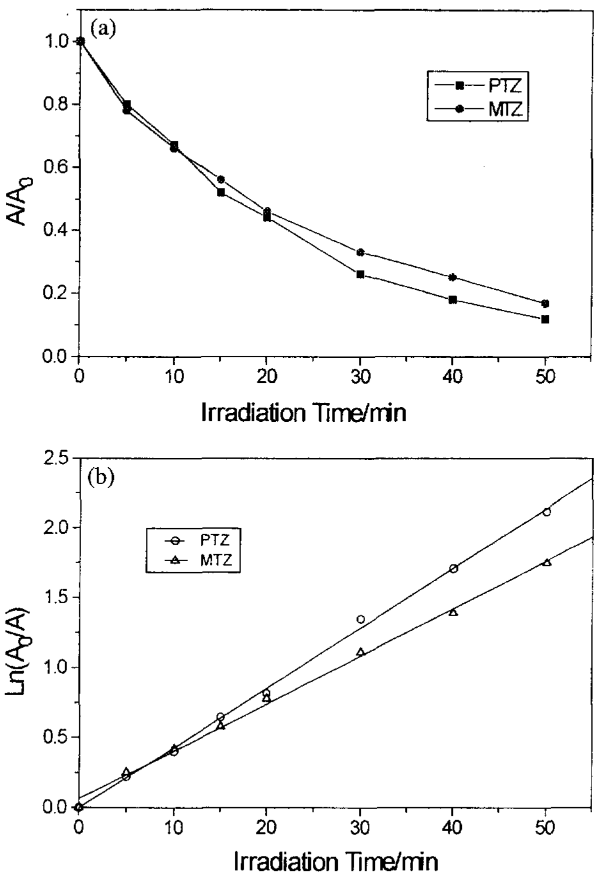


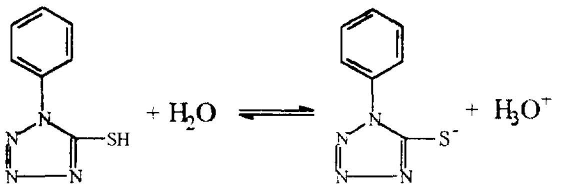
Fig. 6. (a) Relative absorbance vs. time profiles during the irradiation of PTZ and MTZ in an aqueous suspension of TiO_2; pH 3.14. (b) Dependence of $\ln(A_0/A)$ on the irradiation time for PTZ and MTZ in an aqueous suspension of TiO_2; pH 3.14.

photogenerated holes. In addition, two pathways for tetrazole attack are possible: by photogenerated holes and hydroxyl radicals. As noted above, the oxidation of the phenyl group is easier than that of the mercapto group, probably due to differences in the charge distribution on the atoms and oxidation pathways.

3.3. *Effect of pH on the photodegradation*

Fig. 7 shows the variation in pH during the photodegradation of PMT (1×10^{-4} mol l^{-1}). It can be seen that, when the initial pH value of the reaction solution is low, the variation in pH is small, otherwise it is large. According to Eqs. (3), (4) and Eqs. (6a) and (6c), protons are produced during photodegradation; therefore the pH value of the system decreases on reaction. When the initial pH of the system is very low, the H^+ produced by the reaction is negligible compared with the amount of H^+ in the bulk phase. However, in basic solution, the H^+ produced during photodegradation reacts with OH^- making the variation of pH apparent. To some extent therefore, the variation in pH indicates the degradation process of PMT.

PMT is a weak acid with a pK_a value of 3.6 [11]



(7)

As shown in Eq. (7), the existing forms of PMT are related to the pH value of the system. Hence the initial pH value of the system should influence the photodegradation process (see Fig. 8). The reaction rate and degree of photodegradation differ with different initial pH values.

The pH value of the system not only affects the existing forms of PMT in solution, but also the surface state of TiO_2. As shown in Eq. (8), a protonation equilibrium exists for TiO_2 in aqueous solution

$$\mathrm{TiOH_2^+} \overset{-\mathrm{H^+}}{\rightleftharpoons} \mathrm{TiOH} \overset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{TiO^-} \qquad (8)$$

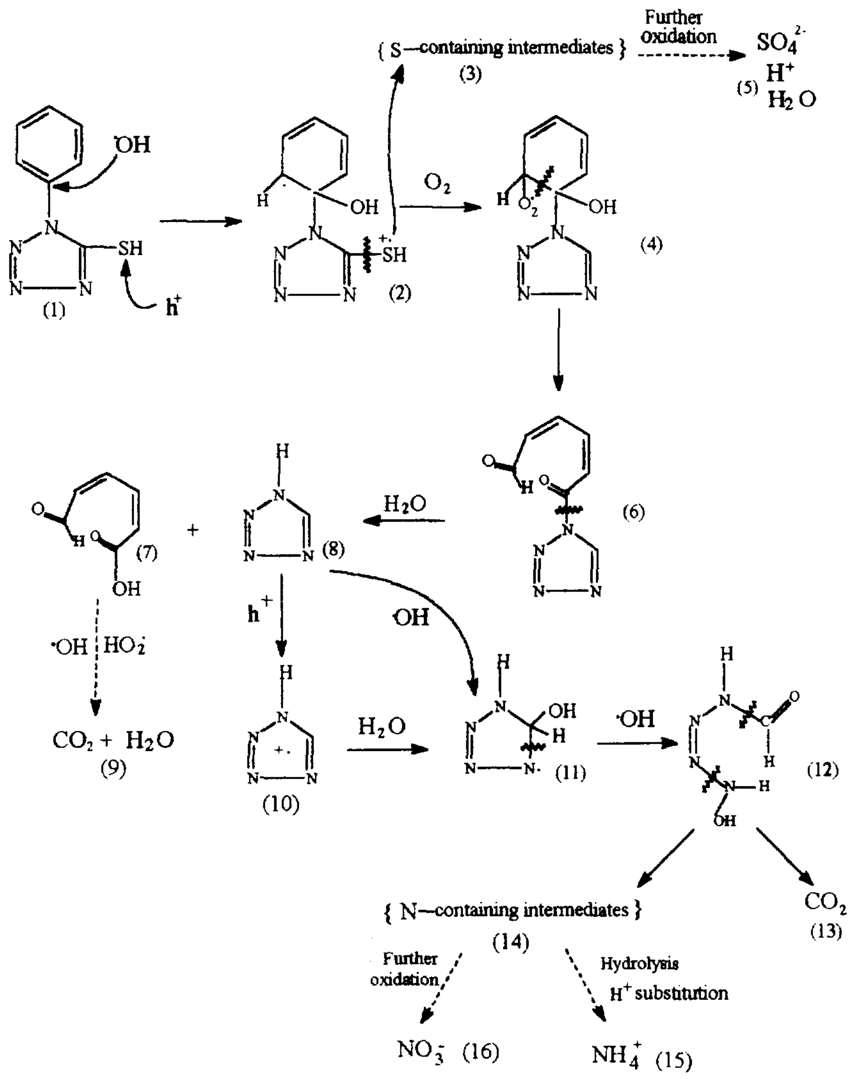
The pH_{zep} value of TiO_2 is 8.9 (23 °C) [13]. When $pH > pH_{zep}$, the surface of TiO_2 is negatively charged; otherwise, it is positively charged. The charged properties of the TiO_2 surface should affect the adsorption of substances existing in solution and the migration of photogenerated charge carriers to the surface, therefore influencing the photodegradation process.

As stated above, the surface of TiO_2 is positively charged at low pH, which facilitates the migration and adsorption of PMT^- anions to the TiO_2 surface. Therefore, at the initial stage of degradation, the concentration of PMT^- at or near the surface of TiO_2 is high, favouring electron injection from PMT to the TiO_2 particles. Therefore the reaction rate is fast at this time. However, as photodegradation proceeds, SO_4^{2-} from the oxidation of –SH will be adsorbed on the surface, decreasing the polarity of the TiO_2 surface and the active centres on the catalyst surface; moreover, the driving force for the migration of PMT and PMT^- to the surface of TiO_2 is also decreased. Therefore the reaction rate slows down as the photodegradation proceeds. Other workers [14,15] have confirmed the inhibitory effect of sulphate ions on the photocatalytic reaction.

At higher pH, the surface of TiO_2 is negatively charged, i.e. unfavourable for the adsorption of PMT^- due to the electrostatic repulsive interaction. However, the migration of photogenerated holes to the surface of TiO_2 is favoured, increasing the production of $^{\bullet}OH$. In addition, the negative charge on the surface suppresses the adsorption of SO_4^{2-} produced during the photodegradation. All of these factors increase the rate of the reaction in basic solution. When the pH of the system is very high (pH 11.7), the initial reaction rate and degree of degradation increase.

3.4. *Effect of ions on the photodegradation*

Anions and cations in the photographic developer can influence the photodegradation. In this work, the influence of



Scheme 1. Postulated mechanism of the photodegradation of PMT.

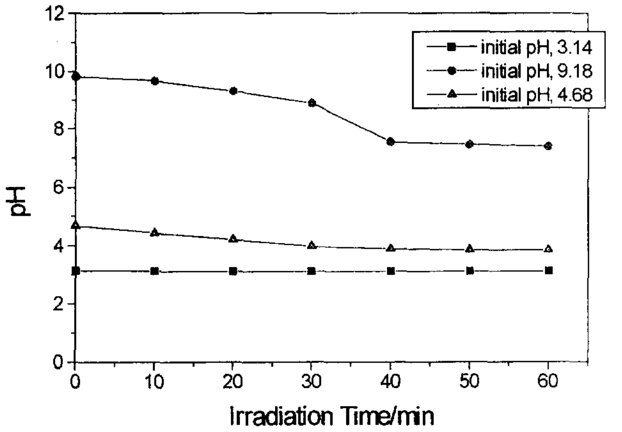


Fig. 7. Variations in the pH values during the photodegradation of PMT (1×10^{-4} mol l^{-1}).

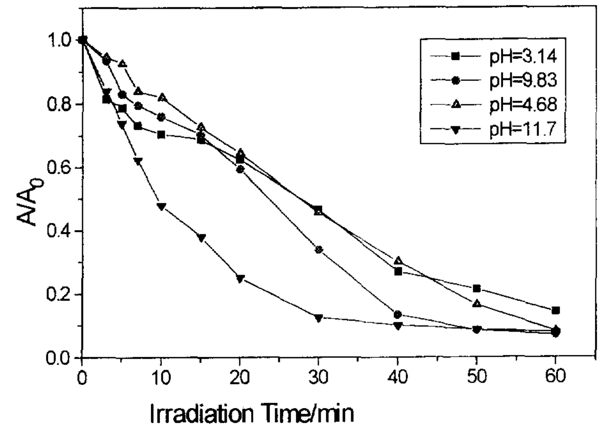


Fig. 8. Dependence of A_0/A of PMT (1×10^{-4} mol l^{-1}) on the irradiation time at different pH values.

anions, such as $S_2O_3^{2-}$, ethylenediaminetetraacetic acid (EDTA), Br^- and Cl^-, were examined. As shown in Fig. 9, $S_2O_3^{2-}$, EDTA and Br^- inhibit the degradation of PMT, whereas Cl^- has little influence; the Cl_2/Cl^- and ClO_3^-/Cl^- potentials are higher, which make the oxidation of Cl^- more difficult. $S_2O_3^{2-}$, EDTA and Br^- are adsorbed on the surface of TiO_2, which decreases the amount of active surface centres; these anions can also be photo-oxidized in competition with PMT. From Fig. 9, it can also be seen that Fe^{3+} (1×10^{-4} mol l^{-1}) accelerates the photodegradation of PMT. The Fe^{3+}

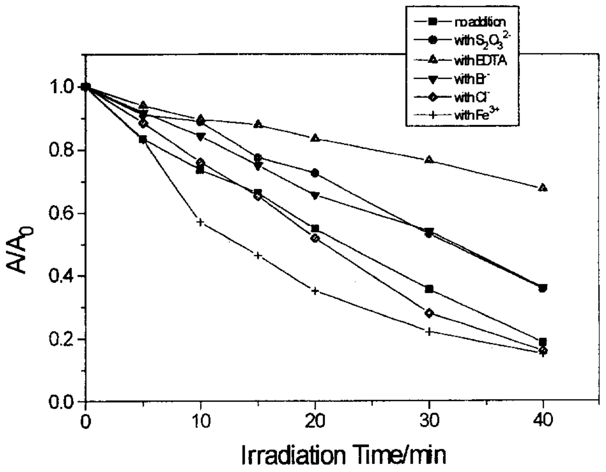


Fig. 9. Effect of ions on the photodegradation of PMT (1.0×10^{-4} mol l^{-1}). Concentration of the ions, 1.0×10^{-4} mol l^{-1}; pH 3.14.

cation may participate in the formation of hydroxyl radicals and behave as a cocatalyst [16].

Silver ions exist in photographic fixing solutions, and can form insoluble salts with PMT^- anions. Therefore the effect of silver ions on the degradation is complicated, and should be investigated further.

4. Conclusions

PMT can be photodegraded in aqueous suspensions of TiO_2 on UV illumination with O_2 bubbling. The phenyl and mercapto groups are relatively easily photo-oxidized compared with the reaction of the tetrazole ring. The reaction activities are in the order: phenyl > mercapto ≫ tetrazole. The reaction environment has an important influence on the photodegradation. $S_2O_3^{2-}$, EDTA and Br^- inhibit the degradation of PMT; Cl^- has little influence on the photodegradation; Fe^{3+} accelerates the photodegradation of PMT.

Acknowledgements

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