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Photocatalytic Degradation of Acid Azo Dyes in Aqueous TiO_2 Suspension II. The Effect of pH Values

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ABSTRACT

The photocatalytic degradation of H/K acid derived 30 dyes in aqueous TiO_2 suspension follows apparent first-order kinetics. The site near the azo bond (C–N=N– bond) is the attacked area in the photocatalytic degradation process, whilst the TiO_2 photocatalytic destruction of the C–N(=) bond and –N=N– bonds leads to fading of the dyes. The pH effect on the TiO_2 photocatalytic degradation of the H/K acid derived azo dyes varies with the different structure of the dyes. Hydroxyl radicals play an essential role in the fission of the C–N=N– conjugated system in azo dyes in TiO_2 photocatalytic degradation. © 1998 Elsevier Science Ltd

Keywords: photocatalytic degradation, acid azo dyes, pH, TiO_2.

INTRODUCTION

In 1971, Fujishima and Honda [1] noted that the semiconductor TiO_2 could produce oxygen from water by photoassisted catalysis. Several studies [2–9] have dealt with the aqueous titanium dioxide mediated photocatalytic degradation of dyes. This paper focuses on the photocatalytic degradation of H/K acid derived azo dyes in aqueous TiO_2 suspension. It has been shown that the light fastness of dyes could be evaluated using kinetic parameters determined in the liquid phase [10]. With the addition of TiO_2 suspension, in part I of this work [11], we have now studied the homogeneous photocatalytic degradation of the dyes, and give a new quick method for testing the light fastness of azo dyes. In this part, we have investigated pH effect on the degradation of acid azo dyes.

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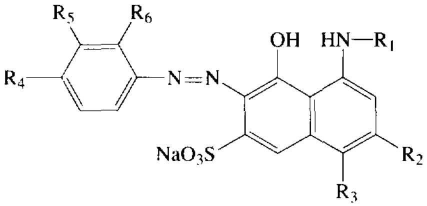
EXPERIMENTAL

The preparation of the TiO_2 suspension is as described in a previous paper [11]. The concentration of the aqueous solutions of the H/K acid azo dyes, (Table 1) was 0.05 mmol litre^{-1}. The aqueous borate or ammonium buffering solution of TiO_2 used was of concentration 0.2 mmol litre^{-1}. The degradation

TABLE 1

The Structures of the Dyes in this Study and Absorption Data of them in Aqueous Solutions



Dye	*R_1*	*R_2*	*R_3*	*R_4*	*R_5*	*R_6*	*λ_{max} (nm)*	*$\varepsilon \times 10^{-4}$ ($l\ mol^{-1}\ cm^{-1}$)*
D–13	COPh	H	$-SO_3Na$	H	H	$-SO_3Na$	506.6	1.876
D–25	COPh	H	$-SO_3Na$	H	H	$-NO_2$	514.8	1.538
D–12	COPh	$-SO_3Na$	H	H	H	$-SO_3Na$	512.2	1.202
D–16	$COCH_3$	$-SO_3Na$	H	H	H	$-NO_2$	516.4	2.324
D–23	COPh	H	$-SO_3Na$	NO_2	H	$-NO_2$	518.2	1.739
D–21	COPh	$-SO_3Na$	H	H	H	$-OCH_3$	523.8	2.231
D–9	$COCH_3$	$-SO_3Na$	H	H	H	$-OCH_3$	517.0	2.573
D–8	$COCH_3$	$-SO_3Na$	H	H	H	–COPh	508.4	2.510
D–11	SO_2Ph	$-SO_3Na$	H	H	H	H	506.6	0.845
D–2	H	$-SO_3Na$	H	H	H	H	527.2	2.473
D–30	$COCH_3$	SO_3Na	H	*p*-Cl–Ph–CO	H	H	508.2	3.48
D–19	H	$-SO_3Na$	H	H	H	$-OCH_3$	547.4	2.473
D–10	COPh	$-SO_3Na$	H	$-NH-CO-CH_3$	H	H	522.0	1.839
D–1	COPh	$-SO_3Na$	H	H	H	H	508.8	1.792
D–4	$COCH_3$	$-SO_3Na$	H	H	H	H	505.2	2.621
D–3	COPh	SO_3Na	H	*p*-Cl–Ph–CO	H	H	508.2	3.167
D–14	COPh	$-SO_3Na$	H	H	$-NH-CO-CH_3$	H	506.6	2.108
D–29	SO_2Ph	$-SO_3Na$	H	*p*-Cl–Ph–CO	H	H	508.4	3.054
D–24	H	$-SO_3Na$	H	$-NO_2$	H	$-NO_2$	642.2	2.022
D–5	$COCH_3$	$-SO_3Na$	H	$-NO_2$	H	H	532.2	2.223
D–20	$COCH_3$	$-SO_3Na$	H	$-OCH_3$	H	H	524.2	2.741
D–18	$COCH_3$	$-SO_3Na$	H	$-SO_3Na$	H	$-NO_2$	536.4	2.205
D–27	$COCH_3$	$-SO_3Na$	H	CN	H	H	505.6	2.115
D–28	$COCH_3$	$-SO_3Na$	H	–O–Ph	H	H	519.6	2.674
D–22	H	$-SO_3Na$	H	$-OCH_3$	H	H	535.4	2.971
D–7	COPh	$-SO_3Na$	H	H	$-NO_2$	H	499.4	1.819
D–15	$COCH_3$	$-SO_3Na$	H	H	$-NO_2$	H	501.2	1.785
D–17	C_2H_5	$-SO_3Na$	H	H	H	$-NO_2$	545.6	1.432
D–6	COPh	$-SO_3Na$	H	H	H	$-NO_2$	519.6	1.347
D–3	COPh	$-SO_3Na$	H	$-NO_2$	H	H	515.8	1.426

of dyes were carried out in a photochemical reaction apparatus (British Applied Photophys. Limited) with a 200 W Hg lamp. Absorption spectra were measured on a Shimadzu UV-260 UV–VIS spectrophotometer. The photocatalytic degradation kinetic constants were obtained by regression of the analytical data and calibration with D-24 (660 nm).

RESULTS AND DISCUSSION

As shown in Fig. 1, the $\pi \rightarrow \pi^*$ band of the C–N=N conjugation in the molecules of the dye locates at 520–550 nm, and at 310–330 nm at pH 10. These results indicate that the C–N=N bond and N=N bond of the dyes in this study are the sites for oxidative attack, especially in the case of TiO_2 photocatalysis. At the same time, the absorption at approximately 410 nm rises with increase of the irradiation time (Fig. 1), probably, more stable azo intermediates are formed.

The heterogeneous photoprocess has been found to be pH dependent, and the properties of the solid–liquid interface are modified as the pH value of the solution is varied. Tang and An [12] have observed that the oxidation kinetics of azo dyes as followed Langmuir-Hinshelwood kinetic model at all pH values studied. The isoelectrical point of acidic oxide TiO_2 is pH 3.5 [3]. In colloidal TiO_2 solution, the protonation of TiO_2 has two equilibria [9].

$$\begin{aligned} &-\mathrm{TiOH}_2^+ \leftrightarrow -\mathrm{TiOH} + \mathrm{H}^+ \quad && \mathrm{pk}_{a1} = 4.95 \\ &-\mathrm{TiOH} \leftrightarrow -\mathrm{TiO}^- + \mathrm{H}^+ \quad && \mathrm{pk}_{a2} = 7.8 \end{aligned}$$

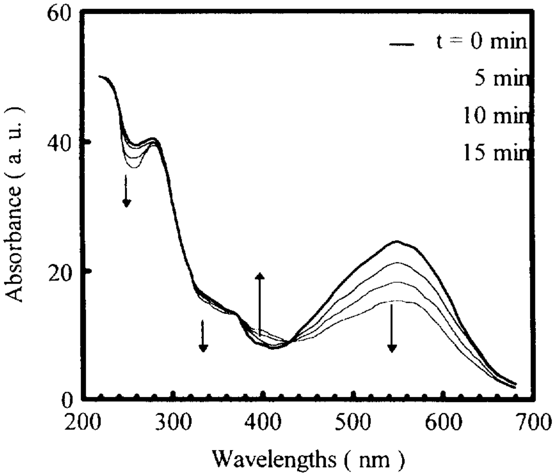


Fig. 1. Photocatalytic degradation of D-3 with irradiation time at pH 10.0.

So, the pH $_{zpc}$ (zero point of charge) of TiO_2 in aqueous solution is $3.5–(pk_{a1}+pk_{a2})/2=3.5–6.4$, at which the reactionless surface of TiO_2 physioadsorbed a sphere of water, and the photocatalytic reaction is inhibited (Fig. 2).

At pH < 3.5, the positive surface of TiO_2 can make the anions of the H/K-acid azo dyes easily aggregate via electrostatic, hydrophillic or hydrogen bonding. The increased acidity of the medium enlarges the energy gap between $E_{Dye}{}'$ /Dye and the valence band of TiO_2. The oxidation potential is increased. More importantly, azo-hydrazone tautomerism has been shown to exist in a wide range of hydroxyazo compounds where the hydroxyl group is ortho or para to the azo group. The hydrazones always absorb at longer wavelengths than their azo tautomer. Table 2 and Fig. 3 show, with increase of acidity of the aqueous solution, that the bathochromic shift of the peaks indicates the presence of more hydrazone tautomer. The hydrazone tautomer

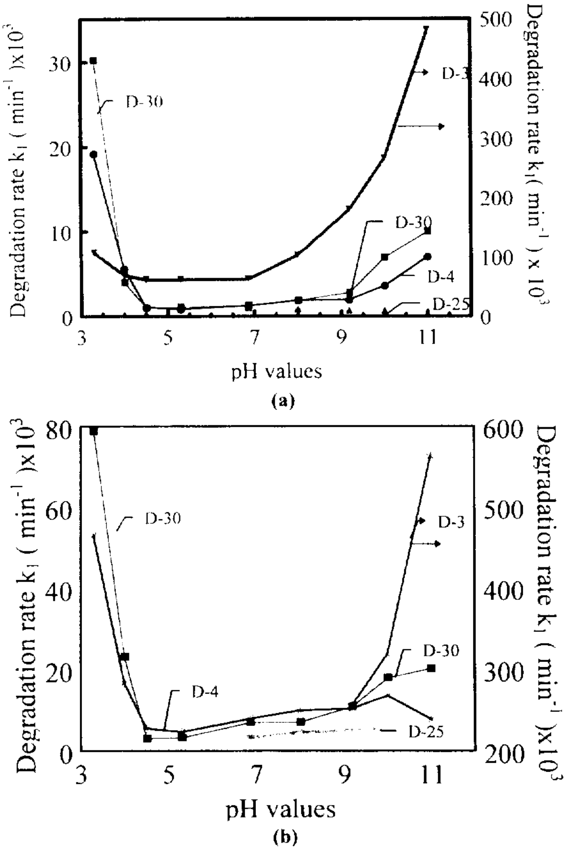


Fig. 2. pH effect on photosensitive and photocatalytic degradation rate k_1 of D-3; D-4; D-25 and D-30: (a) for photosensitive, (b) for photocatalytic.

TABLE 2

Bathochromic shifts of the Visible Spectra of D-29 in Acidic and Basic Aqueous Solutions

pH value	0	1.0	2.0	3.3	4.5	5.3	8.0	9.0	10	11	12	13
λ_{max} (nm)	516	516	515	511	509	573	509	511	512	529	529	529

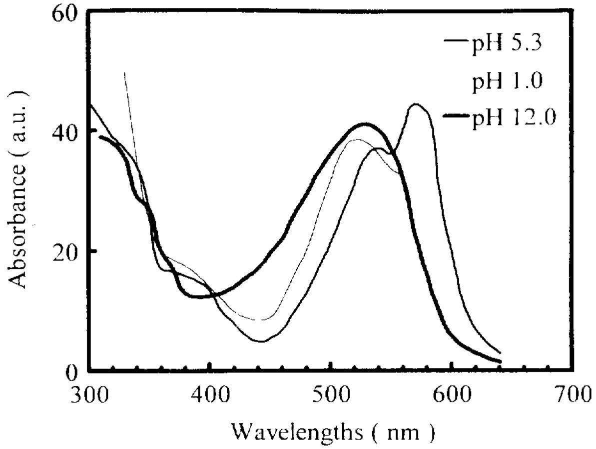


Fig. 3. The absorption spectra of D-29 in aqueous solution at pH 1.0, 5.3 and 12.

is thought to be responsible for both singlet oxygen generation and the reaction with the electrophilic oxidant, $^{\bullet}OH$ via a diazo analogue of the 'ene' reaction [13].

At pH > 6.4, $^{\bullet}OH$ and $O_2^{\bullet -}$ are easier to diffuse from the negative surface of TiO_2 into the bulk of reaction solution, avoiding the recombination of $^{\bullet}OH$ radicals, but this has only little contribution on the decolorization of the H/K-acid azo dyes. The bathochromic shift of about 80 nm in the λ_{max} D-3

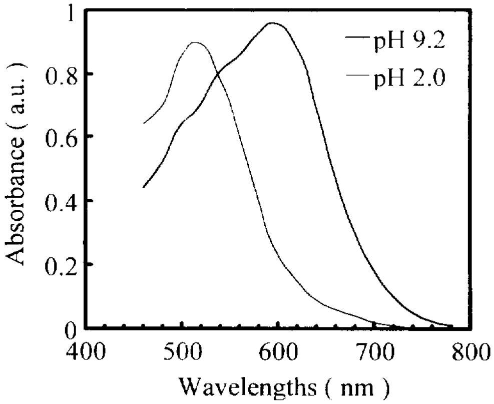


Fig. 4. The bathochromic shift of spectra of D-3 in aqueous solution from pH 2.0 to 9.2.

(Fig. 4) indicates that this dye undergoes subsequential charge separation in basic and polar aqueous solution. This is because, after allowing for resonance interaction, the gap between the ground and excited states in the charge separated form is reduced and a bathochromic shift of the absorption band results (Table 2 and Fig. 4). The charge separated form with lower resonance energy is easily destroyed by $^1O_2$ or the $^{\bullet}OH$ radical. Our experiments show that TiO_2 acts as a strong photosensitizer for $^{\bullet}OH$ radicals which are highly reactive towards *o*-arylazonaphthols. The pH values of solutions can change the structure of dyes, but affect the reactivity of TiO_2 only limitedly.

CONCLUSIONS

The site near the azo bond (C–N=N– bond) is the attacked area in the photocatalytic degradation process. TiO_2 photocatalytic destruction of the C–N(=) bond and –N=N– bond leads to fading of the dyes and TiO_2 acts as a strong photosensitizer for $^{\bullet}OH$, $O_2^{\bullet -}$ and $^{\bullet}OOH$ radicals, which are highly reactive towards azo dyes. The pH of the photolytic solution interferes with the TiO_2 photocatalytic degradation kinetics of the investigated dyes, and the pH effect varies with different dye structures. The pH values of solutions can change the structure of dyes, but affect the reactivity of TiO_2 limitedly.

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