

Role of primary active species and TiO₂ surface characteristic in UV-illuminated photodegradation of Acid Orange 7

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Abstract

Controversy still exists over whether photocatalytic oxidation proceeds via OH• radicals, valence band holes, O₂•⁻ or H₂O₂. In this paper, the role of these primary oxidants in the photodegradation of an azo dye, Acid Orange 7 (AO7) in UV-illuminated TiO₂ suspension was investigated. Little influence of methanol or isopropanol on the degradation indicated that the oxidation was not primarily proceeding by reaction between OH• radicals and AO7, because alcohols could effectively scavenge OH• radicals. But the presence of I⁻ (hole scavenger) significantly inhibited the degradation, thus suggesting that holes played a major role. Then, experiments carried out in acetonitrile, methanol or isopropanol solvent confirmed the major role of holes, since OH• radicals were minimized in dry solvent. In addition, it was suggested that O₂•⁻ and H₂O₂ had a negligible effect when Cr(VI) was used as electron scavenger instead of O₂. The effects of surface modification by F⁻ or SO₄²⁻ on the initial steps of photodegradation were also investigated. The hydroxyl groups on the surface of TiO₂ were replaced by F⁻ or SO₄²⁻ and there were little adsorbed AO7 molecules to be trapped by hole, so the initial process could shift progressively from hole-dominated surface reaction to homogeneous radical reaction in bulk solution. Discussion about the relationship between adsorption and photodegradation indicated that the degradation rate was not strongly affected by the actual location amount of organics on TiO₂ surface.

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Keywords: Photocatalysis; Acid Orange 7; Initial step; Scavenger; Surface modification

1. Introduction

The photocatalytic degradation of pollutants using TiO₂ is attracting considerable attentions for applications to environmental problems and the mechanism of this reaction has been intensively studied [1–3] (see Section 2).

The role of active species leading to the initial photoreaction process has been deeply investigated, but it is still under active controversy [4]. The major uncertainty is whether oxidations proceed via direct electron transfer between substrate and positive holes (Eq. (5)), or via an OH• radical-mediated pathway (Eqs. (6) or (8)).

The OH• radicals (either adsorbed or free) are often assumed to be the major species responsible for the photocatalytic oxidative reactions (Eqs. (6) or (8)), based on evidences including detection of hydroxylated intermediates, distribution of the hydroxylation products, and spin trapping with subsequent ESR detection [5–8].

However controversy exists over whether direct hole oxidation plays a major role (Eq. (6)). Direct electron transfer is thermodynamically feasible since the oxidation potentials of most organic compounds lie below that of valence band holes. Early studies reported that the initial photoreaction process appeared to vary according to the model pollutants and experimental conditions. Carboxylic acids, lacking abstractable hydrogens or C–C unsaturation such as trichloroacetic acid and oxalic acid, seemed to be oxidized primarily by valence band holes via a photo-Kolbe process

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[9]. At pH 3 the initial step of photocatalytic transformation of 2,4-dichlorophenoxyacetic acid was established to be the direct hole oxidation, whereas below and especially above pH 3 it shifted progressively to a hydroxyl-radical-mediated mechanism [10]. The degradation of phenol proceeded predominately via OH• radicals in the presence of dissolved O₂, via the direct hole oxidation in the presence of Ag⁺, and both mechanisms contributed to the degradation in the presence of H₂O₂ [11]. Ishibashi et al. [12] estimated the quantum yields of OH• (7×10^{-5}) and hole (5.7×10^{-2}) and implied that photocatalytic reactions developed mainly via photogenerated holes since the general quantum yield of photocatalytic reaction was 10^{-2} .

Despite the contributions from a number of research groups, detailed mechanisms of the photocatalytic oxidation processes at the TiO₂ surface remain elusive. Further studies are still essential.

Azo dyes, such as Acid Orange 7 (AO7), are a significant portion of wastewaters generated from the textile industry and constitute a major threat to the surrounding ecosystem owing to their non-biodegradability, toxicity and potential carcinogenic nature. Heterogenous photocatalysis has been considered as a cost-effective alternative as pre- or post-treatment of the biological treatment process for the purification of dye-containing wastewater [13]. Information about the reaction types and mechanisms is very important in view of practical applications.

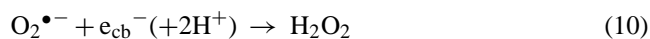
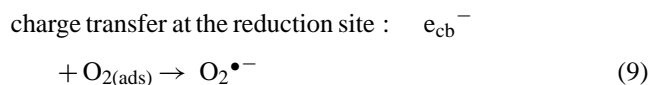
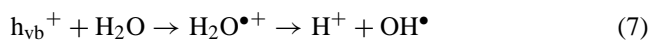
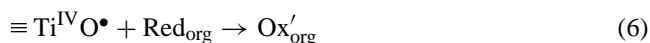
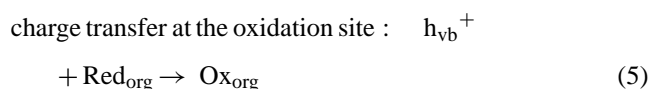
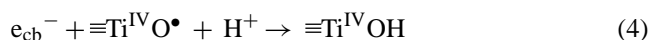
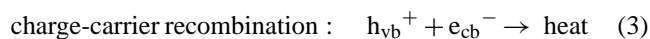
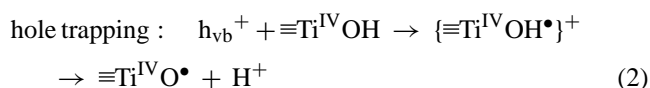
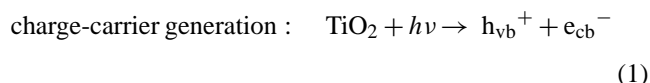
AO7 has commonly been used as a model compound for the photodegradation of dyes [14–23]. The mechanism of visible light-induced photocatalytic degradation of AO7 in aqueous TiO₂ suspensions has been extensively investigated [17,18]. We had focused our attentions on the photodegradation of AO7 on TiO₂/SiO₂ particles under visible light irradiation [24] and on the influence of inorganic anions [25].

In the present work, the role of the main active species during the photodegradation of AO7 under UV light illumination was investigated in detail. To achieve this goal, we suppressed the OH• radical-mediated process by alcohol scavenger, testified the hole mechanism through iodide ion, employed acetonitrile, methanol or isopropanol as solvent to minimize the formation of OH• radicals and introduced Cr(VI) as electron scavenger to eliminate the effect of species generated at the reduction site. The TiO₂ surface modification was attained by addition of F⁻ or SO₄²⁻ to aqueous suspensions. The influence of additives and parameters provided information about the mechanisms and reactive species involved in the reaction. From this study, we could confirm that the hole preferentially reacts with AO7 more than any other photooxidants and the presence of anion may change the surface characteristic of TiO₂ surface and even the photodegradation mechanism.

2. Photocatalytic process

The primary steps occurring in photocatalytic process are summarized in Eqs. (1)–(12) [1–4]. The first step is the pro-

duction of electrons (e_{cb}^-) and holes (h_{vb}^+) in conduction band and valence band (Eq. (1)). The photogenerated holes that escape direct recombination (Eqs. (3) and (4)) reach the surface of TiO₂ and react with surface adsorbed hydroxyl groups or water to form trapped holes (Eq. (2)). The trapped hole ($\equiv TiO^{\bullet}$) is usually described as a surface-bound or adsorbed OH• radical (OH_{ads}•) [10,26,27]. According to Eq. (7), OH• generates at the surface of semiconductor and leaves the surface to bulk solution to form free OH• (OH_{free}•) [28]. If electron donors (Red_{org}) are present at the TiO₂ surface, electron transfer may occur according to Eqs. (5) and (6) and Eq. (8). In aerated systems, oxidative species, such as O₂•⁻ and H₂O₂ generate from the reduction site:



3. Experimental section

3.1. Materials

Acid Orange 7 was obtained from Sigma Chemical Co. TiO₂ (P-25, ca. 80% anatase, 20% rutile; BET area, ca. 50 m² g⁻¹; mean particle size, ca. 30 nm) was supplied by Degussa Co. and was dried at 120 °C in the oven for 12 h before use. KI, K₂Cr₂O₇, NaF and Na₂SO₄ were of analytical reagent grade quality and MeOH, *i*-PrOH and acetonitrile were of HPLC grade quality and dehydrated. All experiments

were carried out using deionized and double distilled water. The pH of the solution was all about 6.0 (unless otherwise reported and adjusted with HClO₄).

3.2. Photoreactor and light source

Photodegradation of AO7 under UV light irradiation was conducted in a quartz reactor of 450 mL capacity at batch mode, and all comparisons were made using the same batch. In the center of cylindrical reactor, two 6 W UV lamps ($\lambda_{\text{max}} = 365 \text{ nm}$) were used as a UV light source. The reactor containing the reaction slurry was kept in the dark and was cooled by recirculation water to $20 \pm 2^\circ \text{C}$ during the experiments.

3.3. Procedures and analyses

The concentration of TiO₂ and AO7 were fixed at 1.0 g L^{-1} and 40.0 ppm (mg L^{-1}), respectively. Prior to irradiation, the dispersions were magnetically stirred in the dark for 1.0 h to achieve the adsorption/desorption equilibrium among TiO₂, AO7 and dissolved oxygen. At given intervals of irradiation, the dispersion was sampled, centrifuged and then filtered through a Millipore filter (pore size $0.22 \mu\text{m}$) in order to remove the TiO₂ particles. The filtrates were analyzed for UV–vis absorbance with a Shimadzu UV1206 spectrophotometer. The degradation of AO7 was monitored by measuring the absorbance at $\lambda = 484 \text{ nm}$ as a function of irradiation time. When a deaerated condition was required, N₂ gas (>99.99%) was continuously purged through the suspension. For the adsorption measurements, the amount of AO7 adsorbed on TiO₂ surface was determined by the decrease in AO7 concentration after reaching equilibrium. The photodegradation rates were described by pseudo-first-order model.

4. Results and discussion

4.1. The role of OH• radical and hole

4.1.1. The effect of alcohol

Our adsorption measurements ($[\text{AO7}]_0 = 40 \text{ ppm}$, $[\text{TiO}_2] = 1.0 \text{ g L}^{-1}$, Fig. 1) showed that nearly ca. 15% of AO7 was adsorbed on TiO₂ surface because of the electrostatic attraction. Early study [29] also reported that the interaction between AO7 and TiO₂ surface was strong, leading to an inner chemisorbed complex. As shown in Fig. 1, in the absence of any scavenger, the rate constant for the photodegradation of AO7 (40 ppm) was 0.50 h^{-1} . And it was well described by pseudo-first-order model ($R^2 = 0.9988$).

The effect of alcohols [10,11,19,30–35], such as MeOH, *i*-PrOH and *t*-BuOH (*tert*-butanol), on the photocatalytic rate has commonly been used to estimate the oxidation mechanism. Though direct oxidation of short aliphatic alcohols

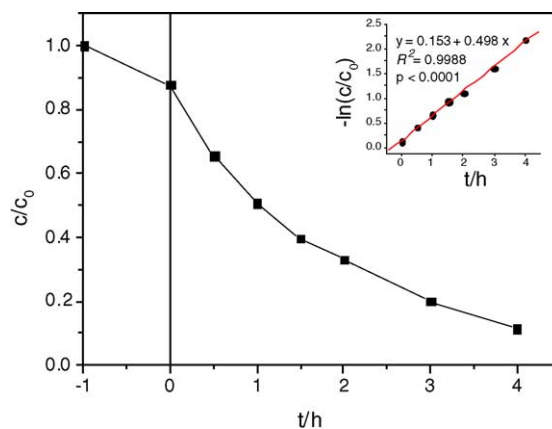


Fig. 1. Photodegradation kinetics of AO7 in aqueous TiO₂ suspension. $[\text{AO7}]_0 = 40 \text{ ppm}$, $[\text{TiO}_2] = 1.0 \text{ g/L}$.

by photogenerated holes probably happens, it is negligible because they have a very weak adsorption power on TiO₂ surface in aqueous media. So alcohols are usually used as a diagnostic tools of OH• radicals mediated mechanism. In a UV/H₂O₂ process [36], the photodestruction of AO7 was inhibited by addition of ethanol as a scavenger. Small amounts of ethanol inhibited the photocatalytic degradation of another azo dye (Acid Red 14, AR14) on ZnO [37]. These experiments suggested that OH• radicals played a major role.

The oxidation potential of MeOH is 0.55 V (versus NHE) [38] and the rate constant of reaction with OH• is $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [39]. Adsorption measurements demonstrated that the presence of 0.10–1.0 M MeOH had negligible influence on the adsorption amount of AO7. Therefore, MeOH cannot compete the adsorption sites with AO7. Due to its low affinity to the TiO₂ surface, MeOH was expected to compete mainly for OH• radicals [11,40]. If OH• radicals dominated the photocatalytic oxidation process of AO7 on TiO₂, the addition of MeOH would inhibit the reaction strongly. The effect of MeOH on degradation of AO7 in air-equilibrated TiO₂ suspension was shown in Fig. 2. It was found that MeOH had little influence on the photodegradation of AO7. The degradation rate only decreased to 0.44 h^{-1} in the presence of 0.10 M MeOH (about 10^3 times higher concentration than AO7). Furthermore, even a little promotion was achieved in the case of 1.0 M MeOH. The results suggested that OH• radicals played a very little role during photocatalytic oxidation.

Isopropanol (*i*-PrOH), a good scavenger like MeOH, is more easily oxidized by OH• radicals. The rate constant of reaction between OH• radical and *i*-PrOH is $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [39], a rate of almost the diffusion limit. Fig. 2 also showed the effect of 0.01 or 0.1 M *i*-PrOH on photodegradation of AO7. The degradation rates decreased to 0.39 and 0.42 h^{-1} , respectively. The inhibitive effect of *i*-PrOH on the photodegradation of AO7 was also not significant. In the presence of *i*-PrOH, the OH• radical-mediated reaction was quenched

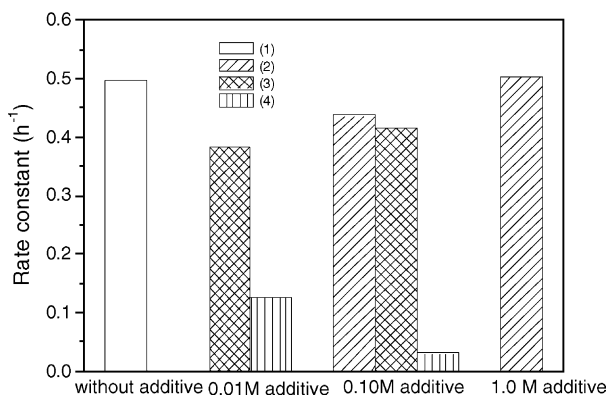


Fig. 2. Effects of MeOH, *i*-PrOH and I^- on degradation rate of AO7 in aqueous TiO_2 suspension: (1) without additives, (2) with $[MeOH]=0.10$ or 1.0 M, (3) with $[i-PrOH]=0.01$ or 0.10 M, and (4) with $[KI]=0.01$ or 0.10 M.

mostly. It was deduced that the contribution of OH^\bullet radicals played a minor role in the photoreaction and that the hole mechanism may be prevailing.

It is worth noting that control experiments under otherwise identical conditions showed that no degradation was observed when the experiments were conducted in the dark or in the absence of the semiconductor. Therefore, both UV light and TiO_2 were indispensable for the degradation of AO7.

4.1.2. The effect of iodide ion

Iodide ion is an excellent scavenger which reacts with valence band hole and adsorbed OH^\bullet radicals [12,27,32]. The valence band hole is easily captured by I^- and pathways due to oxidation by surficial hydroxyl radical are also possible [41].

When iodide ion was used as diagnostic tool for suppressing the hole process, the photocatalytic degradation of AO7 was greatly inhibited, as shown in Fig. 2. In the presence of 0.01 M KI, the rate constant decreased to 0.13 h^{-1} . When the concentration of I^- reached 0.10 M, the degradation reaction of AO7 almost stopped. From the inhibitive effect of I^- , it was deduced that photogenerated holes played an important role in the photodegradation of AO7 under UV light irradiation.

4.1.3. The effect of reaction solvent

TiO_2 is usually surrounded by adsorbed water in aqueous suspension, so water molecules are likely oxidized to hydroxyl radicals by photogenerated holes. The use of non-aqueous reaction medium could rule out the participation of OH^\bullet radicals in the oxidation process.

Acetonitrile is an extremely stable molecule. It is usually used as a solvent in photocatalytic oxidation reactions, and the electron-hole transfer mechanism between substrate and holes was often suggested [47–49]. The lack of transformation of 1,10-dichlorodecane (D_2C_{10}) in acetonitrile solvent indicated that the major oxidants of D_2C_{10} in aqueous TiO_2 suspension were OH^\bullet radicals [32].

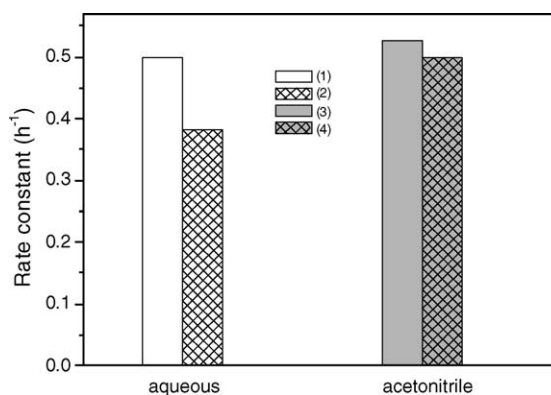


Fig. 3. The photodegradation of AO7 in aqueous or acetonitrile solvent: (1) aqueous, (2) aqueous with $[i-PrOH]=0.10$ M, (3) acetonitrile, and (4) acetonitrile with $[i-PrOH]=0.10$ M.

Experiments were carried out in acetonitrile suspension to minimize the formation of $OH_{ads/free}^\bullet$ since there were no water molecules (Fig. 3). AO7 molecules adsorbed on the surface of TiO_2 were more likely oxidized directly by photogenerated holes. As anticipated, almost the same reaction rate was obtained in H_2O and acetonitrile solvent. Furthermore, just like in aqueous suspension, the presence of 0.10 M *i*-PrOH had little effect on the degradation of AO7 in dry TiO_2 suspension because of the absence of OH^\bullet radicals (both adsorbed and free). So, the direct electron transfer between holes and surface-bound AO7 molecules played a significant role.

As mentioned above, MeOH and *i*-PrOH are known OH^\bullet radicals scavengers. If a photodegradation reaction was dominated by OH^\bullet radicals, it would be quenched when it occurs in anhydrous MeOH or *i*-PrOH solvent. Turchi and Ollis [28] once put forward that direct hole-organic reaction is not believed to be significant because of the lack of reactivity witnessed in water-free organic solution. Experiments were carried out to testify the activity of photodegradation of AO7 in dry MeOH and *i*-PrOH (Fig. 4). As anticipated, it

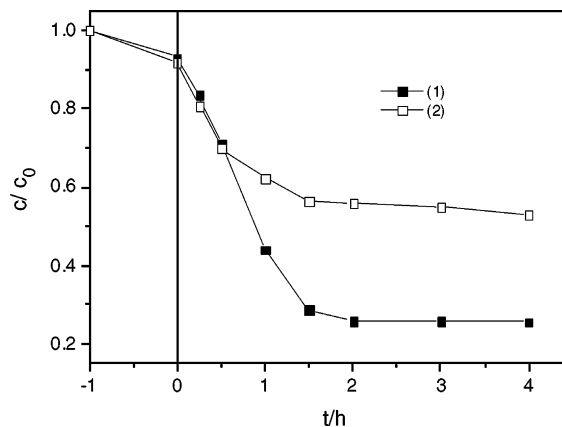


Fig. 4. The photodegradation of AO7 in MeOH or *i*-PrOH solvent: (1) MeOH and (2) *i*-PrOH.

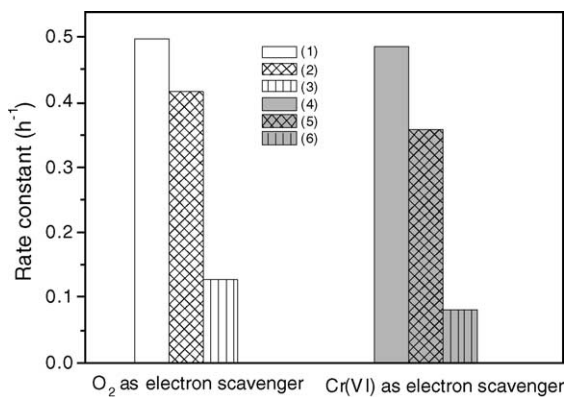


Fig. 5. Effects of electron scavengers on the degradation rate of AO7 in aqueous TiO₂ suspension: (1), (2) and (3) were air saturated, (4), (5) and (6) were N₂ saturated with [K₂Cr₂O₇] = 0.001 M. (1) and (4) without additive, (2) and (5) with [*i*-PrOH] = 0.10 M, (3) and (6) with [KI] = 0.01 M.

was clearly seen that in alcohol solvents AO7 still displayed high degradation efficiency especially at the first 1.5 h. The following cessation may be caused by the accumulation of some inert intermediate organic products on the surface of TiO₂. In any case, these results proved again the major role of holes.

4.2. The role of O₂^{•-} and H₂O₂

The contribution of species generated at the reduction site (Eqs. (13)–(16)), such as O₂^{•-} and H₂O₂, to photocatalytic reactions at the TiO₂ surface remains unclear [42]. It was thought to be less reactive and not so important in the photocatalysis process [43]. However, Ryu and Choi [44] recently confirmed that O₂^{•-} was mainly responsible for the As(III) photocatalytic oxidation.

The use of inorganic compounds such as Cr(VI) and S₂O₈²⁻ has been demonstrated to trap the photogenerated electrons [45,46]. Upon purging with nitrogen, and using Cr(VI) as an electron scavenger, the role of species generated at the reduction site could be neglected since Cr(VI) is easily reduced to Cr(III) by the photogenerated electron.

As presented in Fig. 5, the photodegradation rate of AO7 in the presence of 0.001 M K₂Cr₂O₇ upon purging with nitrogen was almost the same as the case that O₂ was used as electron scavenger. It was observed that the additives showed a very similar influence too. The photodegradation of the dye was little affected by 0.10 M *i*-PrOH and was significantly inhibited by 0.01 M I⁻. These results suggested that O₂^{•-} and H₂O₂ had a negligible effect on the photodegradation of AO7.

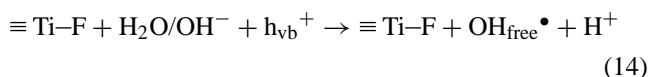
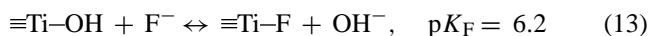
It should be noted that the homogeneous photochemical reaction of Cr(VI) with AO7 was negligible. In addition, the effect of 0.001 M K₂Cr₂O₇ on the determination wavelength for AO7 (484 nm) was very little and the error was less than 3%, so it was not taken into account.

4.3. The effect of TiO₂ surface characteristic

4.3.1. The alterability of mechanism on F⁻-modified TiO₂ system

The redox potential of the couple F[•]/F⁻ is about 3.6 V, which makes fluoride very stable against oxidation, even by TiO₂ valence holes [50]. Furthermore, fluoride shows strong adsorption on TiO₂ (as Eq. (13)) and the concentration of surface hydroxyl group on the catalysts could be controlled by adopting fluoride-exchange [33].

The great promotion of degradation rate in photocatalytic phenol in the presence of fluoride ions has been recently ascribed to the enhanced generation of mobile free OH[•] as Eq. (14) [35,51]:



Our adsorption measurements showed that AO7 adsorption on TiO₂ ([AO7]₀ = 40 ppm, [TiO₂] = 1.0 g/L) was almost inhibited in the presence of 0.01 M F⁻. That is to say, the hydroxyl groups and AO7 on the surface of TiO₂ were almost replaced by F⁻. Park and Choi [19] had also reported the same results very recently.

Fig. 6 presented the effect of F⁻ on the photodegradation of AO7 at pH 6.0 and 3.6 in TiO₂ suspensions. The replacement of the hydroxyls by fluoride ion favored the promotion of reaction too. The degradation at pH 3.6 was more rapid than that at pH 6.0. In the presence of 0.01 M F⁻, the rate constants increased to 0.81 h⁻¹ (pH 6.0) and 1.63 h⁻¹ (pH 3.6) respectively. The diminution of ≡TiOH will decrease the ability to trap the holes as ≡TiO[•] or OH_{ads}[•] according to Eq. (2) and subsequently increase h_{vb}⁺ availability as extensively discussed in the previous paper [19,33–35]. The promotion may be attributed to either the hole direct oxidation or the homogeneous OH_{free}[•] mechanism since the formation of OH_{ads}[•] was significantly inhibited.

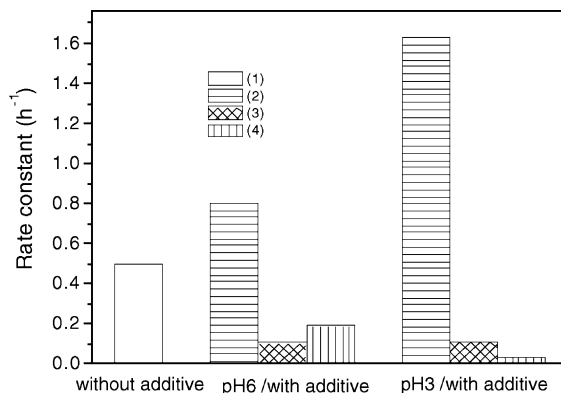


Fig. 6. Effects of fluoride ion and pH on the degradation rate of AO7 in aqueous TiO₂ suspension: (1) without additive, (2) with [NaF] = 0.01 M, (3) with [NaF] = 0.01 M and [*i*-PrOH] = 0.10 M, and (4) with [NaF] = 0.01 M and [KI] = 0.01 M.

As shown in Fig. 6, the role of active species in the photodegradation of AO7 on TiO₂/F system was observed through the addition of the scavengers, *i*-PrOH or I⁻. The inhibition of 0.10 M *i*-PrOH and 0.01 M I⁻ on TiO₂/F⁻ system is pronounced: at pH 6.0, the rate constants decreased to 0.10 and 0.18 h⁻¹; and at pH 3.6, decreased to as much as 0.11 and 0.03 h⁻¹. The OH[•] radical played a significant role in the F⁻-modified system.

What is more interesting, both *i*-PrOH and I⁻ had greater inhibition at pH 3.6 than at pH 6.0, which meant that more h_{vb}⁺ was available and more OH_{free}[•] generated at pH 3.6. At pH 3.6 the surface coverage by fluoride ions was maximum [34] due to electrostatic attraction, the photogenerated holes had to oxidize water molecules to generate OH_{free}[•] since there were little ≡TiOH and adsorbed AO7 molecules to trap. On the other hand, the increased distance between AO7 and the photogenerated holes did not allow direct charge transfer. With very limited AO7 coverage on the surface of TiO₂ occurring, most of the decomposition was probably mediated by enhanced OH_{free}[•] radicals in bulk solution.

To sum up, when AO7 was strongly adsorbed on naked TiO₂ in the absence of F⁻, mechanism involving direct electron transfer was responsible for the reaction progress. The presence of weakly or non-adsorbed species, such as alcohol, had a negligible effect on the degradation pathway of those adsorbed, such as AO7. However, at low AO7 coverage replaced by F⁻ on the surface of TiO₂, the first step involved reaction with free OH[•] radicals, and the presence of alcohol had significant inhibition.

4.3.2. The relationship between adsorption and photodegradation

Previous studies showed that those organics that have better adsorption on the surface are more likely to be degraded in the photocatalytic process [52,53]. Carraway et al. [54] believed that surface-mediated reactions played a significant role for the strongly adsorbed electron donors and homogeneous OH[•] reaction in the bulk solution played a greater role for weakly adsorbed substrates such as alkane.

If organics were easily adsorbed on the surface of TiO₂, they would have more chances to be oxidized by photogenerated hole or OH_{ads}[•]. If the adsorption ability of organic molecules was poor or there were little chance for their adsorption to the surface on some special conditions, such as the coverage of TiO₂ surface was occupied by other species, the degradation rate would decrease accordingly. However, it is not a general case. Sometimes the degradation rate may not be affected or even enhanced though the adsorption was decreased. Maybe some reaction sites at the surface were not the adsorption sites. Maybe there were other active species in the bulk solution. In general TiO₂ photocatalysis occurs at specific active sites on TiO₂. The reaction sites are not assumed to coincide with the adsorption sites for reactants. The degradation rate is not strongly affected by the actual location

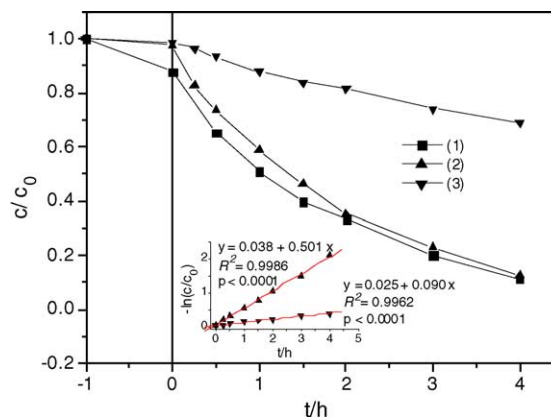
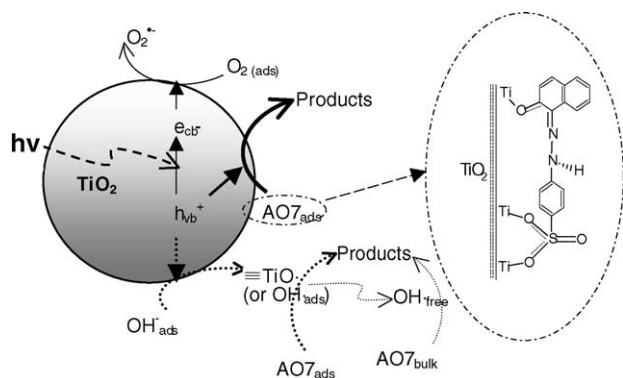


Fig. 7. Effects of SO₄²⁻ on the degradation rate of AO7 in aqueous TiO₂ suspension: (1) without additive, (2) with [Na₂SO₄] = 0.001 M, and (3) with [Na₂SO₄] = 0.001 M and [*i*-PrOH] = 0.10 M.

of organics [55]. In other words, there was no strong correlation between the photodegradation rate and the adsorption amount of AO7 on the surface of TiO₂.

In the present study, the surface modification by fluoride ion inhibited the adsorption of AO7 but strongly accelerated its degradation as a result of its enhanced homogeneous reaction with free OH[•] radical. In our previous study [25], it was also found that in TiO₂/UV system no correlation between the photodegradation rate and the adsorption of AO7 on TiO₂. The presence of SO₄²⁻ or HCO₃⁻ showed significant inhibition on the adsorption of AO7 on TiO₂, but these anions had non-appreciable inhibition effect on the photodegradation of AO7. For example, SO₄²⁻ has strong affinity to the surface of TiO₂ and could replace the hydroxyl groups and the adsorption of AO7 molecules. As shown in Fig. 7, the adsorption sites of AO7 was almost replaced by SO₄²⁻, but the degradation rate constant still kept at 0.50 h⁻¹. SO₄²⁻ could lose an electron to TiO₂ valence band holes or OH[•] radical to become a sulfate radicals which has a very high oxidation potential but a lower rate than OH[•] radical. The inhibitory effect of SO₄²⁻ may be limited by the ability of the sulfate radical itself to oxidize organics or by slowing down further recombination of electron and hole pair. On SO₄²⁻-modified system, *i*-PrOH greatly inhibited the degradation, which suggested that the primary oxidation probably changed from hole-dominated surface reaction to radical reaction in bulk solution (Fig. 7). The radicals probably included sulfate radical or free OH[•] radical generated from the reductive site since more electrons were available as Eqs. (9)–(12).

We have to point out that in our previous paper [25] the general conclusion which the photodegradation of AO7 took place mainly in the bulk solution may remain some uncertainties. The influences of anions on the photodegradation reaction were mixed till today [56–58]. It is a very interesting subject for further study and the mechanism will be discussed in detail in our later papers.



Scheme 1. Illustration of the simplified kinetic pathways for AO7 under photocatalytic condition on TiO₂ and adsorption geometry of AO7 on TiO₂.

4.4. The proposed chiefly direct hole mechanism for AO7 photodegradation

In the OH[•] radicals mediated mechanism, it is believed that h_{vb}^+ reacts with surface hydroxyl groups or water molecule to form a ‘trapped hole’ on the surface or OH_{free}[•] in bulk (Eqs. (2) and (7)). And the OH_{ads/free}[•] radicals subsequently transform organic compounds (Eqs. (6) and (8)).

But if organic molecules are strong adsorbed on the surface of TiO₂, they will compete with adsorbed hydroxyl groups or water as electron donors [59–62] since the oxidation potential of organic molecules lie below that of the holes. Compounds that can adsorb at the ≡TiO[•] radical centers would undergo photooxidation more efficiently than water and OH⁻ ions.

Scheme 1 shows the kinetic pathways for AO7 degradation on UV-illuminated TiO₂. The pH 6.0 was less than the point of zero charge of the TiO₂ (6.8 for Degussa P-25) and the surface was electropositive. So the electronegative AO7 transported to the surface from the solution was easily chemisorbed. The AO7 molecule is linked to three Ti surface metallic cations through one oxygen atom of carbonyl group of the hydrazone tautomer and two oxygen atoms from sulfonate group [29] (Scheme 1). The strong adsorption of AO7 on TiO₂ surface forms an inner-sphere complex, which means ultrafast electron transfer and hot carrier injection between photogenerated carriers and AO7 molecules. The Ti–O bond has a relatively high covalent character, and the oxygen atoms of AO7, being relatively strong electron donors, are able to direct interact with valence band holes. On the other hand, the oxidative potential of AO7 (0.76 V versus NHE) [14] is much lower than that of photogenerated hole. So the direct electron transfer is a thermodynamically feasible process. Therefore, when the valence band hole migrated to the surface, it was primarily captured by the adsorbed AO7 molecules, rather than by the adsorbed water or hydroxyl groups (Eq. (5), Red_{org} = AO7).

On the other hand, OH_{ads/free}[•] produce was thermodynamically admissible too, and the initial steps of attack of AO7 molecules by h_{vb}^+ or OH_{ads/free}[•] were two competitive processes. Under our common experimental conditions, the direct transfer mechanism played a major role. Exception-

ally, it shifted to a radical-mediated mechanism at low AO7 coverage replaced by F⁻ or SO₄²⁻ on the surface of TiO₂.

5. Conclusion

From the fundamental point of view, there are still open questions concerning photocatalytic oxidation mechanism. In the current paper, experiments were developed to testify on the kinetics of photoreaction of AO7 on UV-illuminated TiO₂ through the use of charge-trapping species (h_{vb}^+ and OH[•] scavengers) as diagnostic tools. The degradation was not significantly affected by *i*-PrOH and MeOH, but was notably inhibited by iodide ion, whether the electron scavenger was O₂ or Cr(VI). By suppressing the formation of OH[•] radicals in acetonitrile solvent, the degradation rate was almost the same as that in aqueous and it was little affected by *i*-PrOH too. Moreover, the degradation still took place in anhydrous MeOH or *i*-PrOH solvent. In a word, AO7 molecules first adsorbed strongly on the TiO₂ surface and the following degradation reaction was mostly initiated by the direct electron transfer reaction between a positive hole and a surface-bound AO7 molecule. However, the initial process could shift progressively from hole-dominated surface reaction to radical reaction in bulk solution according to experimental conditions, for example, when there were seldom AO7 molecules adsorbed on the surface of TiO₂ in the presence of F⁻ or SO₄²⁻. There was no correlation between the photodegradation rate and the adsorption amount of organics on the surface of TiO₂.

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