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Synergistic effects of cupric and fluoride ions on photocatalytic degradation of phenol

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Abstract

Synergistic effects of cupric ions and fluoride ions were investigated on the photocatalytic degradation of phenol in TiO_2 (Degussa P25) suspensions at pH 3 under UV irradiation. Under all tested conditions, the phenol photodegradation was observed to follow a pseudo-first-order reaction in kinetics. The rate constant k of the phenol photodegradation was evaluated as 0.010 min^{-1} in the absence of Cu^{2+} and F^- ions, and was increased up to 0.014 min^{-1} by adding 0.4 $mmol\,L^{-1}$ Cu^{2+}, and to 0.022 min^{-1} by adding 5 $mmol\,L^{-1}$ F^- ions. The coexistence of both Cu^{2+} and F^- ions increased the k value further to 0.041 min^{-1}, being 410% of that without any addition of Cu^{2+} and F^- ions. The much increased rate of phenol degradation induced by the coexistence of Cu^{2+} and F^- ions were also confirmed by the monitoring of degradation intermediates. With the aid of the determination of $^\bullet OH$ radicals and H_2O_2 generated during the photodegradation, the observed significant synergistic effects were attributed to the shielding effect of fluoride on the charge separation efficiency and the efficient trapping of the photogenerated electron by the Cu^{2+} adsorbed on TiO_2 surface.

Keywords: Titanium dioxide; Phenol; Synergistic effect; Fluoride; Cupric ion

1. Introduction

TiO_2 photocatalysis has been intensively investigated for its application to the destruction of environmental toxic pollutants [1–3]. The primary event occurring on the UV-illuminated TiO_2 is the generation of photo-induced electron/hole (e^-–h^+) pairs. These charge carriers can rapidly migrate to the surface where they are captured by a suitable electron donor and acceptor, initiating an oxidation and reduction reaction, and/or they are recombined, dissipating the input light energy onto heat. The strong oxidizing ability of TiO_2 photocatalysts has been ascribed to highly oxidative valence band holes (+2.7 V *versus* NHE) and various oxygen-containing radical species (e.g., $^\bullet OH$, $O_2{}^{-\bullet}$, $HO_2{}^\bullet$). Among these species, holes and $^\bullet OH$ radicals play the most important roles in the photodegradation of organic pollutants. Thus, the overall quantum efficiency is expected to be decided by the competition between charge-carrier recombination, trapping, and interfacial charge transfer [4,5]. It is well known that improving photocatalytic efficiency requires primarily a decreased e^-–h^+ recombination rate, which is generally achieved by increase of the rate of photogenerated electrons transfer to the oxidant at the interface and/or the capture of holes via oxidation process.

Among various efforts for enhancing photocatalytic efficiency, the surface modification of TiO_2 seems mostly interesting. The surface modification of TiO_2 can be performed by depositing noble metal clusters on the surface of TiO_2. For example, platinized-TiO_2 photocatalysts show higher photoactivity by increasing the rate of electron transfer from TiO_2 to O_2 [1,3,5]. It can be also carried out *in situ* by adding appropriate compounds into solution during the photodegradation. It has been reported that the photocatalytic decomposition of organic contaminants is greatly accelerated by the addition of metal ions to TiO_2 suspensions, such as Fe^{3+} [6–8], Ag^+ [8–10], Cr^{6+} [10,11], and Cu^{2+} ions [12–15]. This positive effect has been attributed to photoelectron trapping by metal ions, which reduces the electron–hole recombination and results in an increased

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concentration of •OH radicals. The enhancing effects of fluoride anions are also concerned intensely [16–21]. Lv and Xu have found that addition of fluoride anions into TiO_2 dispersions accelerates the photocatalytic degradation of organic dye X3B [17]. Minero et al. have observed that the degradation of phenol is enhanced by using surface fluorinated-TiO_2 [18]. Choi and coworkers have reported similar enhancing effect of F^- ions for the degradation of phenol, acid orange 7 and tetramethylammonium [19–21]. The surface fluoride-enhanced effect is ascribed to accelerating generation of mobile •OH radicals, due to enhanced holes availability for water oxidation through the displacement of ≡Ti–OH by ≡Ti–F.

Although it is known that both the adsorption of metal ions and fluoride ions can promote the photocatalytic degradation of organic pollutants, we have not found any report on the possible synergistic effects of metal ions and fluoride ions. The further enhancing of the photocatalytic efficiency of TiO_2 photocatalysts with the aid of the synergistic effect of metal ions and fluoride ions is very interesting from the view points of both academic and technological aspects in the field of photocatalysis. Therefore, the main purpose of the present work is to investigate the synergistic effects of Cu^{2+} ions and F^- ions. To achieve it, phenol is taken as a model compound to be degraded, because it is an important toxic pollutants with the safety levels in the range of 0.1–1.0 mg L^{-1} and is considered to be an intermediate product in the photooxidation pathway of higher molecular weight aromatic hydrocarbons [22].

2. Experimental section

2.1. Reagents and materials

TiO_2 powders (Degussa P25, ca. 80% anatase, 20% rutile; BET area, ca. 50 $m^2\,g^{-1}$) were used as received. Horseradish peroxidase (POD, specific activity of 300 units mg^{-1}, RZ ≥ 3) was purchased from Tianyuan Biologic Engineering Corp. (China). All other chemicals (*N*,*N*-diethyl-*p*-phenylenediamine sulfate (DPD, from Aldrich), sodium diethyldithiocarbamat (DDTC), $CuCl_2$, NaF, and phenol) were of analytical reagent grade and used without further purification. Distilled water was used throughout. The pH of solutions was adjusted using diluted aqueous H_2SO_4 or NaOH solutions.

2.2. Photodegradation experiments

Photocatalytic degradation was performed at room temperature (25 ± 2 °C) by using a photocatalytic reactor equipped with a 400 mL cylindrical Pyrex vessel [23]. A 11 W UV lamp (Philips) was positioned in the center of the reactor. For typical photocatalytic runs, a load of 0.25 g TiO_2 was suspended into 250 mL aqueous solutions containing 0.4 mmol L^{-1} phenol with or without the addition of Cu^{2+} and/or F^- ions, followed by adjusting pH to pH 3.0. Prior to irradiation, the suspensions were first sonicated for 60 s, and then magnetically stirred in the dark for ca. 30 min to ensure the establishment of adsorption–desorption equilibrium of the concerned chemical substances on the surface of TiO_2. The reaction mixture was maintained in suspension by using a magnetic stirrer before and during the irradiation.

2.3. Analysis

At given time intervals, 2 mL aliquots were sampled, immediately centrifuged at 14,000 rpm for 15 min, and then filtered through a 0.22 μm pore size filter to remove the TiO_2 particles. The filtrates were collected and analyzed. The degradation of phenol and the intermediate products were identified and quantified by HPLC-MS (Agilent 1100 LC-MSD-Trap-XCT) equipped with a diode array detector and a Hiqsil C18 ODS column (4.6 mm × 150 mm). The mobile phase was 35% methanol and 65% water at 0.8 mL min^{-1}. The concentrations of phenol and catechol were determined at the wavelengths of 270 and 275 nm, and the amounts of hydroquinone (HQ) and *p*-benzoquinone (BQ) were determined at 289 and 246 nm, respectively. The total amount of aliphatic acids was determined at two wavelengths, i.e. 220 and 289 nm.

The •OH radical formation in TiO_2 system under UV irradiation was monitored by fluorescence technique using coumarin, which easily reacts with •OH to form the highly fluorescent product 7-hydroxy coumarin [24]. The fluorescence spectra were recorded on a JASCO FP6200 spectrofluorometer. The concentration of total peroxides (including organoperoxides and H_2O_2) formed during phenol degradation was determined immediately by the spectrophotometric DPD method after irradiation and removal of TiO_2 particles by centrifugation and filtration [25]. H_2O_2-oxidized POD reacts with DPD to produce a colored product, DPD^+, which shows an absorption maxima at 551 nm. After being filtered, 2.7 mL sample was mixed with 0.3 mL buffer solution (pH 6.86), followed by rapid addition of 50 μL DPD (10 g L^{-1}) and 50 μL POD (0.5 g L^{-1}). The absorption was measured after a reaction time of 60 s.

To evaluate the adsorption of Cu^{2+} on the photocatalysts, 0.2 g TiO_2 was stirred in 100 mL aqueous solutions containing 0.4 mmol L^{-1} phenol and different concentrations of Cu^{2+} for 1 h in dark. After centrifuging and filtration, the concentration of Cu^{2+} remained in solution was analyzed by using the spectrophotometric DDTC method (GB 7474-87, China).

3. Results and discussion

3.1. Synergistic effect of Cu^{2+} and F^- on photocatalytic degradation of phenol

In control experiments, we confirmed that the disappearance of phenol was negligible when the phenol solution is not irradiated with UV light or no TiO_2 catalyst was added into the solution. The photocatalytic degradation of phenol only occurred over TiO_2 under UV light illumination. As partly shown in Fig. 1, the phenol photodegradation under all the tested conditions was observed to follow a pseudo-first-order reaction in kinetics, which could be expressed as $\ln(c_t/c_0) = kt + y$. Here, c_0 and c_t represent the initial concentration of phenol and the concentration at illumination time t (min), k is the apparent rate constant of the pseudo-first-order reaction, and y is a con-

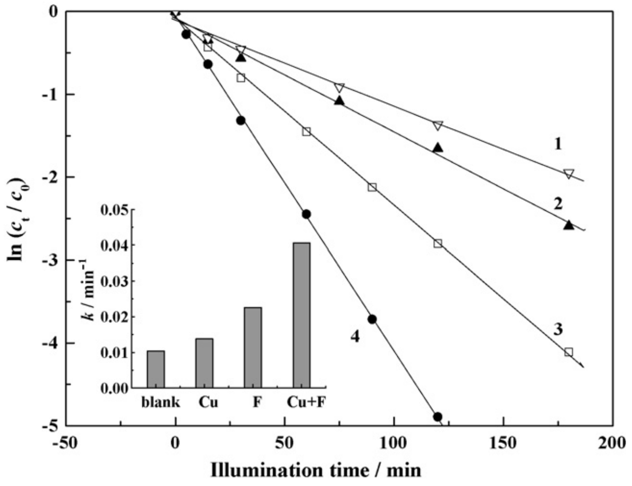


Fig. 1. Kinetics of photodegradation of phenol over TiO_2 in suspensions of (1) 0.4 mmol L^{-1} phenol, (2) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+}, (3) 0.4 mmol L^{-1} phenol + 5 mmol L^{-1} F^-, and (4) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+} + 5 mmol L^{-1} F^-. The inset gives the values of the rate constant *k* of phenol photodegradation.

stant. This is in good agreement with the reported observations [5,7,26].

It is easily seen from Fig. 1 that relative to the phenol degradation over TiO_2 nanoparticles alone, the rate of phenol degradation is slightly increased in the presence of cupric ions, and more strongly promoted by the addition of fluoride anions. It is interesting that the simultaneous addition of both cupric ions and fluoride anions significantly increases the photodegradation of phenol. This strong synergistic effect of cupric and fluoride ions is better known by comparing the values of the rate constant *k* (the inset of Fig. 1).

The synergistic effect of cupric and fluoride ions was further investigated at different levels of the added ions. Fig. 2 compares the values of apparent rate constant *k* of phenol photodegradation over TiO_2 under illumination and the adsorption amounts of Cu^{2+} over TiO_2 in dark in suspensions containing various concentrations of Cu^{2+} ions. As Cu^{2+} concentration in the suspension is increased, the adsorption of Cu^{2+} on the surface of TiO_2 particles is increased, indicative of *in situ* surface modification of the photocatalyst's surface by dissolved Cu^{2+} ions. Corresponding to this surface modification, the rate constant of phenol degradation is slightly increased from 0.010 to 0.014 min^{-1} when Cu^{2+} concentration is increased from 0 to 0.4 mmol L^{-1}. However, the rate constant of phenol degradation is decreased when Cu^{2+} concentration is higher than 0.4 mmol L^{-1}. This suggests that the excessive adsorption of Cu^{2+} ions on the surface of TiO_2 is unfavorable to the phenol photodegradation. From Fig. 2 we can conclude that the enhancing effect of Cu^{2+} on the phenol degradation is rather weak, and this effect is maximized at Cu^{2+} concentration of 0.4 mmol L^{-1}.

Our observation is consistent with Litter's opinion that, in the UV/TiO_2 system, some transition metal ions at appropriate concentrations can accelerate the decomposition of organic pollutants, but can suppress the photooxidation at high concentrations of metal ions [27]. Water oxidation by photogenerated holes can be enhanced by the addition of Cu^{2+} ions through efficient trapping of the photogenerated conduction band electron, resulting in increased $^{\bullet}OH$ radicals and valence-band holes. Fig. 2 correlates the adsorption isotherm of Cu^{2+} with the *k* value of phenol disappearance, indicating that adsorption of Cu^{2+} ions on the TiO_2 surface is an essential factor influencing the phenol degradation rate, only the Cu^{2+} ions adsorbed on the TiO_2 surface can affect the degradation of phenol. However, superabundant adsorbed Cu^{2+} ions hinder photogenerated holes transferring to the mediated oxidations, depressing the positive effect of Cu^{2+} and even having a detrimental influence. Another reason is due to the short circuiting reaction ($Cu^{2+} + e^- \rightarrow Cu^+$, $Cu^+ + h^+ \rightarrow Cu^{2+}$) which usually occurs at high Cu^{2+} concentrations without generation $^{\bullet}OH$ radicals [12].

Fig. 1 shows that the addition of 5 mmol L^{-1} fluoride into the TiO_2 dispersion accelerates the photocatalytic degradation of phenol (curve 3). The fairly strong accelerating effect of fluoride is further confirmed over a very wide range of fluoride concentration. As shown in Fig. 3 (curve 1), when the F^- concentration is increased from 0 to 9 mmol L^{-1}, the rate constant *k* of phenol degradation is increased from ca. 0.010 min^{-1} to

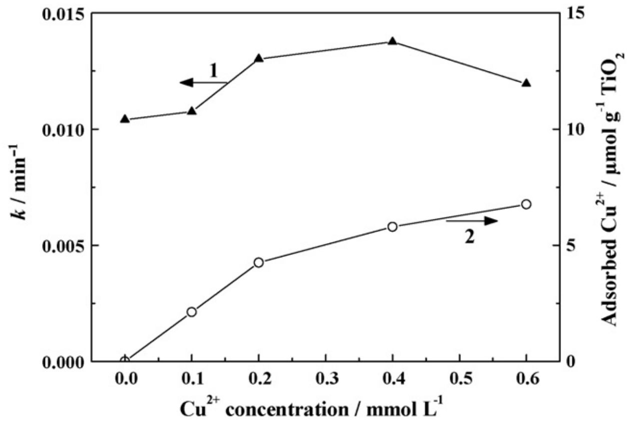


Fig. 2. Effects of dissolved Cu^{2+} concentrations on the rate constant *k* of phenol photodegradation over TiO_2 under illumination and the Cu^{2+} adsorption over TiO_2 in the dark.

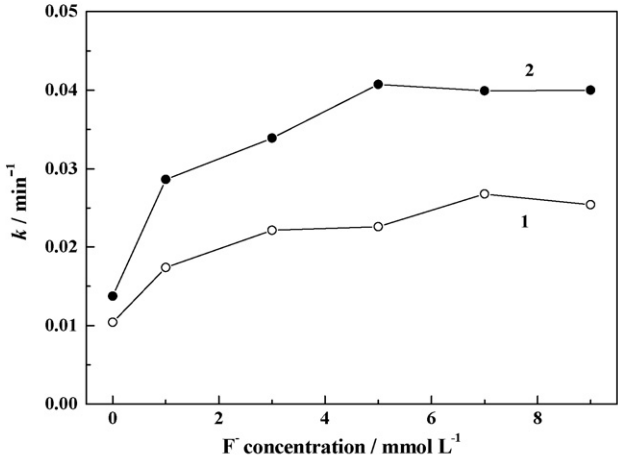
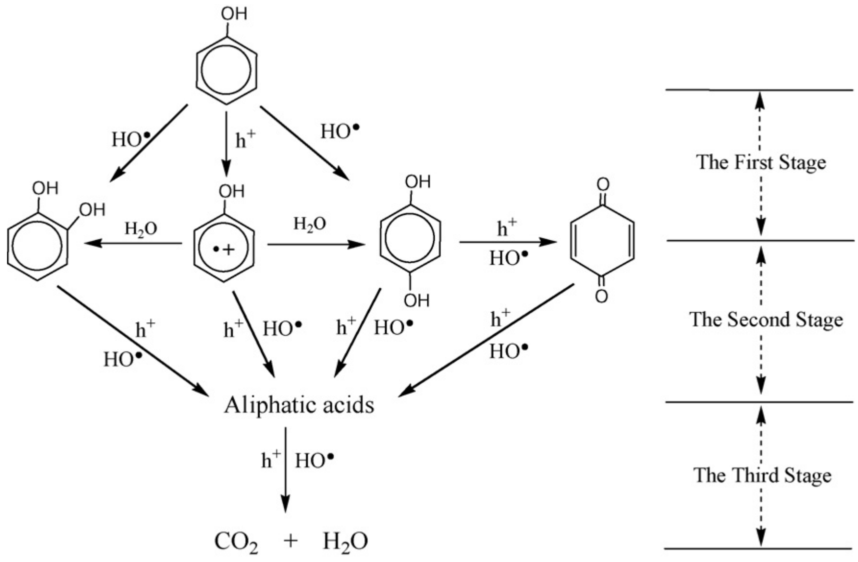


Fig. 3. Dependence of the apparent rate constant *k* of phenol degradation on concentration of F^- ions in the absence (1) and presence (2) of 0.4 mmol L^{-1} Cu^{2+}.



Scheme 1. The three stage pathways for the photocatalytic degradation of phenol over TiO_2.

about 0.027 min^{-1}. To account for the enhancing effect of fluoride ions, it has been proposed that the replacement of surface hydroxyl groups (≡Ti–OH) by fluoride increases holes availability and then accelerates either the generation of free $^{\bullet}OH$ radicals or the direct electron transfer to the organic electron donors [16–21]. The consequence is that the photodegradation of organic pollutants is promoted by the addition of fluoride into solution.

Although the enhancing effect of Cu^{2+} ions on the phenol degradation is rather weak (curve 1 in Fig. 2), a small addition of Cu^{2+} (0.4 mmol L^{-1}) can significantly increase the accelerating effect of fluoride ions on the phenol degradation. Curve 2 in Fig. 3 illustrates that as the F^- concentration is increased in the presence of 0.4 mmol L^{-1} Cu^{2+}, the rate constant k is increased rapidly, achieves a maximum of 0.041 min^{-1} at the F^- concentration of 5 mmol L^{-1}, and then is kept almost constant at greater F^- concentrations. Relative to the k value (0.010 min^{-1}) in the case without any addition of Cu^{2+} and F^-, the addition of 0.4 mmol L^{-1} alone increases k to 0.014 min^{-1} by 40%, the addition of 5 mmol L^{-1} F^- alone enhances k to 0.022 min^{-1} by ca. 120%, and the simultaneous addition of 0.4 mmol L^{-1} Cu^{2+} and 5 mmol L^{-1} F^- promotes k further to 0.041 min^{-1} by ca. 310%. Such strong synergistic effect of Cu^{2+} and F^- ions should be attributed to the surface modification of photocatalyst by adsorbed Cu^{2+} and F^- ions, being related to interactions between the adsorbed Cu^{2+} and F^- ions.

3.2. *Influences of Cu^{2+} and F^- on the formation and accumulation of intermediates of phenol degradation*

It is well known that phenol is photodegraded not directly to CO_2 but to many intermediates, and it is quite difficult to further mineralize these intermediates [1,18,22,26]. Identification of the intermediates is essential for a better understanding of the phenol degradation mechanism and the synergistic effect of Cu^{2+} and F^- ions. Using HPLC-MS, we identified the generated intermediates and monitored the concentrations of these intermediates during the photodecomposition of phenol. Two groups of intermediates, i.e., aromatic and aliphatic ones, were observed as reported in literature [22,26]. The aromatic intermediates mainly included catechol, hydroquinone (HQ) and benzoquinone (BQ), and the aliphatic intermediates were primarily aliphatic acids, including oxalic acid, acetic acid, maleic acid and formic acid [22]. For simplicity, we did not try to distinguish the generated aliphatic acids from each other in the present work.

The whole process of phenol photodegradation may be simply divided into three stages as phenol → aromatic intermediates → aliphatic intermediates → $CO_2 + H_2O$, as proposed in Scheme 1. The first stage for the conversion from phenol to aromatic intermediates is primarily important, and at this stage there are several parallel steps leading to formation of different aromatic intermediates. Santos and coworkers reported that upon conversion of phenol to catechol, higher rate of phenol mineralization was obtained than through the conversion of phenol to HQ or BQ, because catechol oxidation yielded nothing more than oxalic acid which was further mineralized to CO_2 and water, whereas the pathways of mineralization of HQ or BQ were much longer [22]. Fig. 4 illustrates the concentration changes of the intermediates during the phenol degradation. In the case without the addition of Cu^{2+} and F^-, faster generation and larger accumulation of catechol and HQ is observed relative to BQ, indicating that the phenol degradation proceeds main through the routes of converting phenol to catechol and HQ, but BQ is formed very slowly as the initial intermediate in the photodegradation of HQ [22]. At a glance of the concentration profiles for catechol and HQ in Fig. 4, we can find the maximum accumulation is increased in the order of blank < Cu^{2+} < F^- < $Cu^{2+} + F^-$. This order is the same as that observed for the synergistic effects of Cu^{2+} and F^- on the phenol degradation mentioned above, demonstrating that the addition of Cu^{2+} and/or F^- ions can accelerate all of the parallel pathways from phenol to the aromatic intermediates. Moreover, the decrease of the accumulation

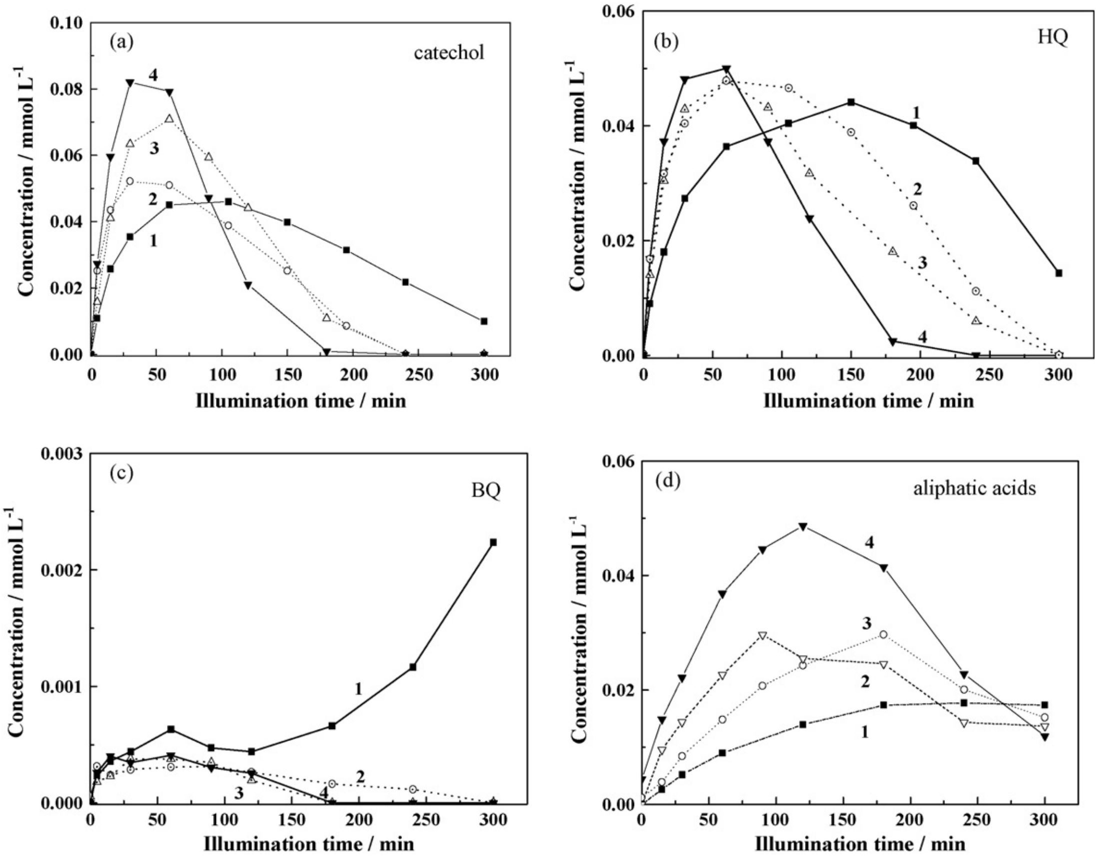


Fig. 4. Concentrations of the intermediates during the phenol degradation in suspensions of (1) 0.4 mmol L^{-1} phenol, (2) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+}, (3) 0.4 mmol L^{-1} phenol + 5 mmol L^{-1} F^-, and (4) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+} + 5 mmol L^{-1} F^-.

is promoted with the same order as mentioned above. Therefore, the addition of Cu^{2+} and/or F^- ions can accelerate all of the parallel pathways from the aromatic intermediates to the aliphatic intermediates. Especially, it is worthy noting that at the illumination time of 180 min, the concentrations of all the aromatic intermediates, as well as phenol, falls to almost zero in the presence of both Cu^{2+} and F^- ions.

The generation and accumulation of the aliphatic intermediates is more complicated. The accumulation of the aliphatic intermediates is dependent on the rate of their generation from the aromatic intermediates at the second stage and the disappearance rate to be mineralized to CO_2 and H_2O at the third stage. It seems apparently from Fig. 4d that higher and rapider accumulation of the aliphatic acids occurred when the phenol photodegradation was started in the case of the co-addition of Cu^{2+} and F^- ions (curve 4), relative to the addition of Cu^{2+} or F^- alone and the no addition of these ions. This is ascribed to the increased of phenol degradation at the stages from phenol to aromatic intermediates and from the aromatic intermediates to the aliphatic intermediates. As long as the added phenol molecules and the generated aromatic intermediates were substantially degraded, the accumulated aliphatic intermediates were rapidly decreased beyond about 120 min. In contrast, the accumulation of the aliphatic acids was low and slightly increased as the illumination time was increased in the case of no addition of F^- and Cu^{2+} ions (curve 1), which is attributed to the slow photodegradation of phenol at all the stages over neat TiO_2. When Cu^{2+} or F^- ions were added, the accumulation of the aliphatic intermediates (curves 2 and 3) was found to stand between the case of no addition of Cu^{2+} and F^- ions and the case of the addition of both Cu^{2+} and F^- ions.

3.3. *Influences of Cu^{2+} and F^- on the formation of H_2O_2 and $^\bullet OH$ radicals*

It is widely accepted that the photo-generated H_2O_2 and $^\bullet OH$ radicals take an important role in the photocatalytic degradation of organic pollutants over TiO_2 catalysts, and it is also well known that the valence band holes or trapped holes often governs the photocatalytic oxidation of organic compounds [28–31]. To clarify further the synergistic effect of Cu^{2+} and F^-, we investigated the influences of Cu^{2+} and F^- on the formation of H_2O_2 and $^\bullet OH$ radicals during phenol degradation.

The surface modification of TiO_2, such as by the adsorption of cations or anions, can drastically influence the interfacial charge transfer processes. Zhao and co-workers found the adsorption of Cu^{2+} on the TiO_2 surface hindered the reduction of oxygen by the conduct band electrons which was the precursor reaction of H_2O_2 generation, thereby influencing the concentration of H_2O_2 formed [32]. In accord with an earlier study [33], we detected no other organoperoxides except H_2O_2 during the irradiation. Fig. 5 shows the formation of H_2O_2 during the photodegrada-

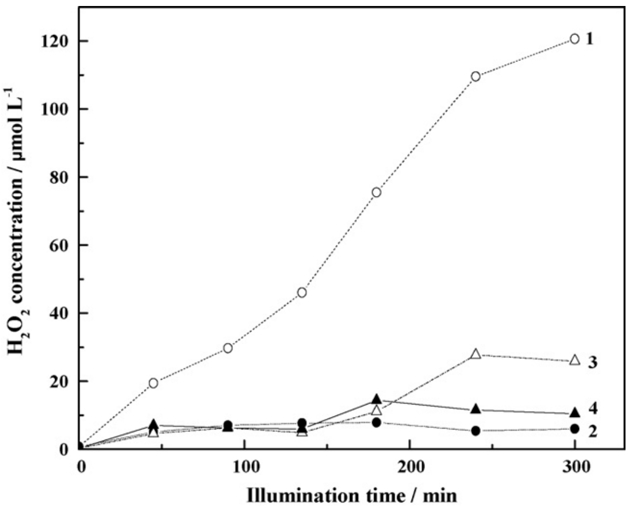


Fig. 5. Generated hydrogen peroxide during the photodegradation of phenol in suspensions of (1) 0.4 mmol L^{-1} phenol, (2) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+}, (3) 0.4 mmol L^{-1} phenol + 5 mmol L^{-1} F^-, and (4) 0.4 mmol L^{-1} phenol + 0.4 mmol L^{-1} Cu^{2+} + 5 mmol L^{-1} F^-.

tion of phenol. It is obvious that relative to neat TiO_2 in the absence of Cu^{2+} and F^- ions, the concentration of photogenerated H_2O_2 is sharply reduced with the addition of Cu^{2+} ions. This was owing to that trapping of the conduction band electrons by the adsorbed Cu^{2+}, reduction of O_2 molecules by the photoelectron becomes rather difficult, and formation of reactive oxygen species (O_2^-, HO_2) is suppressed. In addition, the produced Cu^+ can deplete generated H_2O_2 by the Fenton reaction ($H_2O_2 + Cu^+ \rightarrow OH + OH^- + Cu^{2+}$). In the presence of F^- ions alone, the concentration of generated H_2O_2 is also very low. By the addition of F^- ions, H_2O_2 reacts with F^- to form OF^- ions ($H_2O_2 + F^- \rightarrow OF^- + H_2O$), leading to a decreased H_2O_2 concentration. The effect of co-existence of Cu^{2+} and F^- on the generation of H_2O_2 is roughly the same as that of the added Cu^{2+} or F^- alone.

The above results indicate that the addition of Cu^{2+} as electron scavengers can enhance the charge separation, and results in increasing of photo-induced holes and then increasing of $^{\bullet}OH$ radicals. A fluorescence technique is used to detect of $^{\bullet}OH$ production in the photoirradiated TiO_2 suspension, in which coumarin is added and the photogenerated $^{\bullet}OH$ radicals will react with coumarin, yielding a strongly fluorescent product 7-hydroxy coumarin. The fluorescence intensity of generated 7-hydroxy coumarin is proportional to the amount of $^{\bullet}OH$ formed [24]. Since the fluorescence intensity increased linearly against time during the beginning of irradiation 10 min, the formation rate constant of $^{\bullet}OH$ was calculated from this slope. As shown in Fig. 6, it is observed that more $^{\bullet}OH$ radicals are formed in UV/TiO_2 system in the presence of both Cu^{2+} and F^- ions than that in other cases. Concerning the amount and initial accumulation rate of produced $^{\bullet}OH$ radicals, Cu^{2+}–F^-–TiO_2 shows the highest efficiency, followed by Cu^{2+}–TiO_2, F^-–TiO_2 and then naked TiO_2. It is proposed that the adsorbed Cu^{2+} on TiO_2 surface accelerates the production of $^{\bullet}OH$ radicals, due to electron-trapping by Cu^{2+} and the Fenton reaction ($H_2O_2 + Cu^+ \rightarrow OH + OH^- + Cu^{2+}$), whereas the positive effect of F^- ions is due to the shielding effect by fluoride replacement of surface hydroxyl groups of TiO_2. From a comparison of k for phenol disappearance and for initial $^{\bullet}OH$ generation (Fig. 6b), we can know that in the cases of blank, Cu^{2+}, and $Cu^{2+} + F^-$, a greater k value for initial $^{\bullet}OH$ generation (k_{OH}) matches well with an increased phenol degradation rate constant (k_{phenol}), but the extent of the increasing of k_{phenol} is quite different. Especially, a small k_{OH} yields a fairly greater k_{phenol} in the case of F^-, which is much different from that in the case of Cu^{2+}, where a fairly greater k_{OH} yields a considerably smaller k_{phenol}. This may suggest that the main reactant which governs the degradation of phenol is not $^{\bullet}OH$ radical but photoinduced holes [28–31]. However, added F^- ions increases the degradation of catechol as shown in Fig. 4a, implying the $^{\bullet}OH$-mediated pathway should not be ignored [18], because the displacement of adsorbed catechol by F^- largely makes the direct hole transfer unfavorable. Therefore, we can propose that the phenol degradation involves mainly the direct holes transfer and $^{\bullet}OH$ attack, and the holes-mediated processes are predominant, as demonstrated in Scheme 1. Because the $^{\bullet}OH$ addition reaction is undistinguishable from the combination of the photoinduced trapped holes

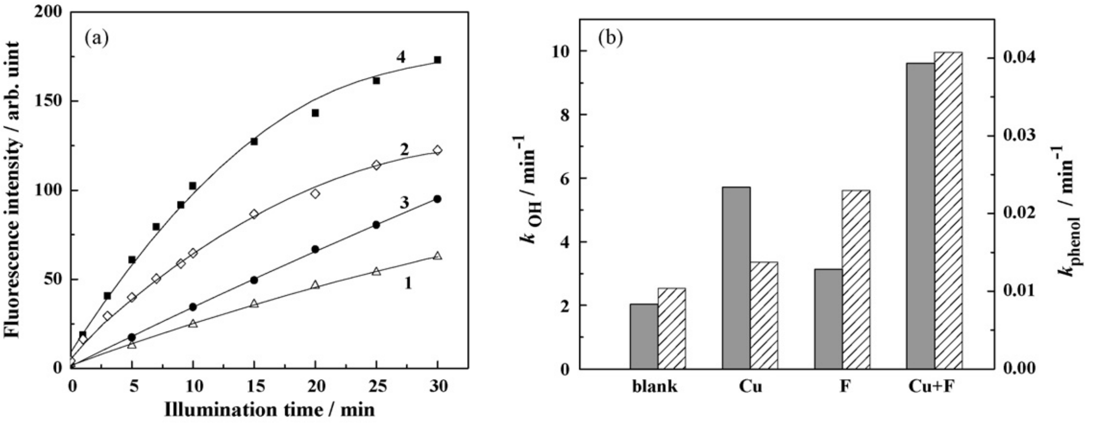


Fig. 6. (a) Formation of 7-hydroxy coumarin during the illumination of TiO_2 in 1.0 mmol L^{-1} coumarin solutions under conditions of Cu^{2+}/F^- addition of (1) blank, (2) Cu^{2+}, (3) F^-, and (4) $Cu^{2+} + F^-$. (b) A comparison between the rate constants of the OH radical formation (k_{OH}, dark bar) and phenol degradation (k_{phenol}, dashed shadow bar).

and the hydration process, [29] the distribution of intermediate products is not changed by the addition of Cu^{2+} or F^- (Fig. 4).

3.4. An explanation to synergistic effect of Cu^{2+} and F^- on the phenol photodegradation

By comparing the influences of Cu^{2+}, F^- and co-existence of $Cu^{2+}$and F^- on the phenol degradation, generation of intermediates, and generation of H_2O_2 and $^\bullet OH$ radicals during the photodegradation, we can propose a tentative explanation to the synergistic effect of Cu^{2+} and F^- on the phenol photodegradation.

When phenol is photocatalytic degraded over TiO_2 without the presence of Cu^{2+} or F^-, phenol degradation proceeds mainly via the actions of photo-generated holes and $^\bullet OH$ radicals, *in situ* produced from the charge separation of photo-induced electron/hole pairs over the surface of the catalyst. The presence of a small amount of Cu^{2+} in the suspension favors to the adsorption of Cu^{2+} on the photocatalyst's surface, leading to a surface modification of the photocatalyst. Instead of O_2, the pre-adsorbed Cu^{2+} ions function as an efficient electron trapping ($Cu^{2+} + e^- \rightarrow Cu^+$), and the produced Cu^+ initiates the Fenton reaction, resulting in acceleration of $^\bullet OH$ radicals generation to an extent. Thus, the phenol degradation is slightly accelerated by the addition of a little amount of Cu^{2+} ions.

Alternatively, the presence of a small amount of F^- in the suspension favors to the adsorption of F^- on the photocatalyst's surface, leading to a surface modification of the photocatalyst with a formation ≡Ti–F species on the surface. It is reported that the $^\bullet OH$ radicals generated on the surface of neat TiO_2 can hardly leave from the TiO_2 surface because it rapidly reacts with surficial $^\bullet OH$ group (≡Ti–OH), [34] unfavorable to the degradation of organic pollutants in the bulk of the suspension. The increased surface coverage of ≡Ti–F species decreases the surface coverage of ≡Ti–OH species. This enhances holes availability for the direct degradation of phenol or water oxidation, promoting the formation of free $^\bullet OH$ radicals [16–21]. Therefore, the addition of a little amount of F^- ions considerably enhances the photodegradation of phenol.

When both Cu^{2+} and F^- ions are simultaneously added into the suspension, the TiO_2 photocatalyst's surface is modified by the adsorbed Cu^{2+} and F^- ions. The function of the electron trapping of Cu^{2+} ions is coupled with the increased holes availability due to the formation of ≡Ti–F species. Therefore, the charge separation at the surface of the photocatalyst is significantly promoted, leading to the much enhanced generation of holes, free $^\bullet OH$ radicals and other reactive species and resulting in greatly enhanced photodegradation of phenol. Hence, we can observe a strong synergistic effect of Cu^{2+} and F^- ions on the photodegradation of phenol. Moreover, the surface charge of TiO_2 and electron-transfer pathway may be somewhat altered due to the TiO_2 surface occupation of Cu^{2+} and F^- ions. The reduced positive surface charge on the surface fluorinated-TiO_2 draws Cu^{2+} cations closer to the photocatalyst surface and triggers the electron trapping more easily and quickly. This also makes a contribution to the observed synergistic effect of Cu^{2+} and F^- ions.

4. Conclusions

By using phenol as a model compound of organic pollutants to be degraded, the effects of dissolved Cu^{2+} and F^- ions were investigated on the photocatalytic degradation of organic pollutants in UV/TiO_2 system. When an appropriate amount of Cu^{2+} or F^- alone was added into the TiO_2 suspensions, the adsorbed Cu^{2+} ions function as an electron scavenger, or the adsorbed F^- ions played a role in increasing holes availability and consequently accelerating to yield more $^\bullet OH$ radicals and/or enhance the direct transfer of holes to phenol. Either of the both functions resulted in the promotion of the phenol degradation. When Cu^{2+} and F^- ions were simultaneously added into the suspension, the favorable function of Cu^{2+} ions was coupled with that of F^- ions, leading to a significant synergistic effect of Cu^{2+} and F^- on the phenol photodegradation. As a consequence of it, the ratios of the phenol degradation rate in the presence of the added substance(s) to that over neat TiO_2 (blank) were found to be about 1.4, 2.2 and 4.1 for the addition of Cu^{2+}, the addition of F^-, and the addition of both Cu^{2+} and F^-, respectively. Because the enhancing effect of Cu^{2+} and/or F^- ions was generally effective to the photodegradation of most organic compounds, the strong synergistic effect of Cu^{2+} and F^- was observed not only for the overall process of phenol degradation, but also for the individual steps of the degradation of the intermediates generated at each of the stages of the overall phenol degradation process. Because of the possible precipitation of Cu^{2+} as hydroxides at high pH values and the association of HF in strongly acidic solutions, we also found that the strong synergistic effect of Cu^{2+} and F^- ions on the phenol photodegradation was best observed in a range of pH from about 2 to 4. The easy establishment and control of the Cu^{2+}–F^-–TiO_2-UV system may provide an alternative way for the rapid degradation of the biorefractory compounds in wastewater treatment.

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