



Enhanced sorption and photodegradation of chlorophenol over fluoride-loaded TiO₂

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ABSTRACT

The presence of NaF in the aqueous suspension of TiO₂ can accelerate the photocatalytic degradation of organic pollutants. However, disposal of such a fluoride-containing wastewater is not allowed by environmental regulation. In the present work, we report on surface modification of TiO₂ with a hardly water soluble salt, fluorite and fluorapatite. The modified catalysts at low loading displayed a higher activity than bare TiO₂ for the sorption and photocatalytic degradation of phenol and 2,4-dichlorophenol in water. A kinetic study using butanol as hydroxyl radical scavenger revealed that the fluoride-modified catalysts produced more hydroxyl radicals than bare TiO₂. Five repeated experiments showed that the fluorapatite-modified TiO₂ was very stable, and could be re-used without significant loss in activity.

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1. Introduction

Photocatalytic degradation of organic compounds over TiO₂ has been extensively studied as a potential technology for water treatment and air purification [1,2]. This is because a variety of organic pollutants can be degraded, and/or mineralized into CO₂ over irradiated TiO₂ at normal temperature and pressure. Many factors that influence the system efficiency have been reported, but they are mainly the physical properties of TiO₂ itself, such as crystal structure, crystallinity, particle size, surface area, and porosity. However, the overall efficiency achieved so far with TiO₂-based system is not sufficiently high to enable practical application. This is mainly ascribed to fast recombination of charge carries on irradiated TiO₂, and thus low quantum yield in generation of the reactive species for organic degradation [3]. Any method that can retard charge carrier recombination would result into improvement in the efficiency of charge separation, and thus in the rate of the interfacial charge transfer to adsorbed substrates.

One of the interesting methods is surface modification of TiO₂ with NaF, which has been shown to significantly enhance the rate of organic photodegradation either in air or in an acidic aqueous suspension [4–14]. The higher rate of organic degradation is ascribed to the higher rate of •OH production, as revealed by a scavenging experiment with alcohol [5], and a spin-trapping electron paramagnetic resonance [9]. Moreover, during the reaction process, fluoride anions are stable against oxidation by valence holes

or •OH. For practical application, such a modified system of TiO₂ with fluoride would be very useful. However, NaF is highly soluble in water. According to environmental regulation, disposal of an industrial wastewater that contains fluoride ions at a concentration higher than 0.5 mM is not permitted. Therefore, fluoride ions must be immobilized onto TiO₂, preferably with enhancement in both sorption capacity and photocatalytic activity toward organic pollutants in water.

In the present work, fluorite (CaF₂) and fluorapatite [Ca₁₀(PO₄)₆(OH)_{2-x}F_x, x = 2], which are hardly soluble in water, have been used as a surface modifier of TiO₂. Result showed that the composite had a higher activity than parent TiO₂, for the photocatalytic degradation of phenol and 2,4-dichlorophenol (DCP) in aqueous suspension under UV light. The samples were prepared through an *in situ* deposition method, followed by routine characterization. Since fluorapatite contains phosphate anions, the samples containing calcium phosphate were also prepared for comparison. Moreover, the modified catalysts showed a higher capacity for uptake of organic substrates in water. Because of that, the adsorption isotherm of DCP on different catalysts was measured, and the effect of substrate concentration on the reaction rate was examined by application of the Langmuir–Hinshelwood (L–H) rate equation [15–17].

2. Experimental

2.1. Materials

Organic substrates (phenol, 2,4-dichlorophenol, benzoquinone and hydroquinone) and inorganic chemicals, such as Ca(NO₃)₂,

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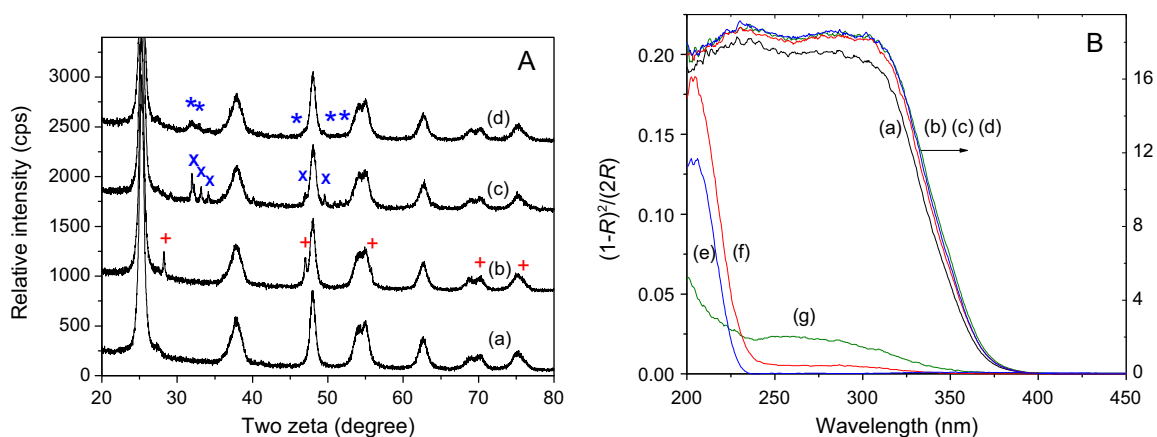


Fig. 1. (A) XRD patterns and (B) diffuse reflectance spectra of (a) TiO₂, (b) 7.2 CaF₂/TiO₂, (c) 9.2 FAP/TiO₂, (d) 9.3 TCP/TiO₂, (e) CaF₂, (f) FAP, and (g) TCP. Symbols in (A) represent fluorite (+), fluorapatite (x), and calcium phosphate (*), respectively. In (B), the y-axis is expressed in the Kubelka–Munk unit, where *R* is the reflectance.

NH₄F, and (NH₄)₂HPO₄, were purchased from Shanghai Chemicals, whereas TiO₂ powder was a gift from Taixing Nanomaterials. Modifiers, CaF₂, Ca₃(PO₄)₂, and Ca₁₀(PO₄)₆(OH)_{2–x}F_x (*x* = 2), denoted as CF, TCP, and FAP, respectively, were prepared by following literature procedures [18,19]. Composite samples were prepared in a N₂-degassed aqueous solution to avoid carbonate contamination. Typically, 1.00 g of TiO₂ was added to 100 mL of calcium solution, followed by pH adjustment to about 11 with 8 wt% ammonia solution. To this suspension was added 100 mL of fluoride or phosphate solution, or a mixed solution of them, the concentration of which was previously calculated by the stoichiometric amount of CF, TCP, and FAP to be loaded onto TiO₂. The suspension at pH 9–10 was heated at 80 °C for 2 h, and stored at room temperature overnight. After filtration and washing, the powder was dried at 60 °C in a vacuum oven. The amount of each modifier loaded onto TiO₂ is represented by *y* in the front of sample. For instance, catalyst 9.2 FAP/TiO₂ means that TiO₂ has been loaded with 9.2 wt% FAP during the sample synthesis.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a D/max-2550/PC diffractometer (Rigaku). Phase content of TiO₂ was estimated from the strongest diffractions of anatase (1 0 1) and rutile (1 1 0), while the crystallite size (*d_s*) was calculated by Scherrer equation. N₂ adsorption was measured at 77 K on a Micromeritics ASAP2020. Pore volume (*V_p*) was estimated at a relative pressure of 0.99. UV–visible diffuse reflectance spectra (DRS) were recorded on a Varian Carry 500 Spectrophotometer using BaSO₄ as a reference. Band gap energy (*E_g*) of TiO₂ was estimated by following literature procedure [20].

2.3. Photocatalysis

Reaction was carried out in a thermo-stated Pyrex-glass reactor, irradiated with a high pressure Hg lamp (375 W, Shanghai Yamin). Due to partial hydrolysis of the modified sample at pH 8, all the reaction suspensions were prepared with 1.0 g/L catalyst and 0.43 mM organic substrate at pH 8.0. The suspension was first sonicated for 5 min, and then stirred in the dark for 30 min. At given irradiation time, some aliquots were withdrawn, filtered, and analyzed with high performance liquid chromatography (HPLC) on a Dionex P680 (Apollo C18 reverse column, and 60% CH₃OH as an eluent). Inorganic anions were analyzed with ionic chromatography (IC) on a Dionex ISC90 (AS14A column, and 10 μM Na₂CO₃/NaHCO₃ as an eluent).

3. Results and discussion

Samples were characterized by XRD, N₂ adsorption, and DRS, and the results are shown in Fig. 1 and Table 1. Parent TiO₂ was a commercial product, and it consisted of anatase and rutile in a ratio of about 97:3. After loading with a modifier (CaF₂, FAP, and TCP), TiO₂ phase remained almost unchanged, in terms of the phase composition, crystallite size, and crystallinity. However, the surface area and pore volume of the modified sample were decreased, as compared to parent TiO₂. The decrease in surface area was balanceable with neat TiO₂, but the corrected pore volume was still significantly lower than that of bare TiO₂ (data in parentheses, Table 1). It implies that porous channels of TiO₂ are partially blocked by modifier particles. In order to prove this, the micropore volume and average pore diameter were then estimated through a *t*-plot and pore size analysis, and the values of composite sample were indeed lower than those obtained with naked TiO₂. Moreover, in the XRD pattern, there also appeared several diffractions, characteristic of fluorite (PDF #35-0816), fluorapatite (PDF #15-0876), and calcium phosphate (PDF #18-0303), respectively. These modifiers did not have influence on the band gap energy of TiO₂ (3.11–3.14 eV), but they showed a different absorption toward light in the wavelength region from 200 nm to 350 nm (Fig. 1). Pure CaF₂ was transparent at λ ≥ 230 nm, whereas pure FAP and TCP had a weak band at 230–380 nm, due to charge transfer from O^{2–} to P⁵⁺ in phosphate. This optical difference may have some effect on the photocatalytic degradation of organic pollutants under UV light at λ ≤ 320 nm, as will be discussed below.

Primary experiment of photocatalysis was performed with bare TiO₂ and 9.2 FAP/TiO₂, for phenol degradation in an aerated aqueous suspension at initial pH 8.0. As shown in Fig. 2, the sample 9.2 FAP/TiO₂ was more active than parent TiO₂. Since phenol degradation in the absence of catalyst was negligible, the observed reaction is surely due to photocatalysis. At the same time, hydroquinone (HQ) and benzoquinone (BQ) as the main intermediates were formed, whose concentration first increased, and then decreased with irradiation time. This indicates that HQ and BQ are also degradable during the reaction process. However, at a given time, the sum of HQ and BQ, and the mole ratio of HQ to BQ, were higher over 9.2 FAP/TiO₂ than those measured with parent TiO₂. Since the intermediates were detected in solution, it implies that the catalysts may have different sorption capacities toward HQ and BQ in water. Separate experiment showed that dark adsorption of HQ and BQ in aqueous suspension were 8.72 and 4.52 μmol/g on bare TiO₂, and 2.00 and 12.1 μmol/g on 9.2 FAP/TiO₂, respectively. Result indicates

Table 1
Physical parameters of representative catalysts.

Samples	P (%)	d_s (nm)	A_{sp} (m ² /g)	V_t (cm ³ /g)	V_m (cm ³ /g)	d_p (nm)	E_g (eV)
Naked TiO ₂	97	11.5	144	0.614	0.0034	14.3	3.11
9.2 FAP/TiO ₂	97	11.4	131 (144)	0.513 (0.565)	0	13.0	3.12
7.2 CaF ₂ /TiO ₂	98	11.8	132 (142)	0.523 (0.564)	0.0020	13.3	3.11
9.3 TCP/TiO ₂	97	11.4	135 (149)	0.536 (0.591)	0.0007	13.3	3.14

P: anatase content; d_s : the diameter of anatase; A_{sp} : BET surface area; V_t : total pore volume; V_m : micropore volume; d_p : average BJH pore width; E_g : bandgap energy. Data in parentheses are the values after correction of a modifier loading.

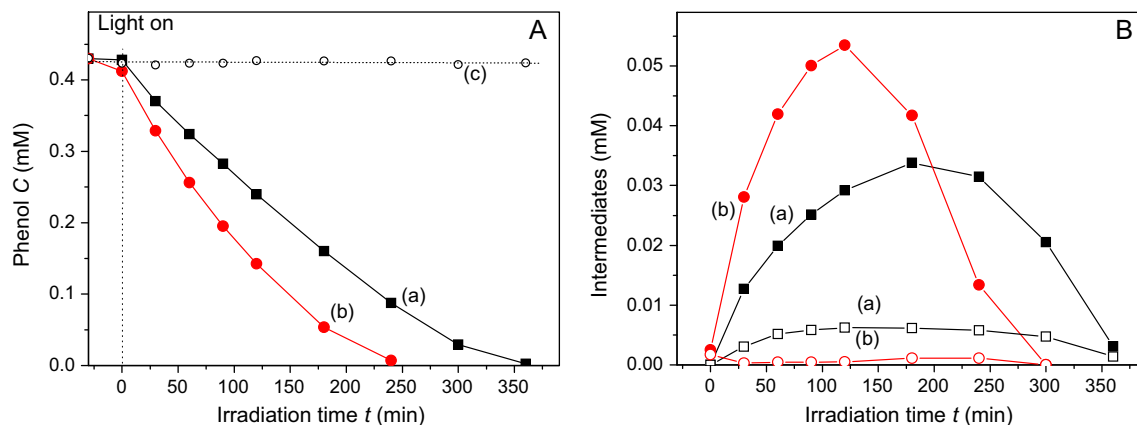


Fig. 2. (A) Photocatalytic degradation of phenol in water over (a) TiO₂, (b) 9.2 FAP/TiO₂, and (c) no catalyst. (B) The intermediates of hydroquinone (solid bars), and benzoquinone (open bars).

that 9.2 FAP/TiO₂ is more photoactive than TiO₂, and it may also prefer to initiate phenol oxidation to form HQ, a possible product of •OH attack to phenol.

The amount of FAP loaded onto TiO₂ has a great influence on phenol degradation, as shown in Fig. 3. Since FAP contains both fluoride and phosphate, the samples containing CaF₂ or TCP were also prepared. As the modifier loading on TiO₂ increased, the apparent rate constant of phenol degradation first increased, and then decreased notably. The optimum loading of FAP, CaF₂, and TCP on TiO₂ were about 4.8, 13.5, and 3.1 wt%, respectively. Separate experiment showed that the rate of phenol degradation over bare TiO₂ increased with TiO₂ concentration present in the reactor, and it then approached a limit at 0.80 g/L of TiO₂. Since the composite catalyst concentration in the reactor was fixed at 1.00 g/L for each measurement, the enhanced activity of the composite catalyst at

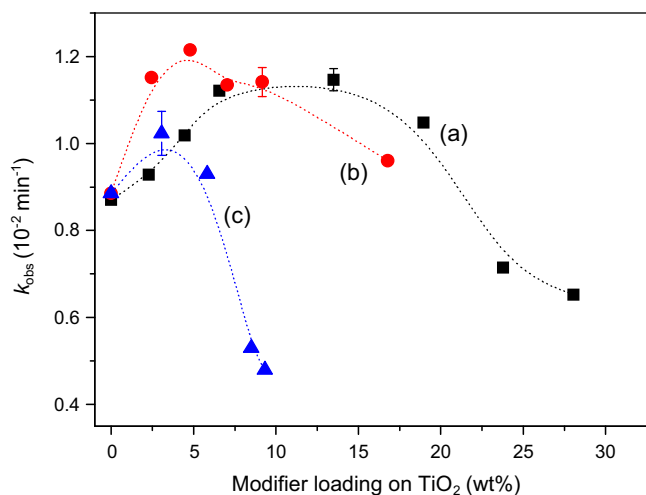


Fig. 3. Apparent rate constant of phenol photodegradation as a function of modifier loading on TiO₂, obtained with (a) CaF₂/TiO₂, (b) FAP/TiO₂, and (c) TCP/TiO₂.

low modifier loading suggests the positive effect of modifier on the photocatalytic degradation of phenol, the reason for which will be discussed below.

On the other hand, the composite catalyst at high modifier loading shows a decreased activity as compared to bare TiO₂, which is ascribed to two factors of the light intensity reaching on TiO₂, and the amount of neat TiO₂ in the reactor. Due to phosphate, both TCP and FAP have a shielding effect on the light absorption by TiO₂ (Fig. 1). Then, the number of charge carrier generated on the irradiated TiO₂ is reduced, and consequently the rate of the interfacial charge transfer to adsorbed substrates is decreased. Since TCP has a higher density of phosphate anions, its loading on TiO₂ displays a fast decay in the rate of phenol degradation, as compared to FAP/TiO₂ (Fig. 3). Pure CaF₂ is transparent at $\lambda > 230$ nm, and its loading on TiO₂ would not have the shielding effect on the light intensity at $\lambda > 320$ nm. Thus, its optimum loading on TiO₂ is high (13.5 wt%). The decrease in activity of CaF₂/TiO₂ at high loading is ascribed to decrease in the concentration of neat TiO₂ in the suspension, because the photocatalytic activity of TiO₂ is the cause, and modifier is only the effect. Among four catalysts at an optimum loading, FAP/TiO₂ is the best one, and its activity is increased by 37%, in relative to that of bare TiO₂.

The composite catalysts in aqueous solution had a weak affinity toward phenol, but a high sorption capacity for uptake of 2,4-dichlorophenol (DCP), due to the increase of substrate hydrophobicity. Fig. 4 shows the adsorption isotherms of DCP on different catalysts in aqueous suspension at pH 8.0. On each catalyst, the amount of DCP adsorbed (q) increased with its equilibrium concentration in solution (C_{eq}). The isotherm was well fitted to the Langmuir adsorption equation, $q/q_s = C_{eq}/(1 + KC_{eq})$, where q_s is the maximum amount of DCP adsorbed, and K is the adsorption constant. The result in Table 2 shows that q_s follows a trend of 9.2 FAP/TiO₂ > 9.3 TCP/TiO₂ > 7.2 CaF₂/TiO₂ > TiO₂, while K follows another trend of 9.3 TCP/TiO₂ > 9.2 FAP/TiO₂ > 7.2 CaF₂/TiO₂ > TiO₂. All modified catalysts exhibit a higher sorption capacity than bare TiO₂ for uptake of DCP from water. Samples 9.2 FAP/TiO₂ and 9.3 TCP/TiO₂ have a similar content of phosphate (0.60 vs 0.66 mmol

Table 2
Parameters of phenol and DCP obtained from dark adsorption and photodegradation.

Samples	q_s ($\mu\text{mol/g}$)	K (mM^{-1})	k_{L-H} (phenol) ($\mu\text{M}/\text{min}$)	K^* (phenol) (mM^{-1})	k_{L-H} (DCP) ($\mu\text{M}/\text{min}$)	K^* (DCP) (mM^{-1})
Naked TiO_2	31	5.98	1.89	29.9	1.95	24.7
9.2 FAP/ TiO_2	106	7.95	2.69	21.3	2.94	18.7
7.2 CaF_2 / TiO_2	61	6.75	2.17	18.2	2.29	18.4
9.3 TCP/ TiO_2	75	8.78	1.01	61.5	1.51	34.5

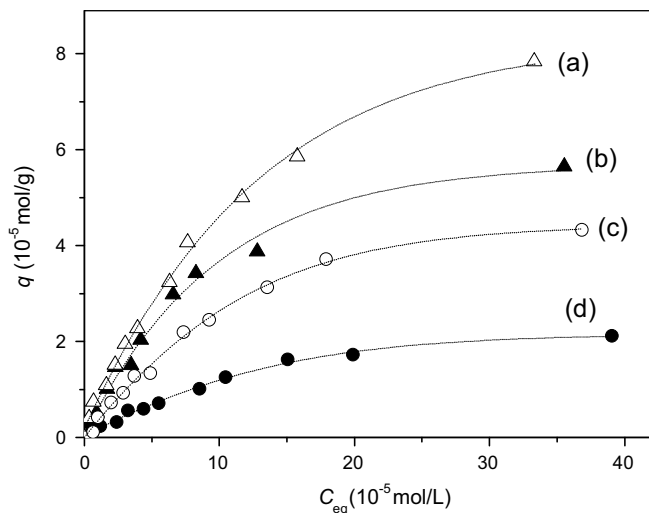


Fig. 4. Adsorption isotherms of 2,4-dichlorophenol in the dark on (a) 9.2 FAP/ TiO_2 , (b) 9.3 TCP/ TiO_2 , (c) 13.5 CaF_2 / TiO_2 , and (d) TiO_2 , in the aqueous suspension at pH 8.0.

per gram of TiO_2). Phosphate anion appears to have a stronger interaction with DCP than fluoride anion, probably through a hydrogen bond. Since FAP contains both phosphate and fluoride, its loading on TiO_2 leads to the highest sorption capacity among the catalysts.

The difference in sorption capacity among the catalysts might be responsible for the difference in activity for organic photodegradation (Fig. 2). In order to exclude the effect of substrate concentration, initial rate of organic photodegradation (r_0) as a function of its initial concentration (C_0) needs to be measured. Such kinetics is usually well fitted to the L-H equation, $r_0 = k_{L-H}K^*C_0/(1 + K^*C_0)$, where k_{L-H} is the rate constant, and K^* is the apparent adsorption constant [15–17]. In the present study, the initial rate of organic loss (r_0) was measured at first 20 min, and C_0

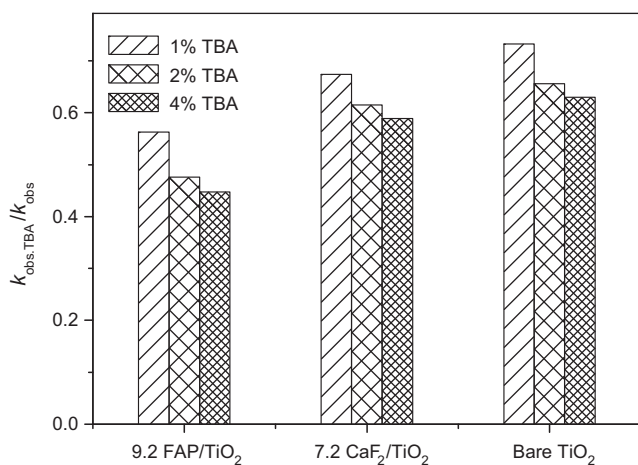


Fig. 5. Effect of TBA concentration on the ratio of $k_{\text{obs,TBA}}$ to k_{obs} , where k_{obs} and $k_{\text{obs,TBA}}$ are the apparent rate constants of phenol photodegradation in absence and presence of TBA, respectively.

was replaced by C_{eq} , the equilibrium concentration of the substrate in solution before light irradiation. A linear relationship between $1/r_0$ and $1/C_{\text{eq}}$ was satisfactory, from which the parameters k_{L-H} and K^* were obtained (Table 2). Both phenol and DCP degradation gave a similar result. That is, the value in k_{L-H} became larger in the order of 9.2 FAP/ $\text{TiO}_2 > 7.2 \text{CaF}_2/\text{TiO}_2 > \text{TiO}_2 > 9.3 \text{TCP}/\text{TiO}_2$, whereas the value in K^* follows a trend of 9.3 TCP/ $\text{TiO}_2 > \text{TiO}_2 > 9.2 \text{FAP}/\text{TiO}_2 > 7.2 \text{CaF}_2/\text{TiO}_2$. Since k_{L-H} is concentration independent, the result clearly shows that among four catalysts, 9.2 FAP/ TiO_2 is the best one, for the photocatalytic degradation of both weakly and highly adsorptive organic substrates in water. Moreover, the value of K^* obtained under UV light is larger than that of K determined in the dark, and also the trend in K^* is not in agreement with that trend in K (Table 2). Such discrepancy between K and K^* is often observed with organic photodegradation over TiO_2 in water (see references in [15]). Ollis has recently ascribed it to the light effect on the equilibrium of substrate adsorption–desorption [15], while Serpone and co-workers have made another explanation [17]. Discussion about the L-H model is out of the present study. At least, the data in Table 2 can be used as a reference. Nevertheless, the result in Fig. 3 has shown that the fluoride-containing catalysts are excellent for the photocatalytic degradation of phenol in water.

Since both fluoride-modified samples exhibit a higher photocatalytic activity than bare TiO_2 , possible involvement of $\bullet\text{OH}$ radicals in the reaction process was then examined by using *tert*-butanol (TBA) as a scavenger [5]. In this study, phenol was used as a model substrate, since it hardly adsorbed on the catalysts. Fig. 5 shows the apparent rate constants of phenol degradation, k_{obs} and $k_{\text{obs,TBA}}$, obtained in the absence and presence of TBA, respectively. With each catalyst, the ratio of $k_{\text{obs,TBA}}$ to k_{obs} was less than 1, and it also decreased with TBA concentration. It implies that $\bullet\text{OH}$ radicals are involved with all catalysts. However, at given TBA, the ratio of $k_{\text{obs,TBA}}$ to k_{obs} follows a trend of 9.2 FAP/ $\text{TiO}_2 < 7.2 \text{CaF}_2/\text{TiO}_2 < \text{TiO}_2$. The larger decrease in rate constant due to TBA means the higher rate of $\bullet\text{OH}$ production in the absence of TBA. This trend in the rate of $\bullet\text{OH}$ production is the same as that in the rates of phenol and DCP degradation (Table 2). The enhanced activity of TiO_2 obtained with a hardly water soluble FAP and CaF_2 is similar to those reported with a highly water soluble NaF [4–14].

Three different mechanisms for the enhanced activity of fluoride-modified TiO_2 have been proposed in the literature. First is the replacement of surface OH^- groups by fluoride ions, which results in enhancement in the rate of $\bullet\text{OH}$ production in solution [4–11]. Second is the enhanced production of singlet oxygen via an energy transfer [12]. The third is the promoted desorption of surface bound $\bullet\text{OH}$ into solution, via a fluorine hydrogen bond [14]. In the present study, the modified catalysts were prepared in an alkaline solution by depositing CaF_2 and FAP onto TiO_2 . Under such conditions, the replacement of surface OH^- groups by fluoride ions is less likely, due to complete deprotonation of TiO_2 [1]. Phenol oxidation by $^1\text{O}_2$ forms BQ as a product [21]. The observed increase in the mole ratio of HQ to BQ, for phenol oxidation over FAP/ TiO_2 (Fig. 2) implies that the production of $\bullet\text{OH}$, other than $^1\text{O}_2$, is enhanced in relative to bare TiO_2 . Therefore, we prefer to the third mechanism that desorption of surface bound $\bullet\text{OH}$ into solution is promoted by fluoride anions immobilized on TiO_2 , thus increasing the rate of organic degradation at a solid–liquid interface.

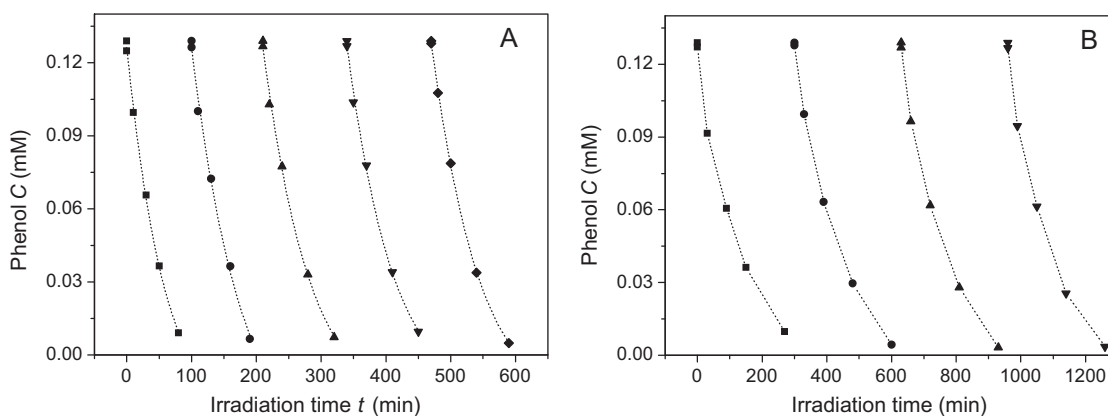


Fig. 6. Repeated experiments for phenol photodegradation over 9.2 FAP/TiO₂ in water at (A) pH 8.0, and (B) pH 4.0. After phenol disappeared completely in each run, a new fresh solution of phenol was supplied so as to maintain its concentration at 0.13 mM.

Last question that needs to be answered is the catalyst stability. Thus, a repeated experiment was performed with 9.2 FAP/TiO₂ as a catalyst for phenol degradation. After five repeated experiments at initial pH 8.0 (Fig. 6A), the catalyst was still active. From the first run to the last, the apparent rate constant of phenol degradation was only slightly decreased, from $3.15 \times 10^{-2} \text{ min}^{-1}$ to $2.61 \times 10^{-2} \text{ min}^{-1}$. Such a decline in the rate of phenol degradation could be ascribed to a gradual loss of catalyst for sampling, and to the HQ and BQ intermediates that compete with phenol for reactive species. IC analysis showed that after the fifth run, the dissolved fluoride and phosphate anions in the filtrate were about 26 and 30 μM , respectively. This is much below the regulation limit for disposal of a fluoride-containing industrial wastewater. Moreover, the catalyst was also quite stable at initial pH 2.6 (Fig. 6B). Comparatively, the reaction at low pH was slower than that at high pH. This is not due to deactivation of the catalyst, but due to lower reducing ability of phenol at low pH [22]. Such the pH effect on phenol degradation over TiO₂ has been reported in literature [4,7,14,23], and confirmed here by a supplemental experiment. The apparent rate constants of phenol degradation at initial pH 4.0 and 8.0 were 0.99 and $4.76 \times 10^{-3} \text{ min}^{-1}$ for bare TiO₂, while the corresponding constants for 9.2 FAP/TiO₂ were 3.83 and $8.83 \times 10^{-3} \text{ min}^{-1}$, respectively. That is, either in an acidic or basic medium, 9.2 FAP/TiO₂ is more active than TiO₂ for the photocatalytic degradation of phenol in water.

4. Conclusions

This work has shown that surface modification of TiO₂ with CaF₂ and FAP at about 10 wt% is an effective way to improve TiO₂ activity for the photocatalytic degradation of organic substrates in water. This is due to enhancement in both organic adsorption and the production of $\bullet\text{OH}$ radicals in solution. The dissolved fluoride anions from the catalyst into solution are below the regulation limit for industrial wastewater disposal. Since a commercial available TiO₂ is optionally selected, this method of fluoride loading would find a wide application for modification of various TiO₂ catalysts.

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