

Effects of Polyoxometalate and Fluoride on Adsorption and Photocatalytic Degradation of Organic Dye X3B on TiO₂: The Difference in the Production of Reactive Species

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Received: September 15, 2005; In Final Form: December 30, 2005

It has been reported that addition of polyoxometalates (POM) or fluoride anions into the TiO₂ dispersions can significantly enhance the photocatalytic degradation (PCD) of weakly adsorptive organic pollutants in water such as chlorophenol. In this work, however, contradictory effects of POM and fluoride were observed on the PCD of highly adsorptive substrate X3B, an anionic organic dye, under similar conditions. The total rate of X3B PCD, determined by total loss of X3B both in solution and on the catalyst surface, was increased in the presence of fluoride, but the rate was decreased in the presence of POM. In both cases, the dark adsorption of X3B on TiO₂ was greatly decreased, ascribed to competitive adsorption of POM or fluoride that reduces the positive charges on the catalyst surface. The spectral analysis and the kinetic study using *tert*-butyl alcohol as hydroxyl radical scavenger revealed that the PCD of X3B on naked TiO₂ was predominately initiated by direct hole transfer, whereas addition of POM or fluoride into the TiO₂ dispersions enhanced the degradation of X3B via hydroxyl radical pathway. It is proposed that the surface occupation of POM on TiO₂ accelerates the production of surface-bound hydroxyl radicals, due to enhanced charge separation, whereas the fluoride replacement of surface hydroxyl groups of TiO₂ increases the production of free hydroxyl radicals in solution, due to enhanced hole availability for water oxidation. Assume that the relative reactivity among various active follows the order of free hydroxyl radicals > subsurface holes > surface-bound hydroxyl radicals, the proposal could account for the observed effects of POM and fluoride on the PCD of both weakly and highly adsorptive organic substrates over TiO₂ such as chlorophenol and X3B.

Introduction

Elimination of organic pollutants by TiO₂ photocatalysis has been widely studied.^{1,2} It is well established that the organic degradation is initiated by reactive species such as conduction band electrons (e_{cb}^-), valence band holes (h_{vb}^+), superoxide radicals (O_2^-), and hydroxyl radicals ($\cdot OH$), produced from illuminated TiO₂ particles. However, the overall efficiency developed so far is still not high enough to satisfy the practical application. The primary event occurring on the UV-illuminated TiO₂ is the generation of e_{cb}^- and h_{vb}^+ . These charge carriers can rapidly migrate into the surface where they are ultimately captured by a suitable electron donor and acceptor, initiating a useful reaction, and/or they are recombined, dissipating the input light energy into heat. Thus, the overall quantum efficiency is determined by the competition between charge carrier recombination and interfacial charge transfer. An increase in the surface concentration of appropriate scavenger or organic substrate would favor the interfacial charge transfer and depress the charge recombination, consequently enhancing the desirable degradation of organic pollutants.

Among various efforts for improvement of photocatalytic efficiency, the surface modification of TiO₂ by polyoxometalate (POM) and fluoride seems mostly interesting. Pelizzetti and co-worker found that addition of a fluoride anion into the dispersions of TiO₂ could significantly accelerate the photocatalytic degradation (denoted PCD below) of phenol under UV irradiation.^{3,4} A similar result was also observed by Choi and co-worker for the PCD of phenol, Acid Orange 7 and tetra-

methyammonium at a specific pH range.^{5,6} This positive effect of fluoride has been ascribed into enhanced production of free $\cdot OH$ radicals in solution, since the surface OH^- groups of TiO₂ are replaced by fluoride and then the valence hole turns out to oxidize water. On the other hand, Ozer and Ferry found that addition of POM such as $PW_{12}O_{40}^{3-}$ into TiO₂ dispersions could accelerate the PCD rate of 1,2-dichlorobenzene (DCB) in water at pH 1.0.⁷ This rate enhancement has been attributed into improved charge separation, due to the fact that POM is a better electron acceptor than O_2 . The one-electron reduction potential of $PW_{12}O_{40}^{3-}$ is +0.218 V versus NHE,⁷ which is more positive than that of O_2 , [$E(O_2/HO_2) = -0.11$ V versus NHE at pH 1 for unit pressure of O_2].^{8,9} Later on, Zhao and co-workers reported a similar result for the PCD of 2,4-dichlorophenol (DCP) on POM–TiO₂, but they also observed the increased production of hydroxylated aromatic intermediates in the presence of POM.¹⁰ Park and Choi have demonstrated that POM is an efficient mediator for the electron transfer from TiO₂ particles to O_2 molecules.¹¹ They further claimed that addition of POM into the TiO₂ dispersion could accelerate the oxidation of As(III) into As(V) species under UV irradiation, due to the enhanced production of $O_2^{\cdot -}$ radicals.¹²

However, all the organic substrates examined above have a rather weak adsorption on TiO₂, i.e., only a few percent from water onto the catalyst.^{3–7,10} If organic substrate is highly adsorbed on TiO₂, the surface modification by POM or fluoride would block the surface sites for organic adsorption, and consequently the substrate oxidation via direct hole transfer may be significantly slowed. In this regard, an optimal loading of POM or fluoride may exist for achievement of maximal efficiency in the PCD of highly adsorptive organic pollutants

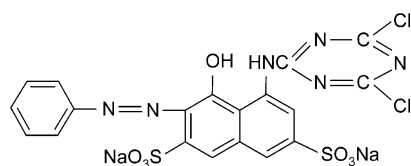
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in water. Second, the adsorbed POM on TiO₂ should not only enhance the conduction band electron transfer, but also enhance, equivalently, the valence hole reaction. Third, POM alone is known to be photoactive for organic oxidation,¹³ which would, more or less, make a contribution into overall PCD rate and be responsible for the enhanced formation of hydroxylated intermediate in POM–TiO₂ system.^{7,10} Answers to these issues are essential to further development of a surface-modified photocatalyst.

In this work, we have investigated the effects of POM (PW₁₂O₄₀³⁻) and fluoride both on the adsorption and PCD of organic dye X3B on TiO₂ in an aerated aqueous suspension. The anionic dye X3B adsorbs highly on TiO₂, relevant to the purpose of this study. It was observed that the adsorption of X3B on TiO₂ was greatly decreased in the presence of either POM or NaF. However, the total rate of X3B PCD, determined by total loss of X3B, both in solution and on the catalyst surface, was increased in the presence of fluoride, but the rate was significantly decreased in the presence of POM. The latter was not in agreement with those previously reported for the PCD of weakly adsorptive substrates on POM–TiO₂.^{7,10} By detailed analysis of the difference in adsorption mechanism, reaction kinetics, spectral change and •OH radical scavenging experiment, we propose that addition of POM results into enhancement in the production of surface-bound •OH radicals, due to enhancement in the separation of charge carriers and subsequently in the hole oxidation of surface OH⁻ groups on TiO₂. This is quite different from the effect of fluoride, which is known to accelerate the production of free •OH radicals in solution, ascribed to enhancement in the hole availability for water oxidation.^{3–6} We further propose that the relative reactivity among various active species follows the order of free •OH radicals > subsurface holes > surface-bound •OH radicals. Then, the proposed mechanism could reasonably account for the observed effects of POM and fluoride on the PCD of both weakly and highly adsorptive organic substrates in water. The origin for such difference is mainly due to the type of adsorption mechanism involved in these systems.

Experimental Section

Materials and Reagents. Phosphotungstic acid hydrate (POM, analytical grade), sodium fluoride (NaF, analytical grade) and *tert*-butyl alcohol (TBA, analytical grade) were purchased from Shanghai Chemicals. POM concentration in water at pH 1.0 was calibrated by its molar absorption coefficient at 265 nm ($\epsilon = 5.0 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$).¹⁴ The titanium dioxide powder was from Degussa P25, and it was a mixture of anatase and rutile (8:2), with a Brunauer–Emmett–Teller (BET) surface area of 50 m²/g. The textile dye, Reactive Brilliant Red X3B (C. I. Reactive Orange 86), was from Jining dye manufacture of China, and was used as received (98%). The solution pH was adjusted with dilute HClO₄ and NaOH solutions.



Structural formula of X3B

Adsorption. The adsorption isotherm of substrate (X3B, POM, and NaF) on TiO₂ was measured in the dark by mixing 50.0 mg of TiO₂ with 50.0 mL of aqueous solution at a specific

pH (pH 1.0 or 3.0) at various initial concentration of substrate C_0 . The suspension was first sonicated for 5 min, and then shaken at a constant rate overnight. After the suspension was filtered through a membrane filter (pore size, 0.45 μm), the filtrate was analyzed on an Agilent 8451 spectrometer to get the equilibrium concentration C_e . The wavelength for analysis of X3B and POM was 510 and 265 nm, respectively, whereas the concentration of fluoride was measured by ion-selective electrode on a PHS–3C pH meter. The amount of adsorption, Q_e , was calculated by the decreased concentration of $(C_0 - C_e)$ divided by the amount of catalyst used, and expressed in unit of moles per gram of TiO₂. In a mixed solution of POM and X3B, the amount of X3B adsorption was directly determined at 510 nm, whereas the amount of POM adsorption was indirectly measured by the decreased absorbance at 265 nm, which was subtracted by the absorbance of X3B at 265 nm on the basis of the determined concentration of X3B at 510 nm.

Photocatalytic Studies. The light source was a mercury lamp emitted mainly at 365 nm (375 W, Shanghai Yamin) and cutoff at 320 nm by the Pyrex-glass reactor. Before light irradiation, all the suspensions containing necessary components (X3B, POM, and NaF) were first sonicated for 5 min, and shaken at a constant rate in the dark overnight. The suspension was divided into two parts under vigorous stirring: 10 mL for the adsorption measurement as above, and 40 mL for the following PCD studies. After the suspension was irradiated for 10 min, the total concentration of X3B left both in the filtrate and on the catalyst surface was analyzed. The total initial rate R_{tot} of X3B PCD was then calculated by $(C_0 - C)$, where C_0 and C were the total concentration of X3B before and after irradiation, and expressed in units of mole per min. Note that the adsorbed X3B on TiO₂ was completely desorbed into an alkaline solution, with an average recovery yield of 99.8%.

Results and Discussion

Effect of POM and NaF on the Adsorption of X3B on TiO₂. The model substrate X3B is an anionic organic dye. Due to electrostatic interaction, the dye adsorbs highly on the positive charged particles of TiO₂ in an acidic medium.¹⁵ However, addition of POM or NaF into the suspension leads to marked decrease in the dye adsorption. Since all the adsorption isotherms displayed the Langmuir-type (Figure 1), the Langmuir equation, $Q_e/Q_{\text{max}} = KC_e/(1 + KC_e)$, was applied, where Q_e is the amount of X3B adsorption at C_e , the equilibrium concentration of X3B in the bulk solution, Q_{max} is the maximum amount of adsorption, and K is the adsorption constant. The resulting adsorption parameters both decreased with the additive concentration (Table 1). It means that the additive (POM or fluoride) competes with X3B for the adsorption sites, and prefers to occupy the strongest sites on TiO₂ due to the surface heterogeneity.

The additive alone could adsorb on TiO₂ under similar conditions. The adsorption isotherms measured in the absence of X3B gave $Q_{\text{max}} = 20.6 \mu\text{mol g}^{-1}$, and $K = 4.4 \times 10^6 \text{ M}^{-1}$ for POM at pH 1.0, and $Q_{\text{max}} = 0.27 \text{ mmol g}^{-1}$ and $K = 1.33 \times 10^4 \text{ M}^{-1}$ for NaF at pH 3.0. The resulting parameters were quite different among POM, fluoride, and X3B (Table 1, first row), implying different adsorption mechanisms involved. Note that the maximal adsorption of POM on TiO₂ obtained here was almost the same as that reported ($Q_{\text{max}} = 26.7 \mu\text{mol g}^{-1}$),¹⁰ but the relevant adsorption constant was much larger than those measured by other groups under similar conditions ($K = 7.1 \times 10^4$ or 467 M^{-1}),^{7,10} probably due to different details in the experiment such as temperature and calibration of POM concentration.

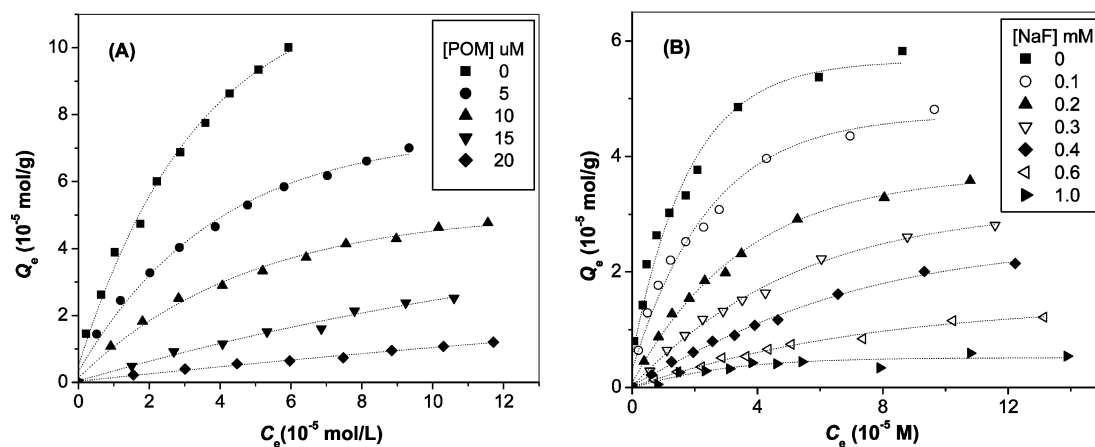
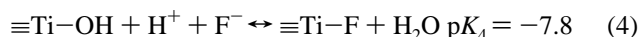
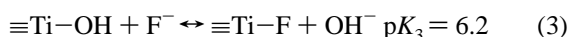
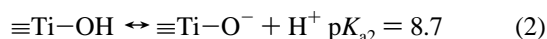
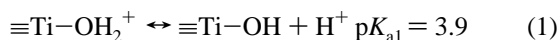


Figure 1. Adsorption isotherm of X3B on TiO_2 in water (A) in the presence of POM at pH 1.0, and (B) in the presence of NaF at pH 3.0. The concentration of POM or NaF is indicated by the legend.

As a naked TiO_2 particle is exposed to water, the surface is hydrated to satisfy the coordination of surface Ti^{VI} ions. Dissociation of the chemisorbed molecular water then gives rise to surface OH^- groups (denoted here as $\equiv\text{Ti}-\text{OH}$), and consequently, the surface of TiO_2 becomes positively charged in an acidic medium (eqs 1 and 2). The surface specification modeling shows that $\equiv\text{Ti}-\text{OH}_2^+$ species accounts for 89% at pH 3.^{3,6} Thus, a high adsorption of anionic X3B on TiO_2 was observed either at pH 1 or at pH 3 (Table 1). Since POM (-3) is more negatively charged than X3B (-2), its adsorption constant was about 2 orders of magnitude larger than that of X3B. However, POM is bulky in size, and its maximal adsorption on TiO_2 is much smaller than that of X3B, determined under similar conditions. Yoon and co-workers have demonstrated that there are three different hydrogen bonds between POM and TiO_2 colloidal particles in aqueous solution, i.e., $\equiv\text{Ti}-\text{OH}\cdots\text{O}_t=\text{W}$, $\equiv\text{Ti}-\text{OH}\cdots\text{O}_e=\text{W}$, and $\equiv\text{Ti}-\text{OH}\cdots\text{O}_w=\text{W}$, on the basis of infrared spectral analysis.¹⁶ But in the present study at pH 1.0, the main adsorption force would be strong electrostatic interaction between POM and $\equiv\text{Ti}-\text{OH}_2^+$ species. This was further supported by a separate experiment performed in a mixed solution of X3B and POM at pH 1.0. Regardless of the initial amount of X3B present (0–0.18 mM), almost all the added POM (4.0, 8.5, or 13 μM) were completely adsorbed on TiO_2 .



Different from POM and X3B, the adsorption of fluoride on TiO_2 is a ligand exchange between F^- and $\equiv\text{Ti}-\text{OH}$ on the surface (eqs 3 and 4).^{3–6} Such complexation is more favorable in an acidic medium, with an equilibrium constant of about 10^8 . The surface specification modeling shows that $\equiv\text{Ti}-\text{F}$ is the dominant species on the surface of TiO_2 at pH 3.^{3,6} The maximal value of adsorbed fluoride was 0.27 mmol g^{-1} at pH 3.0, which could be regarded as the surface site density of TiO_2 (Degussa P25) (note that $Q_{\text{max}} = 0.25 \text{ mmol g}^{-1}$ at pH 4.0).¹⁷ Although the adsorption constant of fluoride was smaller than X3B, in agreement with the anion negative charges, it could not be simply taken as the evidence that fluoride was less strongly

TABLE 1: Effect of POM or NaF Concentration on the Langmuir Adsorption Parameters of X3B on TiO_2 in Water^a

[POM] (μM)	Q_{max} ($\mu\text{mol/g}$)	K ($\times 10^4 \text{ M}^{-1}$)	[NaF] (mM)	Q_{max} ($\mu\text{mol/g}$)	K ($\times 10^4 \text{ M}^{-1}$)
0	141	3.66	0	64	8.86
5	94	2.87	0.1	56	5.20
10	68	1.96	0.2	48	2.63
15	77	0.45	0.3	47	1.33
20	35	0.42	0.4	43	0.87

^a Experiment was performed in water at pH 1.0 in the presence of POM or at pH 3.0 in the presence of NaF. In the Table, Q_{max} and K present the maximum amount of adsorption of X3B and the adsorption constant of X3B on TiO_2 , respectively, obtained by application of the Langmuir adsorption equation into Figure 1 (correlation coefficient = 0.977–0.997).

adsorbed on TiO_2 as compared to X3B, because different adsorption mechanisms were involved in the two systems. In fact, fluoride competed strongly with X3B for the adsorption sites. Both the values of Q_{max} and K obtained for X3B adsorption regularly decreased with the concentration of fluoride present in the mixed solution (Table 1).

The positive charge of TiO_2 was reduced after the surface was occupied by POM or fluoride. This led to a regular decrease in the adsorption of X3B with the increase in the additive concentration (Table 1). Such negative effect of POM was more profound than that of fluoride. Small amount of POM (0–20 μM) present caused a dramatic decrease in the adsorption of X3B, whereas for such variation a large amount of fluoride (0–1.0 mM) was needed (Table 1). Although the anion size was one of the factors, it might also imply that fluoride replaced both $\equiv\text{Ti}-\text{OH}_2^+$ and $\equiv\text{Ti}-\text{OH}$ sites into $\equiv\text{Ti}-\text{F}$ species on the surface (eqs 1–4), whereas POM interacted mainly with $\equiv\text{Ti}-\text{OH}_2^+$ sites without removal of surface hydroxyl groups. This information will be helpful to understand different effects of POM and NaF on the PCD of X3B over TiO_2 , as will be shown below.

Photocatalytic Degradation of X3B over TiO_2 in the Presence of POM or NaF. Because of high adsorption of X3B on TiO_2 , the photocatalytic experiments for the evaluation of additive effect were carefully performed as follows. Prior to light irradiation, the suspension containing all necessary components was first equilibrated in the dark overnight. After 10 min of UV irradiation ($\lambda \geq 320 \text{ nm}$), both the concentrations of X3B left in the bulk solution and on the catalyst surface were analyzed and used thereafter for the determination of total initial rate of X3B PCD.

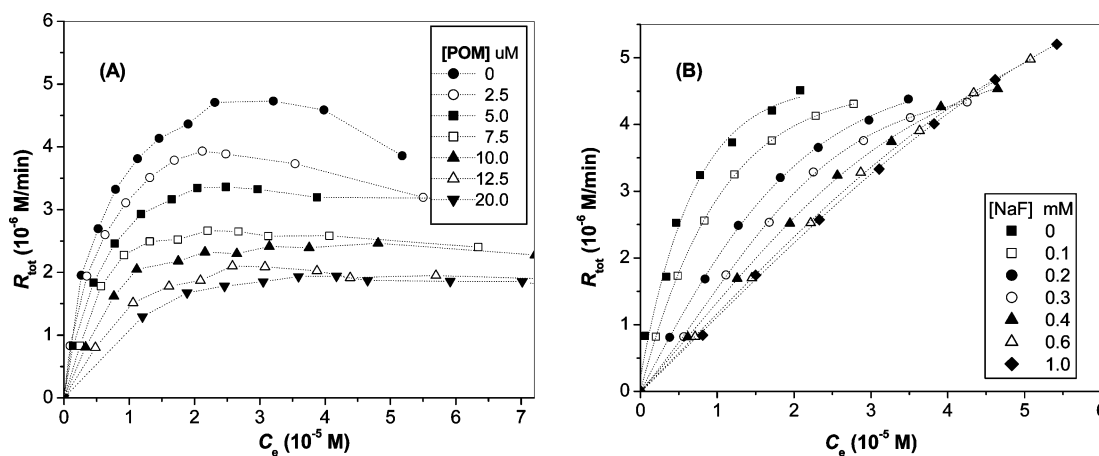


Figure 2. The total initial rate of X3B PCD in an aerated aqueous suspension of TiO₂ as a function of initial equilibrium concentration of X3B (A) in the presence of POM at pH 1.0, and (B) in the presence of NaF at pH 3.0. The additive concentration (POM or NaF) is given by the legend.

TABLE 2: Effect of POM on the Apparent First-Order Rate Constants for the PCD of X3B on TiO₂ in Water at pH 1.0^a

[POM](mM)	k_{first} (min ⁻¹)	[POM](mM)	k_{first} (min ⁻¹)
0	0.0578	1.0	0.0266
0.01	0.0386	2.0	0.0250
0.20	0.0337	3.0	0.0238
0.50	0.0282	4.0	0.0228

^a The kinetic data was well fitted by the apparent first-order rate equation, $\ln(C/C_0) = -k_{\text{app}} t$, where k_{app} is rate constant, C and C_0 are the total concentration of X3B at irradiation time $t = 0$ and t , respectively. The initial concentration of X3B used was 88 μM and TiO₂ at 1.00 g/L.

Figure 2A and B show the total initial rate of X3B PCD, R_{tot} , as a function of initial equilibrium concentration of X3B, C_e , determined at pH 1.0 in the presence of POM (0–20 μM), and at pH 3.0 in the presence of NaF (0–1.0 mM), respectively. In this region, the dark adsorption of X3B was very sensitive to the additive concentration used, [POM] or [NaF]. We see that the effect of POM was significantly different from that of fluoride. In POM–TiO₂ system, R_{tot} increased first with C_e , approached a limit, and then decreased with C_e (Figure 2A). The limit rate appeared to decrease with [POM]. This was confirmed by measurement of the total concentration of X3B as a function of irradiation time. The resulting apparent first-order rate constant, k_{first} , decreased with [POM], as shown in Table 2. This negative effect of POM on the PCD rate of X3B was opposite to those previously reported for the PCD of weakly adsorptive substrates DCB⁷ and DCP¹⁰ on POM–TiO₂ under similar conditions. In F–TiO₂ system, R_{tot} increased always with C_e , without appearance of rate saturation (Figure 2B). But a separate experiment showed that the apparent first-order rate constant k_{first} for the PCD of X3B (88 μM) at pH 3.0 was greatly increased in the presence of NaF (1.0 mM), from 0.0974 min⁻¹ on naked TiO₂ to 0.173 min⁻¹ on F–TiO₂. This positive effect of NaF was in agreement with that reported previously for the PCD of phenol^{3,4} and Acid Orange⁵ on F–TiO₂ under similar conditions.

To get the concentration-independent rate constant, the Langmuir–Hinshelwood (L–H) equation, $R = k_{\text{LH}} K' C / (1 + K' C)$, is often applied in photocatalysis,¹ where R is the PCD rate of X3B at X3B concentration C in solution, and k_{LH} is the rate constant and K' is the apparent adsorption constant. However, the fitting of the L–H equation is silent about the reaction mechanism, i.e., whether the PCD reaction between substrate and active species occurs on the catalyst surface or in solution.

In fact, Turchi and Ollis proposed, very early, the same analytical equation for four possible pathways, only with a difference in the expression of K' .¹⁹ Very recently, Ollis formulated another rate equation (eq 2), based on a pseudo steady-state hypothesis.²⁰ The newly developed equation is similar in form to the original one, but K' is replaced by $K_{\text{ad,app}}$, which is useful to explain the effect of light intensity.

Therefore, the modified L–H equation was applied here, without consideration of specific mechanism. All the reciprocal plots of $1/R_{\text{tot}}$ versus $1/C_e$ for F–TiO₂ system were satisfactorily linear. But the linear plots for POM–TiO₂ system resulted only in the limited region of C_e , especially at high [POM]. The resultant parameters of k_{LH} and $K_{\text{ad,app}}$ as a function of additive concentration are summarized in Figure 3. It showed that, in the F–TiO₂ system, k_{LH} increased with [NaF], whereas, in the POM–TiO₂ system, k_{LH} decreased with [POM]. Since k_{LH} is concentration-independent, it is reliable to conclude that POM has a negative effect, whereas NaF has a positive effect on the TiO₂-mediated PCD of X3B. This contradictory effect could not be simply attributed to the effect on the X3B adsorption, since the adsorption was decreased in the presence of either POM or fluoride (Figure 1). On the other hand, the value of $K_{\text{ad,app}}$ in both cases decreased consistently with the additive concentration, similar to the trend of K observed in the dark (Table 1). According to Ollis's new model that $K_{\text{ad,app}}$ is fundamentally proportional to K at a given light intensity,²⁰ the present result might suggest that the additive also prefers to adsorb on the strongest sites of TiO₂ even in the initial period of irradiation time.

An interesting feature came out when the total initial rate of X3B PCD, R_{tot} , was re-plotted as a function of the initial amount of adsorption of X3B, Q_e (Figure 4). In the absence of additive (Figure 4, curve a), R_{tot} increased linearly with Q_e , and then began to decrease at a value of Q_e larger than 40 $\mu\text{mol/g}$. Such rate decrease at high surface coverage has been attributed to the screening effect of the adsorbed dye.^{2,15} In the presence of an additive, the PCD rate changed differently with Q_e . First of all, in the POM–TiO₂ system, R_{tot} increased first with Q_e , and then approached a platform at certain Q_e (Figure 4A). The limit rate decreased with [POM], similar to the result presented above (Figure 2A). In the F–TiO₂ system, however, such limit rate was not observed (Figure 4B). Instead, R_{tot} increased linearly with Q_e , with a slope proportional to [NaF]. Second, as [POM] or [NaF] increased, the rate curve shifted gradually from right side to the left (Figure 4, curves b–g). In other words, the observed R_{tot} at a given Q_e is higher than that expected from

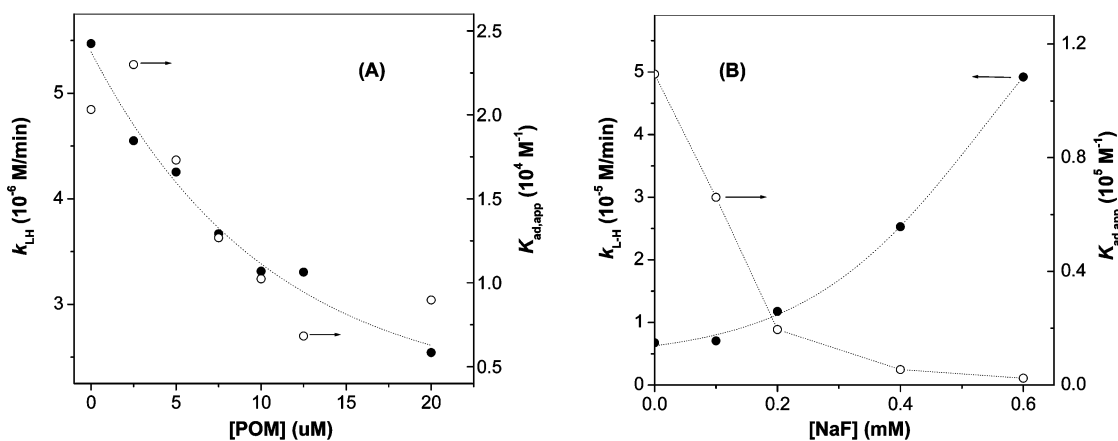


Figure 3. Effect of [POM] (A) and [NaF] (B) on the rate constant k_{LH} (solid symbol) and the apparent adsorption constant $K_{ad,app}$ (open symbol) for the PCD of X3B on TiO_2 .

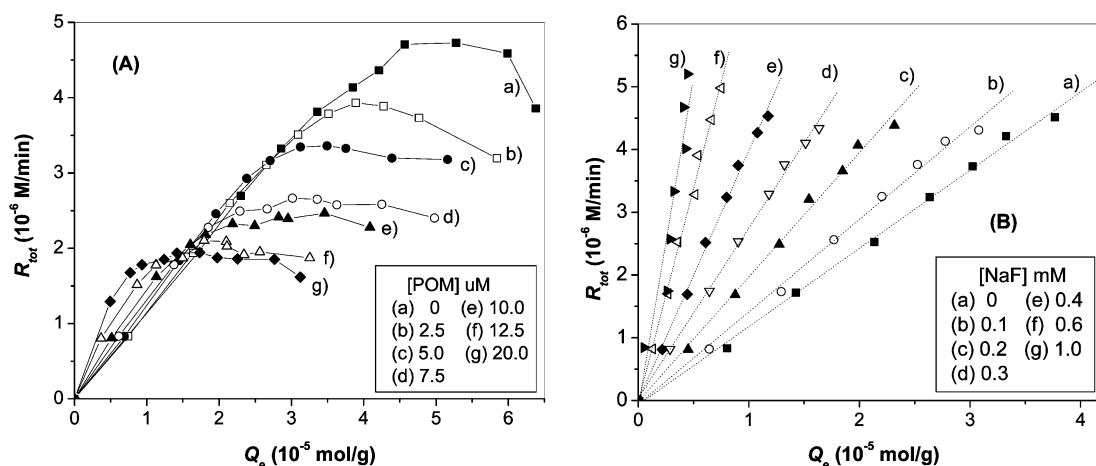


Figure 4. The total initial rate of X3B PCD as a function of initial amount of X3B adsorption on TiO_2 in the presence of POM (A), and in the presence of NaF (B). The additive concentration is indicated by the legend.

the intrinsic relationship between PCD rate and initial amount of X3B adsorption on naked TiO_2 (Figure 4, curve a). It implies that some active species are produced upon addition of the additive, making a notable contribution into the overall rate of X3B PCD in the two systems. Such an effect was strikingly evident in the F- TiO_2 system, which will be further discussed below in the section on reaction mechanism.

The spectral change, recorded during the PCD process, gave some useful information about the reactive species proposed above. In the dispersions of TiO_2 alone, the visible bands of X3B decreased in a whole with irradiation time, without a significant band shift (Figure 5A). In POM homogeneous solution, however, the dye bleaching was accompanied by a band red-shift, together with appearance of a weak band centered at 750 nm (Figure 5B). This new species at 750 nm is assigned to so-called heteropoly blue (the reduced POM),⁹⁻¹³ formed from the reaction between excited POM and organic substrates or solvent water.^{18,21,22} In the POM- TiO_2 system, the spectral change (Figure 4C and D) was similar to that in POM solution, but the expected heteropoly blue was not found in the filtrate, probably due to its strong adsorption on TiO_2 . The band red-shift was more obvious at high [POM] (0.20 mM) (Figure 4D) than that at low [POM] (0.015 mM) (Figure 4C). In F- TiO_2 system at pH 3.0, the band red-shift was also seen (Figure 5E), while the corresponding spectral change on naked TiO_2 was almost the same as that at pH 1.0 (Figure 5A). The similarity in spectral change suggests that the reactive species proposed above might be the same in both the systems of POM- TiO_2 and F- TiO_2 . In an early study, $\cdot OH$ radicals has been proposed

as the main species responsible for the POM-mediated photo-oxidation of organic substrates such as X3B¹⁸ and 4-chlorophenol,²¹ and also responsible for the rate enhancement in the PCD of phenol on F- TiO_2 .³⁻⁵ Thus, it is highly possible that the $\cdot OH$ radicals are also involved in the present study for the PCD of X3B on POM- TiO_2 and F- TiO_2 .

Effect of *tert*-Butyl Alcohol on the PCD of X3B. To verify whether $\cdot OH$ radicals are involved, the PCD of X3B was carried out in the presence of *tert*-butyl alcohol (TBA), a widely used $\cdot OH$ scavenger ($k = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).⁴⁻⁶ Figure 6 shows first the total concentration of X3B as a function of irradiation time, determined for the PCD of X3B on F- TiO_2 at pH 3.0. The presence of TBA greatly depressed the PCD rate of X3B on F- TiO_2 (Figure 6, curves c and d). The relevant rate constant k_{first} was decreased from 0.173 min^{-1} to 0.0177 min^{-1} . At the same time, the band red-shift observed in the absence of TBA (Figure 5E) completely disappeared. For the PCD of X3B on naked TiO_2 , no such inhibitory effect of TBA was observed (Figure 6, curves a and b). The result suggests that the PCD of X3B on naked TiO_2 is predominately initiated by direct hole transfer, whereas the reaction on F- TiO_2 is mediated by both $\cdot OH$ radicals and valence holes. This explanation is similar to those reported previously for the rate enhancement of weakly adsorptive substrate phenol on F- TiO_2 .³⁻⁵ The present study also shows that the generation of such $\cdot OH$ radicals upon addition of fluoride is not significantly affected by the organic adsorption.

Figure 7 shows the effect of TBA on the PCD rate of X3B on POM- TiO_2 at pH 1.0. Similarly, the addition of TBA greatly

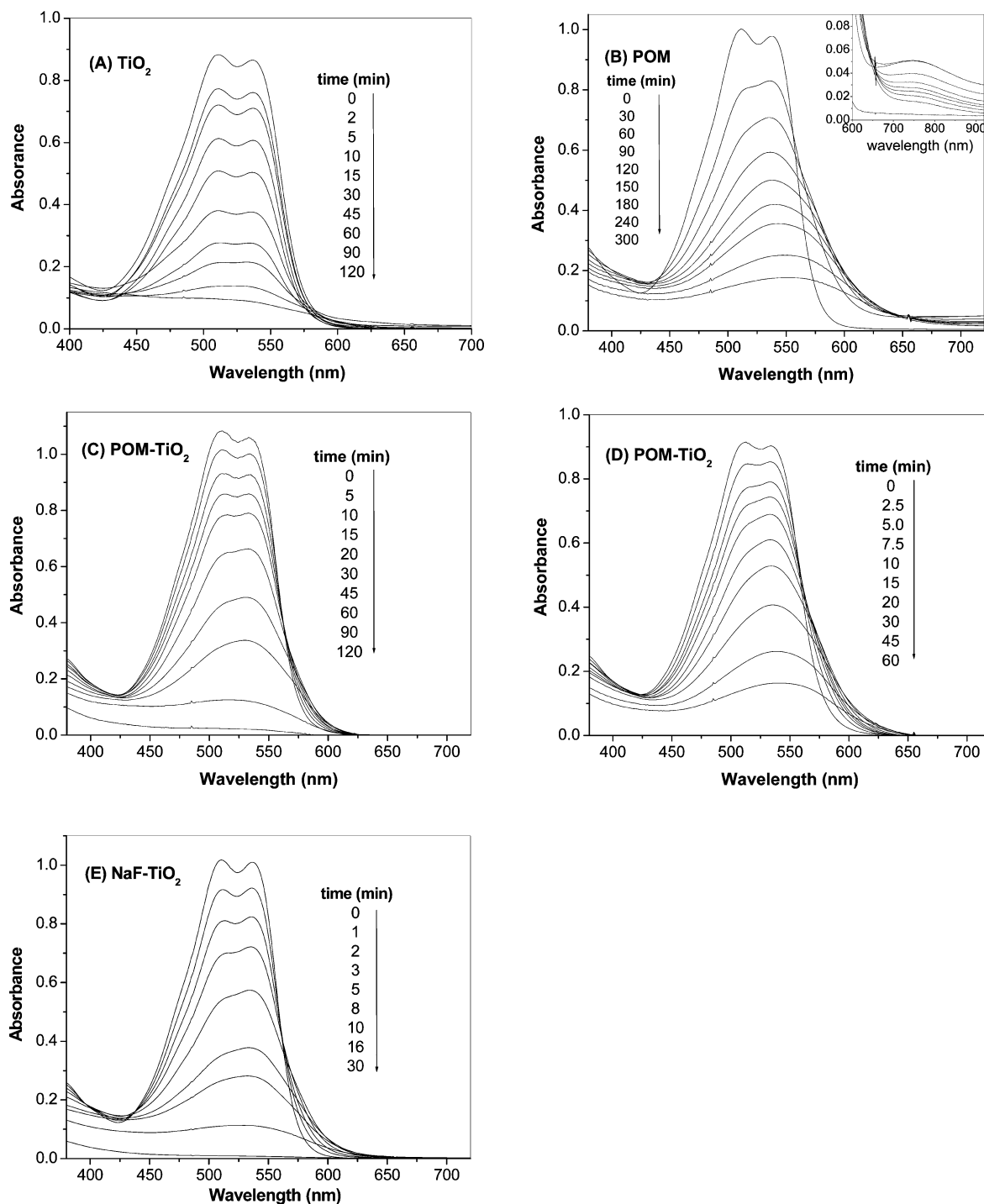


Figure 5. Spectral change of the filtrate recorded during the PCD of X3B at pH 1.0 under different conditions of (A) TiO₂, (B) POM (1.25 mM), (C) TiO₂ + POM (0.015 mM), and (D) TiO₂ + POM (0.20 mM). The spectral change (E) was for TiO₂ + NaF (1.0 mM) at pH 3.0. The initial concentration of X3B was at 88–127 μM and TiO₂ at 1.00 g L⁻¹.

decreased the PCD of X3B on TiO₂–POM (0.20 mM) (Figure 7, curves c and d). The rate constant k_{first} was decreased from 0.0337 min⁻¹ to 0.00950 min⁻¹. It was also noted that the band red-shift, observed previously in POM–TiO₂ (Figure 5D), completely disappeared in the presence of TBA. No inhibitory effect of TBA was observed on naked TiO₂ at pH 1.0 (Figure 7, curves a and b), as that observed at pH 3.0 (Figure 6, curves a and b). It suggests again that the PCD of X3B on naked TiO₂ is predominated via direct hole transfer. The addition of POM increases the organic degradation initiated by $\cdot\text{OH}$ radicals. In a homogeneous solution of POM, $\cdot\text{OH}$ radicals were also involved during the degradation process of X3B.¹⁸ This was

evidenced here by the effect of TBA (Figure 7, curves e and f) and the spectral analysis (Figure 5B). However, such contribution from homogeneous POM was negligible over the total PCD of X3B on POM–TiO₂. The rate constant k_{first} , obtained from the PCD of X3B on POM–TiO₂ at [POM] = 0.50 mM, was 0.0282 min⁻¹, much larger than $k_{\text{first}} = 0.00725$ min⁻¹ resulted from the PCD in a homogeneous solution of POM (0.50 mM). Therefore, the $\cdot\text{OH}$ radicals detected in the TiO₂–POM system are mainly produced from POM-modified TiO₂.

The above TBA experiments confirm the same active species of $\cdot\text{OH}$ radicals produced as the consequence of POM or NaF addition into the dispersions of TiO₂. The $\cdot\text{OH}$ radicals are

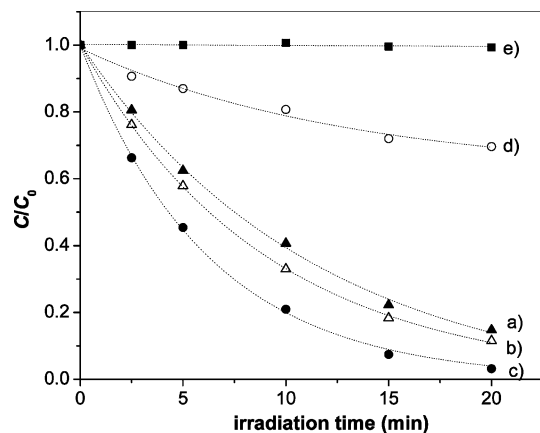


Figure 6. Effect of *tert*-butyl alcohol (TBA) on the photocatalytic degradation of X3B at pH 3.0 under different conditions: (a) TiO_2 , (b) TiO_2 + TBA, (c) TiO_2 + NaF (1.0 mM), (d) TiO_2 + NaF (1.0 mM) + TBA, (e) without catalyst. Other conditions: TiO_2 at 1.00 g/L, X3B at 88 μM and TBA at 4% (v/v). C_0 and C were the total concentration of X3B determined before and after irradiation.

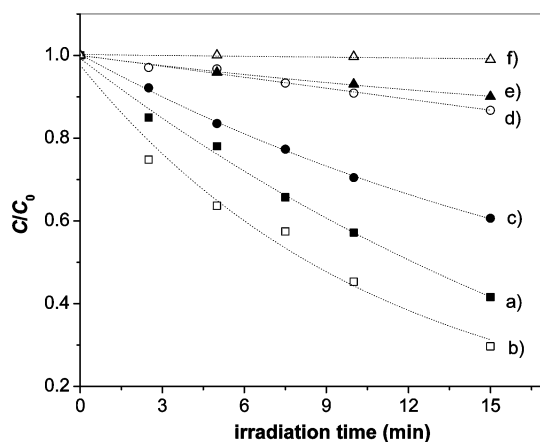


Figure 7. Effect of *tert*-butyl alcohol (TBA) on the PCD of X3B at pH 1.0 under different conditions: (a) TiO_2 , (b) TiO_2 + TBA, (c) TiO_2 + POM (0.20 mM), (d) TiO_2 + POM (0.20 mM) + TBA, (e) POM (0.50 mM), and (f) POM (0.50 mM) + TBA. Others were the same as Figure 6, except TBA at 10% (v/v).

responsible for the observed enhancement in the PCD rate of X3B. If it follows, the concentration of such $\cdot\text{OH}$ radicals would increase with the additive concentration. This was verified by the effect of TBA on the PCD of X3B at different [POM] in the POM– TiO_2 system at pH 1.0. In the presence of TBA, the rate constant k_{first} was decreased by 0.0035 and 0.0242 min^{-1} at [POM] = 0.010 and 0.20 mM, respectively. The larger decrease in k_{first} implied higher concentration of the $\cdot\text{OH}$ radicals produced at higher [POM].

Reaction Mechanisms. It has been reported that addition of POM or NaF into the TiO_2 dispersions can lead to significant enhancement in the PCD rate of weakly absorptive substrates such as chlorophenol in water under UV irradiation.^{3–7,10} The positive effect of fluoride was confirmed here for the PCD of highly adsorptive X3B, but POM exhibited a negative effect, not in agreement with those reported. In the presence of the additive, the dark adsorption of X3B on TiO_2 was greatly decreased (Figure 1), and under UV irradiation the production of $\cdot\text{OH}$ radicals was also enhanced (Figures 5–7). However, the contribution of such $\cdot\text{OH}$ radicals into the overall rate of X3B PCD was strikingly different between two systems of F– TiO_2 (Figure 4B) and on POM– TiO_2 (Figure 4A). This is only the clue to find a understanding for the opposite effects of POM and fluoride observed on the PCD of X3B.

In the absence of POM or fluoride, the anionic dye of X3B adsorbs highly on TiO_2 , due to strongly electrostatic interaction between X3B and $\equiv\text{Ti}-\text{OH}_2^+$ sites in an acidic medium (Figure 1). The kinetic study (Figures 5–7) demonstrates that the PCD of X3B on naked TiO_2 is initiated predominantly by direct hole transfer. More importantly, the initial total rate of X3B PCD was observed to increase almost linearly with the initial amount of adsorption of X3B on the catalyst (Figure 4, curve a). Only a few of such examples could be found in the literature that there exists an intrinsic relationship between organic adsorption and its PCD rate, such as carboxylic acid and aromatic sulfide, evaluated, respectively, by photoelectrolysis²³ and time-resolved spectroscopy.²⁴ Since the kinetic data was well fitted by the L–H-type equation (Figure 3), the result, together with others,^{23,24} might serve as the direct evidence that the PCD of highly adsorptive substrates on TiO_2 is dominated by the L–H bimolecular mechanism. At a high surface coverage ($\theta > 0.3$), the PCD rate decreases with the adsorption, attributed to the screening effect of the adsorbed dye (Figure 4).^{2,15} Control experiments have shown that the direct photolysis of X3B in the absence of catalyst and/or the photosensitized degradation of X3B in the presence of catalyst under visible light irradiation ($\lambda \geq 450$ nm) are very slow under the present conditions. Thus the observed PCD rate of X3B on TiO_2 is almost entirely attributed by the photocatalysis of TiO_2 under UV irradiation ($\lambda \geq 320$ nm).

In the presence of fluoride, both $\equiv\text{Ti}-\text{OH}_2^+$ and $\equiv\text{Ti}-\text{OH}$ on TiO_2 are replaced by fluoride to form $\equiv\text{Ti}-\text{F}$ species. Since fluoride ions [$E^\circ_{\text{NHE}}(\text{F}^\cdot/\text{F}^-) = 3.6$ V]²⁵ are not reactive to the valence holes of irradiated TiO_2 ($E_{\text{NHE}} = 2.9$ V at pH 3), the decrease in the number of surface OH^- groups would facilitate the hole reaction with adsorbed organic substrate to form organic cation radicals, and/or with adsorbed water to produce surface-bound $\cdot\text{OH}$ radicals. The latter process is expected when the organic substrate is not adsorbed on the catalyst. In this case, the production of surface-bound $\cdot\text{OH}$ radicals would be slowed somewhat, since oxidation of adsorbed water would be slower than that of surface OH^- groups. Then, the PCD rate of weakly adsorptive organic substrate over TiO_2 would be slowed in the presence of fluoride. However, the rate enhancement was observed during the PCD of phenol on TiO_2 in the presence of fluoride.³ Such increased rate of PCD could not be ascribed to the change in flat-band potential, since it shifts to negative value upon adsorption of fluoride on TiO_2 in acetonitrile.²⁶ Since the production of $\cdot\text{OH}$ radicals was also greatly enhanced on F– TiO_2 , Pelizzetti and co-workers proposed that the hole reaction with solvent water in the surface/solution monolayer to generate free $\cdot\text{OH}$ radicals would be also possible. The free $\cdot\text{OH}$ radicals is more reactive than surface-bound $\cdot\text{OH}$ radicals, consequently resulting to observed acceleration in the PCD of phenol.³ They have further verified that on naked TiO_2 about 90% of phenol oxidation proceeds via surface-bound $\cdot\text{OH}$ radicals,⁴ but almost entire oxidation of phenol on F– TiO_2 proceeds via homogeneous $\cdot\text{OH}$ radicals. This interpretation for the enhanced production of free $\cdot\text{OH}$ radicals upon addition of fluoride seems somewhat ambiguous, but no alternative explanation is available at present. The hydrogen bonding, that causes desorption of the adsorbed H_2O into solution, between adsorbed H_2O and $\equiv\text{Ti}-\text{F}$ might be formed, consequently facilitating the oxidation of solvent water by the hole into free $\cdot\text{OH}$ radicals.

If organic substrate is highly adsorbed on TiO_2 , the total PCD rate would be determined by the complicated competitions among various reactions initiated by subsurface h_{vb}^+ , surface-bound $\cdot\text{OH}$ radicals and free $\cdot\text{OH}$ radicals. Assume that the

relative reactivity among these reactive species for organic oxidation follows the decreasing order of free $\cdot\text{OH}$ radicals $>$ subsurface h_{vb}^+ $>$ surface-bound $\cdot\text{OH}$ radicals, the surface fluorination would result to enhancement in the PCD of highly adsorptive substrate such as X3B. In the presence of fluoride, both the number of surface OH^- groups and the amount of organic adsorption on TiO₂ are decreased. The latter would be not favorable to the organic oxidation by subsurface h_{vb}^+ and surface-bound $\cdot\text{OH}$ radicals. But the surface fluorination increases the generation of free $\cdot\text{OH}$ radicals, which could initiate the organic reactions either in solution or on the catalyst surface. As result, the observed rate constant for the PCD of X3B increases first slowly and then quickly with [NaF] present (Figure 3B). It also explains the plot of R_{tot} vs Q_{e} , where R_{tot} increases linearly with Q_{e} of X3B adsorption on the catalyst, without apparent saturation, and the plot slope is proportional to [NaF] present (Figure 4B). Since the TiO₂ surface was not fully covered by fluoride within the [NaF] region studied (0–1.0 mM), the organic reaction could occur either in solution or on the surface or both, depending on the amount of adsorbed fluoride. The surface adsorption of target substrate is important to any surface reaction, but it is not a determining factor here for the PCD of X3B on F–TiO₂.

Different from fluoride, the POM anions interact mainly with $\equiv\text{Ti}-\text{OH}_2^+$ sites, instead of surface hydroxyl group replacement. It means that the number of surface OH^- groups remains unchanged after the catalyst surface is covered by POM. After X3B is further adsorbed, the total number of surface OH^- groups would not change, since the adsorption also proceeds mainly via $\equiv\text{Ti}-\text{OH}_2^+$ sites. Also different from the adsorbed fluoride, the adsorbed POM can capture the conduction band e_{cb}^- from TiO₂ ($E_{\text{NHE}} = -0.189$ V at pH 1.0), and enhance the charge separation. Since the driving force for the electron transfer to POM is larger than that to O₂, the production of charge carrier would be faster than that on naked TiO₂ or on F–TiO₂. Since the reduced POM is relatively long-lived (it can last a few minutes in air),^{9,13} such enhanced charge separation would also result to equivalent enhancement in the generation of valence hole. If there is not enough organic substrate nearby on the surface, the increased holes would be first trapped by $\equiv\text{Ti}-\text{OH}$ species to generate surface-bound $\cdot\text{OH}$ radicals (resonance with $\equiv\text{Ti}-\text{O}\cdot$).⁷ Thus, the rate of PCD is expected to increase with [POM] present. This reasoning is consistent with the previous finding that addition of POM into the TiO₂ suspension results into significant enhancement in the PCD rate of weakly adsorptive substrates (DCB and DCP).^{7,10} It may also offer an alternative explanation for the observed enhancement in the formation of hydroxylated intermediate from DCP oxidation on TiO₂–POM,¹⁰ since the intermediates are formed from the $\cdot\text{OH}$ attack of the aromatic ring.

If the organic substrate is highly adsorptive, the increased holes could oxidize $\equiv\text{Ti}-\text{OH}$ species or adsorbed organics on the catalyst. However, the surface-bound $\cdot\text{OH}$ radicals are only detected in POM–TiO₂, but not obviously found in the dispersions of TiO₂ alone (Figures 5–7). It implies that the increased holes are used to oxidize the $\equiv\text{Ti}-\text{OH}_2^+$ species previously linked to the adsorbed POM. The resulting surface-bound $\cdot\text{OH}$ radicals can react with the adsorbed X3B nearby, and/or deactivate back to $\equiv\text{Ti}-\text{OH}$ species due to the limitation in surface diffusion. As result, the PCD of X3B on POM–TiO₂ at a given Q_{e} is only slightly faster than that expected from the intrinsic relationship between PCD rate and adsorption of X3B on naked TiO₂ via direct hole transfer (Figure 4A, curve a). The production of such surface-bound $\cdot\text{OH}$ radicals is expected

to increase with [POM]. Thus the rate curve gradually shifts from curve (a) to curve (g) in Figure 4A. However, the valence holes are more reactive than surface-bound $\cdot\text{OH}$ radicals. Consequently, the overall PCD of X3B is still determined by the amount of X3B adsorption. The plot of R_{tot} vs Q_{e} is almost linear even in the presence of POM (Figure 4A).

As Q_{e} further increased, however, R_{tot} remained almost unchanged. It reached a plate, and the limit rate decreases with [POM] (Figure 4A). One reasonable hypothesis for such limit rate is that not all surface sites are photoactive enough to initiate the degradation of adsorbed X3B. This may arise when substrates and/or reactive species do not migrate on the surface at rates competitive with charge carrier recombination. The surface-bound $\cdot\text{OH}$ radicals, produced as a consequence of POM addition, may partially deactivate before its effective reaction with the adsorbed X3B. This may arise when the adsorptive sites occupied by POM are also the photoactive sites. Due to surface heterogeneity, there is a distribution both in the adsorption sites and in the photoactive sites. The surface sites, that are originally adsorbed by X3B and are photoactive to initiate the adsorbed X3B oxidation via direct hole transfer on naked TiO₂, are now occupied by POM, leaving the nonphotoactive sites for X3B adsorption. The number of these ineffective sites is expected to increase with [POM]. Consequently, the limit rate decreases with [POM], and the rate platform appears at low Q_{e} when [POM] is high (Figure 4A). This picture is quite different from that of F–TiO₂ system, where the free $\cdot\text{OH}$ radicals produced can react with organic substrate in solution, and thus no rate platform is seen in Figure 4B.

It is noted that both POM and X3B are the light absorbing species. It means that the adsorbed POM species may function as a screening filter, decreasing the light intensity reaching on the catalyst and thus decreasing the PCD of X3B. However, this is less possible. Significant enhancement in the PCD of DCB and DCP on TiO₂ has been observed in the presence of POM (0–0.16 mM) under similar conditions.^{7,10} The adsorbed dye functioning as a screening filter is also less possible in the region of Q_{e} studied (<40 $\mu\text{mol/g}$). In this region, the plots of R_{tot} vs Q_{e} are all basically linear (Figure 4A). On the other hand, the photodegradation of X3B in a homogeneous solution of POM was very slow. The reaction rate was about 1 order of magnitude slower than that over TiO₂.¹⁸ The dye X3B is also quite stable against UV irradiation in solution. The dye degradation under visible light irradiation ($\lambda \geq 450$ nm) via photosensitization pathway is also much slower than that under UV irradiation.¹⁵ Therefore, the light-absorbing properties of POM and X3B would not significantly alter the reaction pathways presented above.

When the surface of TiO₂ is completely covered by POM, the rate of surface-bound $\cdot\text{OH}$ production would reach a maximum. This maximal rate constant has been observed for DCB and DCP oxidations on TiO₂–POM at [POM] = 0.10 or 0.16 mM, respectively.^{7,10} After that, the PCD rate of DCB or DCP begins to decrease with [POM], ascribed to the solution filter effect of POM.¹⁰ In the present study, the reaction rate always decreases with [POM] (Table 2), without optimal [POM]. Therefore, the decrease in the PCD rate at low [POM] (0–0.020 mM) is attributed to the decreased adsorption of X3B on the catalyst, whereas the rate decrease at high [POM] is ascribed similarly to the inner-filter effect of free POM.¹⁰

At high [POM], the free POM remaining in solution is also able to produce $\cdot\text{OH}$ radicals under UV irradiation ($\lambda \geq 320$ nm) (Figures 5B and 7). We have recently proposed that the

generation of reduced POM (POM^-) is the rate determining step both for dichromate reduction and organic oxidation (X3B and 2-propanol) in POM solution under UV light irradiation.²² It implies that the $\cdot\text{OH}$ radical is most likely produced from the reaction between POM^* and solvent H_2O . The reduced POM species was detected, but its maximal absorbance at 750 nm (Figure 5B) was much lower ($A = 0.051$) than that expected ($A = 2.5$) if all POM (1.25 mM) were totally converted into POM^- ($\epsilon_{750} = 2000 \text{ cm}^{-1} \text{ M}^{-1}$).¹¹ The reoxidation of POM^- by O_2 back to POM is very slow.^{9,13} Definitely, the free OH radicals, produced from POM photolysis, will make some contribution into the overall PCD rate of X3B, but it is quite small, as shown above in the section of TBA effect.

Conclusions

The surface modification of TiO_2 by POM or fluoride leads to great change both in the adsorption and in the photocatalytic activity for organic degradation. Due to the surface occupation of these anions (POM or fluoride), the positive charges of TiO_2 are greatly reduced, consequently resulting in significant decrease in the adsorption of anionic dye X3B. Due to different adsorption mechanisms involved, this results into different pathways of the hole reactions. The fluoride replacement of surface hydroxyl groups give the enhanced production of free $\cdot\text{OH}$ radicals, whereas the adsorption of POM on TiO_2 predominantly via $\equiv\text{Ti}-\text{OH}_2^+$ sites, accelerates the production of surface-bound $\cdot\text{OH}$ radicals, due to enhanced charge separation. Although it is somewhat speculative, the proposed mechanism could satisfactorily account for the observed contradictory effects of POM and fluoride on the PCD of highly adsorptive X3B and other weakly adsorptive substrates such as DCP and DCB, assume that the relative reactivity among the reactive species for organic oxidation follows the decreasing order of free $\cdot\text{OH}$ radicals > subsurface holes > surface-bound $\cdot\text{OH}$ radicals. The organic adsorption is critical to the PCD on $\text{POM}-\text{TiO}_2$, but it is not a determining factor for the PCD on $\text{F}-\text{TiO}_2$. It suggests that $\text{POM}-\text{TiO}_2$ would find a limited application for the PCD of highly adsorptive organic pollutants such as X3B. On the other hand, the $\text{F}-\text{TiO}_2$ system, which works well for the PCD of both weakly and highly adsorptive organic

contaminants, is worthy of further development such as catalyst fixation. The present work also outlines the difference between adsorption sites and photoactive sites on the TiO_2 surface and the importance of surface migration of substrates and/or reactive species. The different limiting rate at different low surface coverage may open new issues for further investigation.

Acknowledgment. This work was supported by the Natural Science Foundation of China (nos. 20273060, 20477038, and 20525724).

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