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Photocatalytic degradation pathways and adsorption modes of H-acid in TiO₂ suspensions

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Effect of adsorption mode on photodegradation of H-acid in TiO₂ suspension was studied using DFT calculation, UV-Vis spectroscopy, FTIR, and ionic chromatography. At pH 2.5, H-acid was adsorbed on TiO₂ surfaces by one dissociated sulfonic group. The adsorbed sulfonic group was attacked by surface ·OH, resulting in the production of SO₄²⁻ and the cleavage of the naphthalene ring. At pH 5.0, H-acid was adsorbed on TiO₂ surfaces by two sulfonic groups. The two adsorbed sulfonic groups were simultaneously attacked by surface ·OH, leading to a faster initial production of SO₄²⁻ and initial degradation rate of H-acid than those under pH 2.5. Microscopic adsorption structures may be more important than adsorption amount in controlling the photodegradation pathways of organic pollutants.

H-acid, TiO₂, photocatalytic degradation, adsorption, organic pollutants

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The heterogeneous photocatalytic degradation of organic compounds on TiO₂ surfaces has been extensively investigated with a view to mineralizing environmentally harmful organic compounds. The adsorption of organic molecules is critical in determining photocatalytic degradation pathways; these pathways are directly related to the equilibrium and kinetic properties of photocatalytic degradation reactions. The process is initiated through band-to-band excitation of the TiO₂ particles by ultraviolet (UV) radiation to generate free ·OH radicals derived from valence band hole oxidation of terminal OH⁻ groups and hydration water on the particle surfaces. These radicals have been assumed to be the dominant oxidizing agents, with a preference for attacking organic compounds adsorbed on or near the TiO₂ surfaces for quick quenching [1]. Since surface adsorption is required for interactions between the organic molecules and the photo-excited electrons or holes, differences in adsorption modes should affect photocatalytic degradation pathways.

Many authors have investigated the adsorption of organic

compounds on TiO₂ surfaces [2–6]. However, few studies have correlated adsorption mechanisms in aqueous solutions with degradation behavior occurring under the same conditions. Recently, a metastable-equilibrium adsorption (MEA) theory has been developed by Pan et al. [7,8], which points out that the adsorption density Γ (mol/m²) has been incorrectly used in the past as a thermodynamic state variable in the theoretical foundations of classical surface thermodynamics. Once this deficiency is removed from classical surface thermodynamics, a new principle, called MEA inequality, is obtained, based on strict theoretical deductions from first principles. The MEA inequality indicates that real “equilibrium” adsorption constants decrease as the actual MEA states deviate from the ideal equilibrium state. Equilibrium adsorption constants or adsorption isotherms, when expressed in terms of Γ , are fundamentally influenced by kinetic factors such as reaction rate and the reversibility of the adsorption process [9–12]. This implies that the equilibrium constants of heterogeneous catalytic reactions can be fundamentally influenced by MEA states. This work investigates whether different MEA adsorption states (i.e.,

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different microstructures and energy states of adsorbates), not just the adsorption capacity, can determine, through different degradation pathways, both the kinetic and equilibrium properties of photocatalytic degradation reactions.

As an important intermediate in the production of synthetic dyes (e.g., direct dyes, reactive dyes, and azo dyes), H-acid (8-amino-1-naphthol-3,6-disulfonic) occurs widely in wastewaters from dye manufacturing. Photocatalytic degradation of this pollutant has therefore already been studied. However, these studies treated H-acid as a simple substance and ignored its different structural forms in different solutions. The mechanisms of adsorption, photocatalytic degradation pathways, and the relationships between these were therefore not clear, or even conflicting, in the past [13–15]. There are two sulfonic groups and one amine group on the naphthalene ring of H-acid, and this makes different structural forms possible by dissociation of the sulfonic groups and deprotonation of the amine group under different pH conditions [16]. H-acid was therefore chosen as a model environmental organic pollutant molecule to study the relationship between adsorption modes and photocatalytic degradation pathways in aqueous TiO₂ suspensions.

1 Materials and methods

1.1 Materials

P25-TiO₂ (ca. 80% anatase, 20% rutile; BET area, ca. 50 m²/g) was purchased from Degussa. H-acid (8-amino-1-naphthol-3,6-disulfonic acid, monosodium salt, 97%) was obtained from Alfa Aesar. PFOS (heptadecafluorooctanesulfonic acid, potassium salt, 98%, Fluka) was used to study competitive adsorption with H-acid. All other chemicals were of analytical grade. The pH values of the solutions were adjusted with either dilute HClO₄ or NaOH.

1.2 Analytical methods

An ultraviolet-visible spectrophotometer (UV-Vis) (Hitachi U-3100, Japan) was used to analyze the structural forms of H-acid and to measure the concentrations of H-acid at 342 nm and pH 2.5. Solutions of other pH values were adjusted to pH 2.5 with HClO₄ or NaOH before measurement. A fourier transform infrared spectrometer (FTIR) (Thermo Nicolet NEXUS 670 FTIR, USA) was used to determine the H-acid groups adsorbed on the TiO₂ surfaces. Concentrations of SO₄²⁻, produced during the photocatalytic degradation reaction, were monitored using ion chromatography (DioneX Series 4500i, USA).

1.3 Calculation methods for determining structural forms of H-acid

The geometries of the H-acid structures were calculated us-

ing semi-empirical MNDO/d method, and the theoretical UV-vis spectra were then obtained by ZINDO/S method [16].

1.4 Adsorption-desorption experiments

Adsorption and desorption isotherms were measured using batch experiments at (273 ± 2) K. The H-acid solutions and TiO₂ aqueous suspensions were all adjusted to the required pH using HClO₄ or NaOH solutions. The 15-mL aliquots of solutions containing different concentrations of H-acid were added to 31-mL glass screw-cap tubes sealed with Teflon tops. Each tube was then quickly filled to 25 mL with a fixed concentration of TiO₂ aqueous suspension to initiate the adsorption reactions. The suspensions were equilibrated for about 17 h in a temperature-controlled incubation shaker (200 r/min) in darkness. After centrifugation at 4000 r/min for 10 min, 10-mL aliquots of the supernatants were filtered through a Millipore filter (Polytetrafluoroethylene, pore size 0.2 μm). Each batch of samples included controls containing no TiO₂. The filtrates were analyzed using an UV-Vis spectrophotometer following a previous method [13]. The amount of adsorbed H-acid was calculated from the difference between the mass added and the mass remained in the solution. The remaining residues were dried at room temperature and then characterized by FTIR. FTIR spectra were obtained using samples in the form of KBr pellets (2:100) [17] on a FTIR spectrometer of resolution 0.2 cm⁻¹.

After the adsorption reached equilibrium, desorption experiments were conducted by replacing 20 mL of supernatant with 20 mL of deionized water at the same pH [18]. The tubes were resealed and mixed for another 17 h. The concentrations of H-acid in solution were determined as described in Section 1.2. The amount of adsorbed H-acid was calculated from the difference between the initial mass and the mass left in the solution. The adsorption/desorption cycles were repeated three times.

PFOS has a sulfonic group which could compete with the sulfonic groups of H-acid for the binding sites on TiO₂ surfaces. PFOS is barely degraded in TiO₂ suspensions under UV irradiation because of the stability of the C–F bond [19]. Thus, to investigate the role of sulfonic groups in the adsorption of H-acid on TiO₂ surfaces, the adsorption of H-acid on TiO₂ covered with PFOS was also studied. The experimental protocols were similar to those described above, except that the TiO₂ suspensions were preconditioned with PFOS (500 mg/L) for at least 1 d before the H-acid adsorption, as described by Makarova et al. [20].

1.5 Photocatalytic degradation experiments

The laboratory-scale photoreactor used had a quartz column of height 220 mm, external diameter 70 mm, and wall thickness 1.5 mm. The UV light source was a 40-W low-pressure mercury lamp (Institute of Electric Light Source, Beijing, China) positioned inside a quartz jacket of external

diameter 55 mm. The quartz jacket was inserted in the photoreactor. A pump was used to bubble air into the reaction solution from the bottom of the photoreactor to ensure a constant supply of oxygen and complete mixing of the solution and TiO_2 during the photoreaction.

In the experiment, 0.45 g of TiO_2 were suspended in 150 mL of a solution containing 100 mg/L of H-acid, and the suspension was adjusted to the required pH. In all the experiments, prior to irradiation, the suspension was mixed continuously in the dark for 30 min to allow adsorption equilibrium to be reached [21]. During the photocatalytic degradation reaction, 10-mL aliquots of the suspensions were collected at different intervals over a period of 270 min. The collected suspension samples were centrifuged at 4000 r/min for 10 min, and the supernatants were filtered through a Millipore filter (Polytetrafluoroethylene, pore size 0.2 μm) before analysis for H-acid concentration. The amounts of SO_4^{2-} in the samples were determined using ion chromatography.

Control experiments at pH 2.5 and 5.0 were conducted; all the protocols for the photocatalytic degradation reactions were the same as those mentioned above except that no TiO_2 was added. This is to test whether different photocatalytic degradation pathways observed at these pH conditions were determined by different adsorption modes or simply by the acidity (pH) of the solutions.

2 Results and discussion

2.1 Structural forms of H-acid in aqueous solutions at different pH values

Figure 1 shows the UV-Vis spectra of H-acid solutions in the pH range 2.03–10.21. At pH 2.03, H-acid showed a maximum absorption at 339 nm. With increasing pH, the maximum absorption band shifted towards longer wavelengths. The maximum absorption occurred at 358 nm for pH 4.69, and 372 nm for pH 10.21, indicating that the compound existed in different forms at different pH values, but, at a given pH, it mainly existed in a dominant form [22].

According to theoretical predictions [16], H-acid can exist in three structural forms under different pH conditions

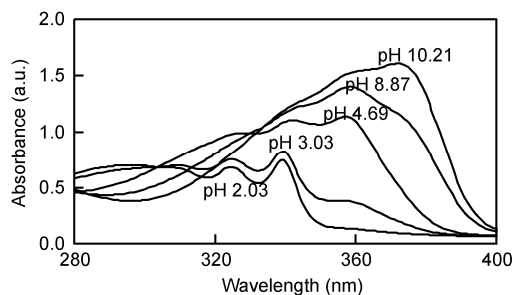


Figure 1 UV-Vis spectra of H-acid solutions under different pH conditions (concentration: 60 mg/L).

(A, B, and C in Figure 2). Since there are two sulfonic groups in the H-acid molecule, one of the sulfonic groups dissociates at low pH, and protonation of the nitrogen atom in the amine group is possible (Figure 2, A). With increasing pH, all the sulfonic groups dissociate (Figure 2, B). In alkaline solutions, the hydroxyl group deprotonates and forms H-bonds with the deprotonated amine group (Figure 2, C).

The UV-Vis spectra of the structural forms (A, B, C in Figure 2) were calculated using quantum chemical calculations. Figure 3 compares the calculated maximum absorptions of the UV-Vis spectra of the three structural forms with those shown in Figure 1. The calculated results agreed well with the experimental data, suggesting that H-acid mainly existed in form A in acidic solutions at pH lower than 3, form B at weakly acidic conditions around pH 5, and form C in alkaline solutions at pH higher than 10.

2.2 Adsorption modes of H-acid on TiO_2

The FTIR spectra of H-acid adsorbed on TiO_2 at pH 2.5, 5.0, and 10.0 are shown in Figure 4(a). The TiO_2 spectrum (Figure 4(a), 2) contained a band in the 1635 cm^{-1} region, characteristic of adsorbed water bending [20]. The FTIR spectrum of H-acid mixed with KBr (Figure 4(a), 1) was characterized by symmetric and asymmetric stretching bands of

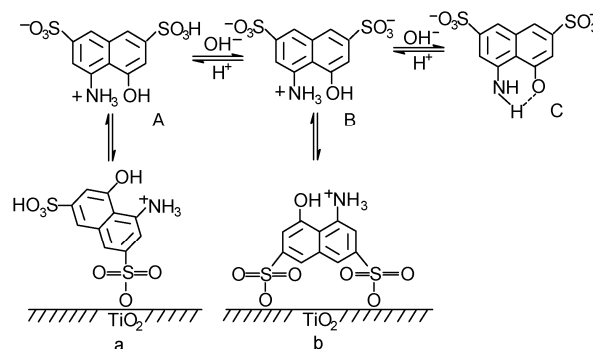


Figure 2 Structural forms of H-acid under different pH conditions: acidic (A), weakly acidic (B), and alkaline (C); proposed adsorption modes of H-acid on TiO_2 at pH 2.5 (a) and 5.0 (b).

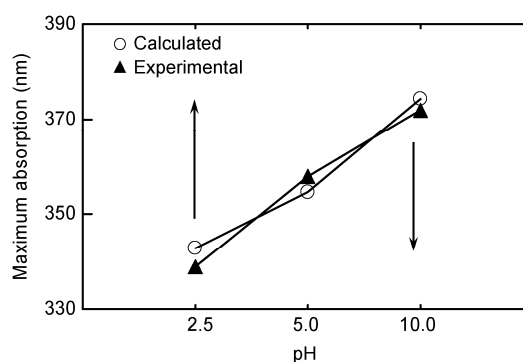


Figure 3 Comparison of calculated and experimental maximum absorption wavelengths of UV-Vis spectra of H-acid.

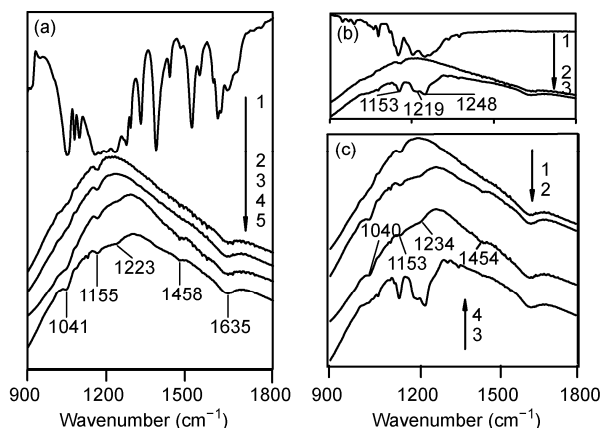


Figure 4 FTIR spectra. (a): 1) H-acid, 2) bare TiO_2 , 3) H-acid adsorbed on TiO_2 at pH 10.0, 4) adsorption sample at pH 5.0, and 5) adsorption sample at pH 2.5; (b): 1) PFOS, 2) bare TiO_2 , and 3) PFOS-modified TiO_2 at pH 2.5; (c): 1) bare TiO_2 , 2) H-acid adsorbed on TiO_2 , 3) PFOS-modified TiO_2 , and 4) H-acid adsorbed on PFOS-modified TiO_2 at pH 2.5.

the sulfonic groups at 1043 and 1148–1221 cm^{-1} , respectively [20,23]. In the spectrum of H-acid adsorbed on TiO_2 at pH 2.5 (Figure 4(a), 5), the positions of these bands were influenced by different metal ions and, upon interaction with TiO_2 , the symmetric and asymmetric stretching vibrations of the sulfonic groups appeared at 1041 and 1155–1223 cm^{-1} , respectively. In the spectrum of H-acid adsorbed on TiO_2 at pH 5.0 (Figure 4(a), 4), these peaks were smaller and, at pH 10.0 (Figure 4(a), 3), they were hardly visible in these regions. The FTIR spectra of PFOS mixed with KBr and of PFOS adsorbed on TiO_2 at pH 2.5 are shown in Figure 4(b). In the spectrum of PFOS adsorbed on TiO_2 (Figure 4(b), 3), the positions of the symmetric and asymmetric stretching vibrations of the sulfonic groups appeared strongly at 1153 and 1219–1248 cm^{-1} , respectively, as a result of a strong interaction between PFOS and TiO_2 through the sulfonic groups. There were similar peaks at 1040 and 1153–1234 cm^{-1} in the spectrum of H-acid adsorbed on TiO_2 covered with PFOS at pH 2.5 (Figure 4(c), 4). The adsorption isotherms of H-acid on TiO_2 at pH 2.5 in the absence or presence of PFOS (Figure 5) showed that the adsorption capacity in the absence of PFOS was higher than

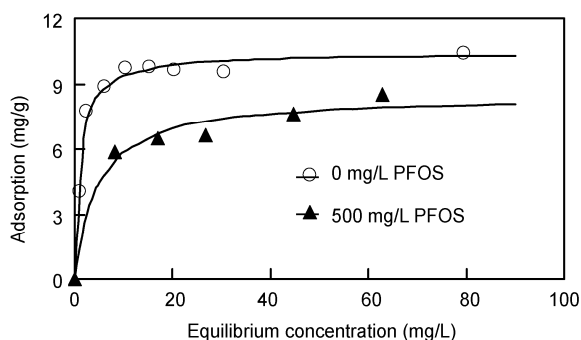


Figure 5 Effects of PFOS on adsorption isotherms of H-acid adsorbed on TiO_2 at pH 2.5 (TiO_2 concentration: 2 g/L).

in the presence of PFOS, suggesting strong competition for binding sites by the PFOS sulfonic groups. The adsorption of PFOS alone on TiO_2 surfaces, before addition of H-acid, has been reported previously [22]. These data confirmed that at low pH, the H-acid was adsorbed on TiO_2 by sulfonic groups.

Figure 6 shows the adsorption-desorption isotherms of H-acid on TiO_2 at pH 2.5, 5.0, and 10.0. The adsorption capacity decreased significantly with increasing pH. The difference between adsorption and desorption isotherms is called adsorption hysteresis, and is an approximate measure of adsorption irreversibility [7–9]. The adsorption hysteresis for the H-acid- TiO_2 system is very large (irreversible), and the irreversibility increased with increasing pH (Figure 6). It was therefore more difficult for adsorbed H-acid to be desorbed at pH 5.0 than at pH 2.5, although the adsorption capacity at pH 5.0 was much less than that at pH 2.5. According to MEA theory, for a given adsorbate and adsorbent, the MEA effect is stronger for adsorption that is more irreversible, and this is known to be the result of stronger adsorption bonds [10]. It will be shown in the following that the photodegradation pathway of H-acid at pH 2.5 was different from that at pH 5.0 as a result of different MEA adsorption states (i.e., adsorption modes and the affinity/reversibility of the adsorption bond). It was noted that at pH 2.5 the adsorption density was significantly different for different particle concentrations (compare Figures 5 and 6). This particle concentration effect corresponded to the fact that adsorption at this pH was largely irreversible; this agreed with the interpretation using MEA theory [7–9].

For P25- TiO_2 , the surface acidity constants are $\text{p}K_{a1}^s = 4.5$ and $\text{p}K_{a2}^s = 8$, which yields $\text{pH}_{zpc} = 6.25$ from the equation $\text{pH}_{zpc} = 1/2 (\text{p}K_{a1}^s + \text{p}K_{a2}^s)$ [24]. At pH values of 2.5, 5.0, and 10.0, the surface charges of P25- TiO_2 are very positive, near neutral, and very negative, respectively, and the H-acid forms are mainly A, B, and C (Figure 2), respectively. H-acid should therefore be adsorbed on TiO_2 surfaces in form A by one dissociated sulfonic group (Figure 2, a) at pH 2.5, and form B by two dissociated sulfonic groups (Figure 2, b). Since the latter adsorption mode (form B, Figure 2, b) is stronger than the former (form A, Figure 2, a),

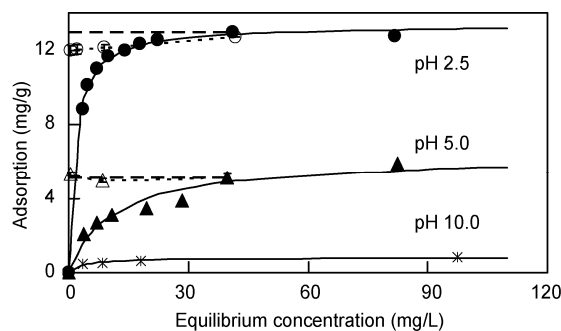


Figure 6 Effects of pH on adsorption-desorption isotherms of H-acid on TiO_2 (TiO_2 concentration: 3 g/L). Solid symbols: adsorption; open symbols: desorption.

adsorption at pH 5.0 is more irreversible than that at pH 2.5. It is important to note that stronger adsorption bonds, which cause a higher degree of adsorption irreversibility, do not necessarily lead to a higher adsorption capacity. Two mechanisms explain why the adsorption capacity at pH 2.5 was higher than that at pH 5.0 (Figure 6). First, the adsorption mode of form A, by one sulfonic group, occupied a smaller surface area than that of form B, by two sulfonic groups, so the monolayer adsorption capacity of form A was higher than that of form B. Secondly, the positive surface charge on TiO₂ decreased as the pH increased, so the adsorption of negatively charged H-acid decreased as the pH increased. At pH 10.0, H-acid and the TiO₂ surfaces were all negatively charged, and the adsorption capacity was too low to be experimentally determined to identify the adsorption mechanism.

2.3 Effects of adsorption modes on the photocatalytic degradation pathway

The concentration of H-acid as a function of radiation time at different pH values is presented in Figure 7. It has been suggested [14] that the adsorption of organic molecules on the catalyst surface is generally an important step in determining photocatalytic degradation rates, and the Langmuir-Hinshelwood model has been used to describe the kinetics of adsorption-photodegradation reactions [25,26]:

$$r = \frac{dc}{dt} = k_1 \frac{Kc}{1 + Kc}, \quad (1)$$

where r is the reaction rate ($\text{mg L}^{-1} \text{min}^{-1}$), c is the H-acid concentration (mg/L), K is the Langmuir-Hinshelwood adsorption equilibrium constant (L/mg), and k_1 is the rate constant of the surface reaction ($\text{mg L}^{-1} \text{min}^{-1}$). A significant correlation was obtained using this model with constants $k_1 = 1.33$, $K = 0.029$ at pH 2.5, and $k_1 = 62.27$, $K = 0.00083$ at pH 5.0. The correlation coefficients r were 0.888 at pH 2.5 and 0.791 at pH 5.0 ($r_{99\%, f=7} = 0.798$, $r_{95\%, f=7} = 0.666$), respectively. The equilibrium adsorption constant K at pH 2.5 was bigger than that at pH 5.0, which agreed with the results shown in Figure 6. However, a higher adsorption

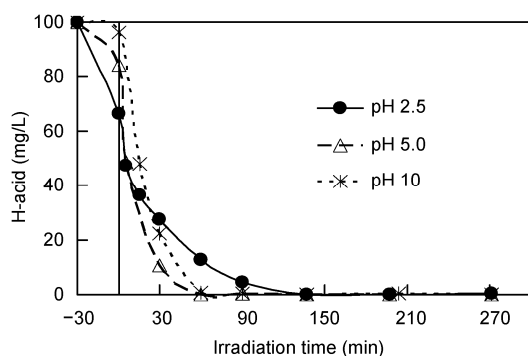


Figure 7 Effects of pH on H-acid concentrations in TiO₂ suspensions under UV irradiation (TiO₂ concentration: 3 g/L; C₀: 100 mg/L).

equilibrium constant did not correspond to a higher rate constant of the surface reaction. Since there was only one sulfonic group adsorbed on TiO₂ at pH 2.5, the surface photocatalytic degradation rate at pH 2.5 was slower than that at pH 5.0, where two sulfonic groups were adsorbed on the TiO₂ surfaces. These results suggested that the photocatalytic degradations of H-acid at pH 2.5 and 5.0 were controlled by the attack of free radicals on the sulfonic groups adsorbed on the TiO₂ surfaces. The adsorption mode of form A by one sulfonic group at pH 2.5 and form B by two sulfonic groups at pH 5.0 explained the kinetic parameters obtained by Langmuir-Hinshelwood modeling.

The photocatalytic degradation behavior at pH 10.0 could not be described by a Langmuir-Hinshelwood kinetics model because of the low adsorption capacity. H-acid may be photocatalytically degraded in non-adsorbed forms at pH 10.0 by the free-radical groups produced during radiation-TiO₂ interactions. Assuming a constant $\cdot\text{OH}$ concentration under irradiation, the reaction kinetics can be described by a first-order reaction model as follows

$$r = \frac{dc}{dt} = k_2 c, \quad (2)$$

where r is the reaction rate ($\text{mg L}^{-1} \text{min}^{-1}$), c is the concentration of H-acid (mg/L), and k_2 is the rate constant of the first-order reaction (min^{-1}). Good regression results ($r = 0.983$) of the reaction at pH 10 are obtained with $k_2 = 0.05618$. These results supported our previous studies [27], which showed that the photocatalytic degradation reactions predominantly occur on the catalyst surface when the adsorption ratios are high, whereas at lower adsorption ratios, the photocatalytic degradation reactions occur near the catalyst surfaces.

A conclusive verification of the mechanism in which photocatalytic degradation pathways were controlled by the adsorption modes, rather than just the adsorption amounts as is conventionally assumed, is presented in Figure 8. Figure 8(a) shows that the kinetic processes of degradation of H-acid at pH 2.5 and 5.0 followed significantly different pathways before equilibrium was reached. These degradation pathways corresponded to the different kinetics of SO_4^{2-} formation; SO_4^{2-} was produced during the attack of free radicals on the adsorbed sulfonic groups (Figure 8(b)) on the TiO₂ surfaces. It can be seen that, although the adsorption amount was higher at pH 2.5 than that at pH 5.0 (see Figure 8(a), adsorption processes before irradiation), removal of H-acid by photocatalytic degradation was much slower at pH 2.5 than at pH 5.0 (Figure 8(a)) since H-acid was adsorbed on the TiO₂ surfaces by one sulfonic group at pH 2.5, but two sulfonic groups at pH 5.0. The initial removal rate of H-acid by photocatalytic degradation was $4.75 \text{ mg L}^{-1} \text{min}^{-1}$ at pH 2.5 but $9.03 \text{ mg L}^{-1} \text{min}^{-1}$ at pH 5.0, and the SO_4^{2-} production rate was $0.11 \text{ mg L}^{-1} \text{min}^{-1}$ at pH 2.5 and $0.85 \text{ mg L}^{-1} \text{min}^{-1}$ at pH 5.0 (Table 1). Control

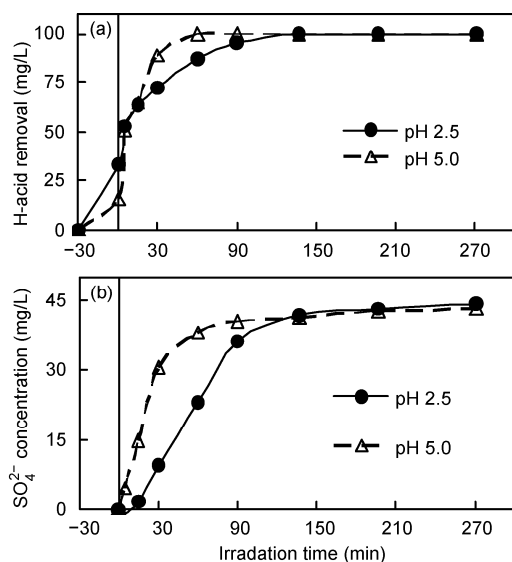


Figure 8 Effects of pH on the kinetic pathways of (a) H-acid removal and (b) SO_4^{2-} production, resulting from the photocatalytic degradation of H-acid in TiO_2 suspensions (TiO_2 concentration: 3 g/L; C_0 : 100 mg/L).

Table 1 Results of adsorption and photocatalytic degradation of H-acid

pH	2.5	5
Main structural form	A	B
Surface charge of TiO_2	Positive	Neutral
Adsorption capacity (mg/g)	13.36	6.24
Adsorption modes	One- SO_3^-	Two- SO_3^-
Removal rate of H-acid ($\text{mg L}^{-1} \text{min}^{-1}$) ^{a)}	4.75	9.03
Formation rate of SO_4^{2-} ($\text{mg L}^{-1} \text{min}^{-1}$) ^{a)}	0.11	0.85

a) Initial rate during the first 15 min (TiO_2 : 3 g/L; H-acid C_0 : 100 mg/L).

experiments indicated that no SO_4^{2-} was produced and little H-acid degradation was observed (less than 20%) during UV irradiation of the same solutions at pH 2.5 and 5.0 when no TiO_2 was added, hence no adsorption was introduced (data not shown here). Since the SO_4^{2-} production kinetics was entirely controlled by the adsorption modes, and H-acid degradation was always accompanied by the cleavage of sulfonic groups (Figure 8(a) and (b)) [28], the MEA adsorption states of form A (less irreversibly adsorbed) and form B (more irreversibly adsorbed) of H-acid (Figure 2) were therefore the real reasons for the different photocatalytic degradation pathways observed at pH 2.5 and 5.0.

Based on the above discussion and previous studies [27], two possible photocatalytic degradation pathways of H-acid were proposed. (i) When H-acid is adsorbed on the TiO_2 surfaces by one sulfonic group, the adsorbed sulfonic group is first attacked by $\cdot\text{OH}_{\text{ads}}$, resulting in the production of SO_4^{2-} and cleavage of the naphthalene ring. The other non-adsorbed sulfonic group is then transformed to SO_4^{2-} after cleavage of the naphthalene ring. (ii) When H-acid is ad-

sorbed on the TiO_2 surfaces by two dissociated sulfonic groups, during the photocatalytic degradation reaction, the two adsorbed sulfonic groups are simultaneously attacked by $\cdot\text{OH}_{\text{ads}}$. The naphthalene ring is cleaved after formation of SO_4^{2-} . This hypothesis needs to be further studied by identifying the intermediates at different stages of adsorption and photocatalytic degradation reactions.

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