Photodegradation of acetaminophen in TiO_2 suspended solution

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Abstract

This study investigated the photocatalytic degradation of acetaminophen (APAP) in TiO_2 suspended solution under a 250 W metal halide lamp. The influence of some parameters on the degradation of acetaminophen was studied and described in details, such as initial APAP concentration, initial pH value and TiO_2 dosage. After 100 min irradiation, about 95% of APAP is decomposed in the $1.0\,g\,L^{-1}$ TiO_2 aqueous solution with an initial concentration of $100\,\mu mol\,L^{-1}$. The effect of adsorption at three different pH values has also been analyzed and it has been conducted that pH 3.5, at which APAP was readily adsorbed also degraded at a faster rate. Reaction rate at pH 6.9 and pH 9.5 was 2.84 and $2.96\,\mu M\,min^{-1}$, respectively. Direct hole (h^+) oxidation and *ipso*-substitution was found to be the main initial step for APAP degradation. Main reaction intermediates and products were identified by GC/MS analysis. The mechanism of acetaminophen photocatalytic degradation in TiO_2 suspended solution was studied not only experimentally but also theoretically by calculating the frontier electron density of APAP. The results obtained indicated that TiO_2 photocatalytic degradation is a highly effective way to remove APAP from wastewater and drinking water without any generation of more toxic products.

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Keywords: Acetaminophen; Photocatalytic degradation; Frontier electron density; TiO_2

1. Introduction

In recent decades, the presence of Pharmaceuticals and Personal Care Products (PPCPs) in the environment is emerging as a new environmental concern to the scientists as well as the public, which has low concentration in the environment and usually does not show acute toxicity. After digestion and metabolism of these compounds in body, residual parts with their metabolites are excreted in human urine and manure, which are the main inlets of them to enter the environment [1,2]. There are still some residual parts of them getting into the surface and groundwater during and after the sewage treatment [3–5].

Acetaminophen (paracetamol, abbreviated as APAP) is one of the top 200 prescriptions in the United States in 2003, which is widely used as pain relief. Muir et al. [6] found 58–68% of acetaminophen was excreted from the body during therapeutic use and the median concentrations of $0.11\,\mu g\,L^{-1}$ was detected in US streams by Kolpin et al. [7]. Most researches on APAP

are focused on its mechanism of analgesic action and its toxicity [8–12]. Only a few researches on its treatment have been published. Lorphensri et al. found acetaminophen exhibited virtually no sorption and no retardation in aquifer sand studies [13]. Based on HPLC, 2D ^1H, ^{13}C, ^{15}N NMR and GC/MS analysis, Vogna et al. found the main degradation pathways for acetaminophen were derived from three different hydroxylation steps [14]. Andreozzi et al. found acetaminophen could be mineralized up to 30 and 40% while using ozonation and H_2O_2 photolysis, respectively [15]. When treated with hypochlorite, acetaminophen has significant transformation efficiency in 1 h. The two quinoidal oxidation products, 1,4-benzoquinone and *N*-acetyl-*p*-benzoquinone imine (NAPQI), which are more toxic than acetaminophen, accounted for 25 and 1.5% of the initial acetaminophen concentration, respectively [16].

China is the second largest APAP manufacture country and many kinds of cold medicine used in China contain APAP, which turn APAP into an important environmental research object. In this work, kinetic study of photocatalytic degradation of APAP in TiO_2 suspended solution at three different pH values was demonstrated, adsorption experiments were carried out in order to explaining the pH effect on the photodegradation rate. The

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mechanism of photocatalytic degradation of APAP was put forward on the basis of the nature and content of the final reaction products, which was verified by the quantum calculation using Gaussian 98 soft package [17].

2. Materials and methods

2.1. Reagents

Acetaminophen (98%) was purchased from Alfa Aesar (Alfa Aesar, Britain) and was used without further purification. Methanol was spectroscopic grade (TEDIA, USA). The photocatalyst nano-TiO_2 (20–40 nm, surface area 120 $m^2 g^{-1}$) was purchased from High Technology Nano Co. Ltd. (Nanjing, China). BSTFA + TMCS (99:1, Supelco, USA) were used as derivatization reagent. $HClO_4$ and NaOH aqueous solutions were used to adjust pH. The reaction solutions were prepared in doubly distilled water.

2.2. Photocatalytic degradation experiment

A 250 W metal halide lamp ($\lambda \geq 365$ nm, Chenguang Illumination Instrument, Jinzhou, China) was used in the photocatalytic experiments, which was placed in a cooling trap for maintaining the constant temperature by water circulation. Aqueous solutions of APAP with TiO_2 were placed in photochemical reactor and purged with air at a fixed flow rate throughout the experiments. A schematic representation of the reactor setup was shown in Fig. 1. The TiO_2 suspended solutions containing APAP were equilibrated in the dark for 20 min before irradiation. Samples were collected and centrifuged at 10,000 rpm for 30 min in a 5415D centrifuge (Eppendorf, German) at different time intervals during the irradiation.
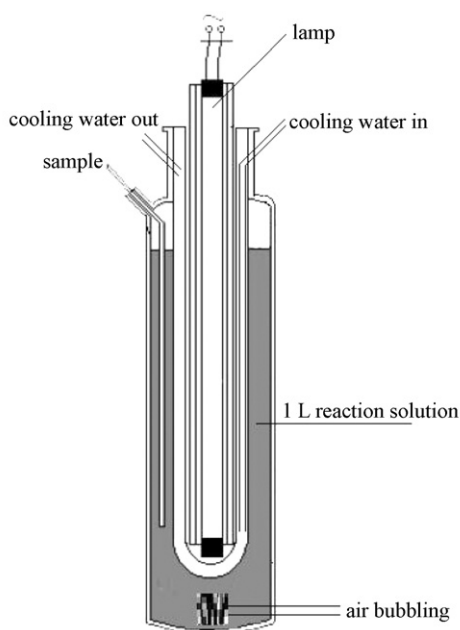

Fig. 1. Schematic representation of the reactor setup.

2.3. Adsorption experiment

The adsorption studies were performed in the darkness with aqueous suspensions containing 20–200 μM of APAP and 2 g L^{-1} catalysts in continuously stirred 250 mL glass vessels for 14 h. All the experiments were performed at constant temperature of 15 °C. Samples (5 mL) were taken for the analyses. The equilibrium concentration was determined by HPLC after centrifugal purification. Langmuir isotherms were used to quantify the adsorption of APAP on TiO_2 surface. K_L and θ were determined by means of a non-lineal regression fit of the Langmuir equation:

$$q_e = \frac{\theta K_L C_e}{1 + K_L C_e}$$

where q_e was the amount of solute adsorbed by gram of TiO_2, K_L was Langmuir equilibrium constant and θ was the adsorption maximum capacity of the solute on the TiO_2 surface and C_e was the solute concentration in the equilibrium.

2.4. Quantum calculation

Quantum calculation using Gaussian 98 was carried out to get the frontier electronic density of APAP. Hartree–Fock (HF) theory was chosen for the full optimization of geometries and 6-31G was used as the basis set which was of moderate size and accuracy. All the optimization was carried out without any symmetry restrictions, which was followed by a harmonic frequency analysis to ensure the optimized conformation was the true global minima. All the calculations were performed on a personal computer.

2.5. Analysis

The acetaminophen concentrations were analyzed by HPLC [Shimadzu LC-6A pump, Kromasil 100-5C18 column (4.6 × 250 mm, 5 μm)] with a flow rate of 1.0 mL min^{-1} and UV absorbance detection (Waters 481 detector) at 243 nm. The mobile phase was CH_3OH/H_2O mixture (30/70, v/v). The injection volume was 20 μL.

GC/MS was used to detect the photodegradation products. About 50% of APAP was degraded after 30 min reaction in 1 g L^{-1} TiO_2 suspended solution, and this was selected as a reasonable reaction time for investigation of early intermediates. 50 mL aqueous solution of APAP was collected at different time intervals and concentrated by vacuum freeze drying method. Then the samples were derivatized by 200 μL BSTFA + TMCS at 70 °C for 1 h to convert all free –OH and –COOH groups into their volatile TMS-ether(–$OSiMe_3$) and TMS-ester (–CO_2SiMe_3) derivatives. 1 μL was analyzed on a Saturn 2000 (Varian, USA) setup. The GC/MS column was a ZB5 (30 m × 0.25 mm × 0.25 μm, Zorbax). Helium was the carrier gas (flow rate 1.0 mL min^{-1}). The GC injection port temperature was 250 °C, and the column temperature was fixed at 80 °C for 1 min, and then programmed from 80 to 150 °C at 7 °C min^{-1}, and hold for 5 min, then from 150 to 200 °C with the same rate, the final temperature maintained for 5 min. The transfer line and

manifold were maintained at 170 and 80 °C, respectively. The MS detector was operated in the EI mode (70 eV).

3. Results and discussion

3.1. Control experiment

Aqueous solutions of APAP were irradiated using a 250 W metal halide lamp. The effect of oxygen was carried out as well as TiO_2, which was shown in Fig. 2. The concentration of APAP in the absence of TiO_2 hardly had any change during the 80 min irradiation. This was because APAP has weak absorption in the range from 350 to 800 nm, which means only few amount of APAP could have direct photolysis when a metal halide lamp was used as the irradiation source. However, oxygen had showed its importance in the photocatalytic degradation of APAP. After 80 min irradiation, almost 96% of APAP disappeared in the air bubbling solution, while only 6.5% of APAP was photodegraded in the nitrogen bubbling solution. According to the published results [18], this was mainly because hydroxyl radical ($^\bullet OH$) was formed not only via hole pathway but also via electron pathway that was initiated by the reaction of conduction band electron with molecular oxygen resulting in the formation of superoxide radical ($O_2^{\bullet -}$), which participated in further oxidation. Furthermore, Heller's group found that the actual oxidizer was a reduced form of oxygen using TiO_2 as photocatalyst, although the oxidation reaction was initiated by the valence band holes. Besides this, reduction of oxygen in aerated aqueous solution maintained charge neutrality of the TiO_2 particles [19].

3.2. Effect of the initial pH

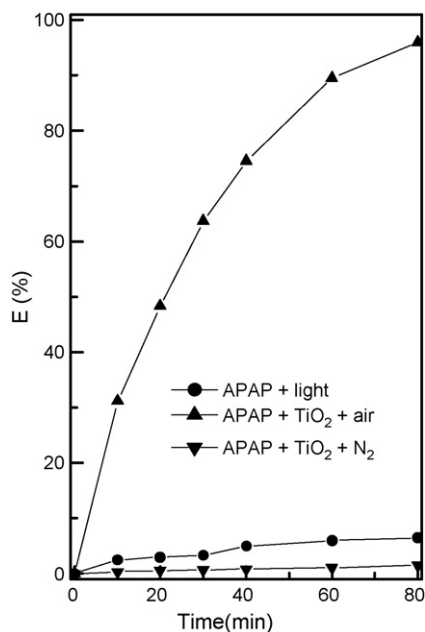The photocatalytic degradation of APAP aqueous solutions with different initial pH values was shown in Fig. 3. Photo-
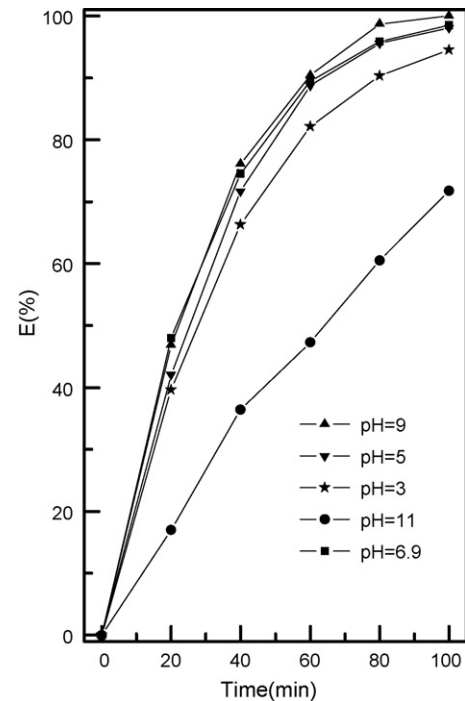
Fig. 3. Effect of pH on photocatalytic efficiency. $[APAP]_0 = 50 \, \mu M$, $TiO_2 = 0.5 \, g \, L^{-1}$. pH varies from 3.0 to 11.0.

catalytic degradation efficiency of APAP became a little higher when the pH value changed from acidic (pH 3.0) to weakly alkaline (pH 9.0), and 9.0 was the optimum pH value for the TiO_2 photocatalytic degradation of APAP in our study. Since the difference was small, the following experiments were carried out at 6.9, which was the natural pH of APAP with a concentration of 50 μM (the pK_a value of APAP was 9.38).

However, when the solution became more alkaline (pH 11.0), the degradation efficiency of APAP was much lower than in acidic and neutral solutions. This was because the surface of TiO_2 was amphoteric and pH-dependent [20]. At higher pH, the surface became more negative, and the hydroxyl group in APAP changed into phenolic anion. Thus, there was higher repulsion between the negative surface and APAP resulted in the lower degradation efficiency.

3.3. Effect of TiO_2 concentration

The photocatalytic degradation of APAP aqueous solutions with various TiO_2 concentrations was shown in Fig. 4. Apparently, in this work, the photodegradation efficiency of APAP increased when the concentration of TiO_2 increased from 0.25 to 1.0 g L^{-1}, After 100 min irradiation, about 95% of APAP decomposed in the aqueous solution with 1.0 g L^{-1} TiO_2, while only 36% of APAP was photodegraded at 0.25 g L^{-1} TiO_2 suspended solution. This was mainly because of the increase of hydroxyl radical produced from irradiated TiO_2. The optimum amount of TiO_2 should be added in order to avoid superfluous catalyst and also to ensure total absorption of radiation photons for efficient photodegradation [21,22]. When we increased the dose of the catalyst, of course, it would in crease the adsorp-
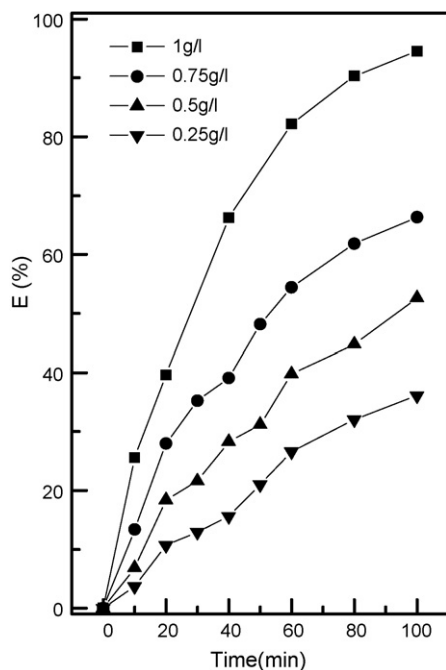

Fig. 2. Control experiments of photocatalytic degradation. $[APAP]_0 = 50 \, \mu M$, $TiO_2 = 1.0 \, g \, L^{-1}$, pH 6.9. $E(\%)$: degradation efficiency of APAP at different time.

Fig. 4. Effect of TiO$_2$ dosage on photocatalytic efficiency. [APAP]$_0$ = 50 μM, pH 6.9.

Fig. 5. Effect of APAP initial concentration on photocatalytic efficiency. TiO$_2$ = 1.0 g L^{-1}, pH 6.9.

tion amount of the reaction target resulting in a faster degraded rate. However, high concentration of TiO$_2$ particles became much easier to aggregate and reduced the light transmission. Hence different results be obtained when increment of catalyst in degradation of various compounds. Wiszniowski et al. found that for higher concentration of TiO$_2$, the removal efficiencies of humic acid decreased with increasing amount of TiO$_2$ [23], while Evgenidou et al. found when the concentration of TiO$_2$ was above 100 mg L^{-1} the photodegradation rate of prometryn had almost no change [24].

3.4. Photocatalytic degradation kinetics

In this experiment, a semi-log plot of concentration of APAP versus irradiation time was linear, indicating overall pseudo-first-order kinetics. The experiment was repeated in the range of initial concentrations from 25 to 100 μM (Fig. 5). The result shown in Fig. 5 indicated that the higher initial APAP concentration, the lower degradation efficiency was. When the initial concentration of APAP increased from 25 to 100 μM, the degradation efficiency of APAP decreased from 92 to 61% after 40 min irradiation. The initial rate of APAP photodegradation increased with increasing of the concentrations of APAP, and the initial rate of 100.0 μM APAP was 1.5 times that of 25.0 μM APPAP.

The initial rates for each concentration were determined from the pseudo-first-order rate constants and initial concentrations. The data were then fitted to the Langmuir–Hinshelwood kinetics rate model, which has been applied to the initial rates of photocatalytic degradation of many organic compounds [18(b),25,26]. The rate law is shown in Eq. (1),

$$R_0 = \frac{-\mathrm{d}C}{\mathrm{d}t} = \frac{k_{\mathrm{re}}K_s C_0}{1 + K_s C_0} \qquad (1)$$

where R_0 is the initial rate of disappearance of substrate and C_0 is the initial concentration of APAP. k_{re} is the reaction rate constant and K_s is taken to be the Langmuir adsorption constant.

Calculation results of k_{re} at three different pH values were shown in Table 1. The reaction rate was much greater with an initial pH 3.5 than that of the others. In an acid solution (pH < pK_a), it followed that the adsorption of APAP should be markedly favored when the oxygen atoms of APAP can interact with the positively charged surface. The reaction rate sequence was the same as the obtained from K_{ad} which was determined by means of a non-lineal regression fit of the Langmuir equation as described in the above section. k_{re} was slightly greater at pH 9.5 than that of pH 6.9, this was probably because of the photoenhanced hydrolysis of APAP in the alkaline solution.

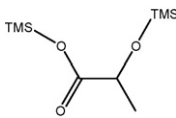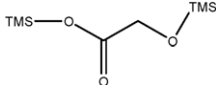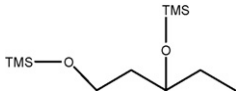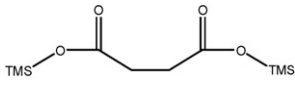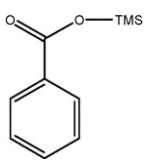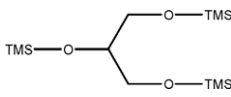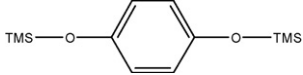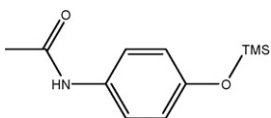### 3.5. Preliminary reaction mechanism study
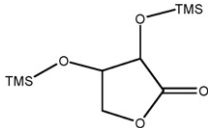
Reaction mechanism of photocatalytic degradation of APAP was concluded from GC/MS results and supported by the frontier electron density (FED). Detected products of the samples were given in Table 2.

We first proposed hydroxylation and direct hole (h$^+$) oxidation two routes as the initial step for APAP degradation. For the direct hole oxidation, the first reaction site was predicted on

Table 1
Kinetics analysis of the photodegradation of APAP

pH	θ (μM g^{-1})	K_{ad} (M^{-1})	Reaction constant (μM min^{-1})
3.5	270.0	330.76	8.09
6.9	320.0	224.49	2.84
9.5	300	260.39	2.96

Table 2
Detected intermediates by GC/MS

| No.	Proposed products	Retention time (min)/molecular weight	Major ion peaks (relative intensity)
1		6.965/234	219(20), 191(100), 147(93), 117(90), 73(63), 66(2), 45(19), 43(17)
2		7.174/220	205(12), 190(1), 177(24), 161(6), 147(100), 133(7), 131(6), 117(5), 103(6), 73(66), 59(8), 43(30)
3		7.461/248	233(5), 147(20), 143(15), 131(100), 103(41), 83(13), 73(88), 45(19)
4		9.820/262	262(5), 247(30), 218(1), 147(93), 129(11), 116(19), 73(45), 45(21)
5		9.996/262	262(1), 247(20), 219(47), 147(90), 131(35), 116(26), 103(22), 101(10), 73(100), 59(40), 45(42), 43(19)
6		10.255/194	194(5), 179(100), 135(43), 105(45), 89(39), 77(37), 59(33), 43(16)
7		10.848/308	293(3), 218(16), 205(51), 191(11), 177(5), 147(100), 133(15), 117(26), 103(18), 73(87), 45(35)
8		13.635/254	254(100), 239(17), 223(5), 147(8), 133(3), 112(2), 73(33), 45(20), 43(15)
9		22.604/223	223(100), 208(13), 181(78), 166(28), 147(3), 73(13), 43(26)

the basis of $2FED^2_{HOMO}$ value [27,28], which was found higher especially at C4 and C9 atoms, Table 3. Therefore, C4 and C9 should be the first sites at which the electron was extracted. Then the formed phenolic radical cation loses a proton and the resulting phenoxy radical reacts with superoxide radical to yield corresponding quinoneimine, which could be susceptible to hydrolysis to generate 1,4-benzoquinone (Path1 in Scheme 1). Hydroquinone and 1,4-benzoquinone was known to be in equilibrium in UV-irradiated TiO_2 aqueous suspensions [29]. Similar reactions have been reported for the TiO_2 photocatalytic degradation of 17β-estradiol by Ohko et al. [30].

Hydroxylation reaction, on the other hand, was also considered as a main initial step for APAP degradation at first. In the Frontier Orbital Theory, for the radical reaction, the

Table 3
Frontier electron density and atom point charge of APAP

Atom label[a]	$2FED^2_{HOMO}$	$FED^2_{HOMO} + FED^2_{LUMO}$
O1	0.0616	0.0366
C2	0.00688	0.0177
N3	0.256	0.128
C4	0.289	0.183
C5	0.0770	0.238
C6	0.0848	0.390
C7	0.119	0.496
C8	0.0922	0.311
C9	0.259	0.141
O10	0.171	0.0867
C11	0.0016	0.00462

[a] Atom label was depicted in Scheme 1.
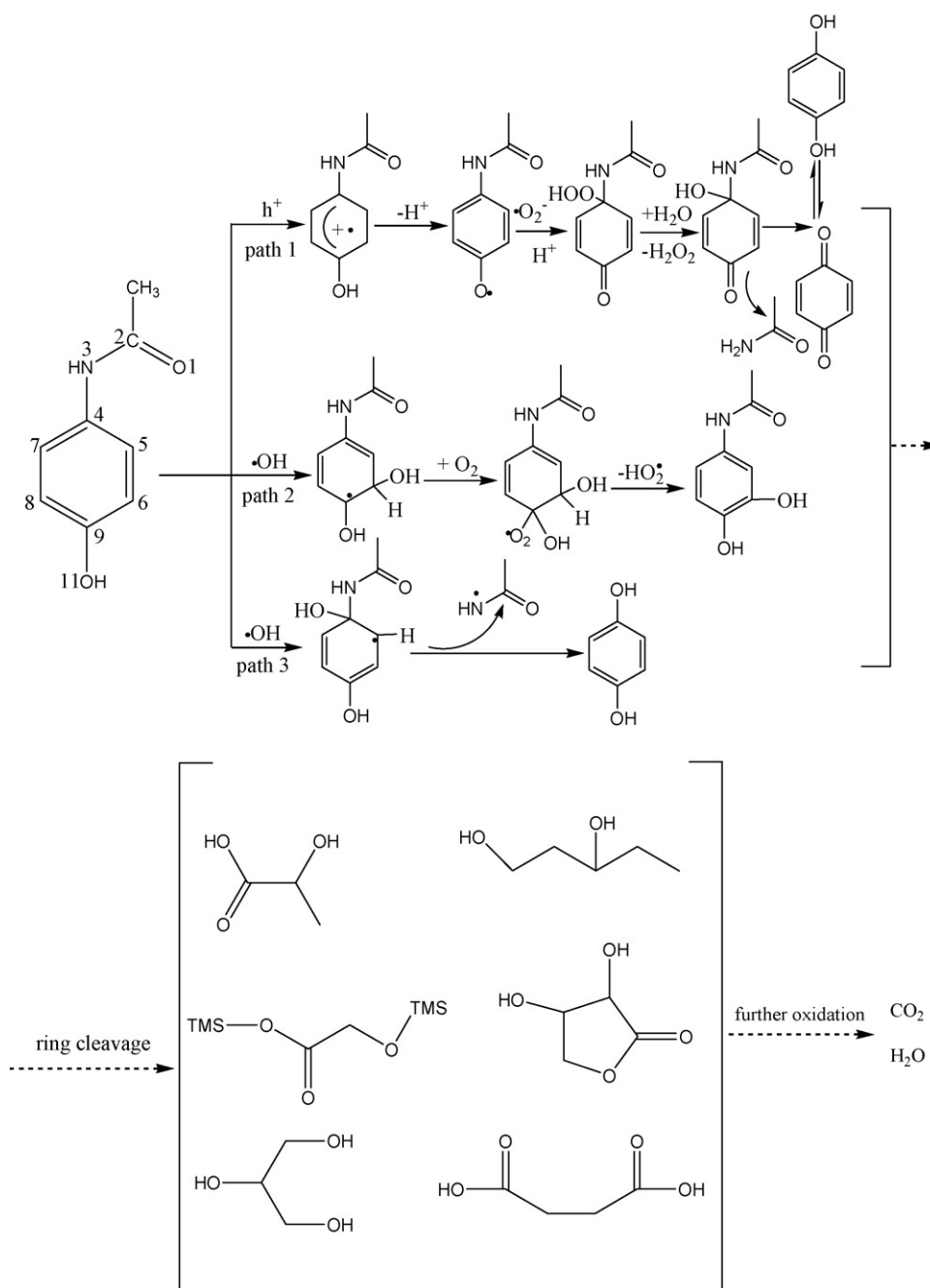
Scheme 1. Proposed pathway for photocatalytic degradation of APAP in TiO$_2$ suspended solution.

first addition probably happened on the atom with highest $FED_{HOMO}^2 + FED_{LUMO}^2$ value [27,28], which has been proved to be reasonable by the published work [30–32]. In this study, as for APAP, the most reasonable site at which the first addition of hydroxyl radical was at C6 and C7. If this predicated reaction occurred at C6 site, the subsequent reaction with oxygen should produce N-(3,4-dihydroxyphenyl) acetamide (Path 2). N-(2,4-dihydroxyphenyl) acetamide will be the resulting product if the reaction occurred at C7. In the two previous works, at least one of them was found during photodegradation of APAP by means of UV/H$_2$O$_2$. But actually none of them was detected in this work. However, as hydroquinone was the main detected intermediate, we concluded that the *ipso*-substitution should be

the main channel for the reaction with hydroxyl radical (Path 3). The main intermediates, hydroquinone or 1,4-benzoquinone, could be attacked by the hydroxyl radical to form hydroxylation product [33]. Subsequently, further oxidation of the early intermediates and the hydroxylation products would result in the breakdown of their aromatic structures followed by the formation of carboxylate acid and carbon dioxide.

4. Conclusion

In summary, we studied the photocatalytic degradation of APAP in TiO$_2$ suspended solution. Under the experimental condition, TiO$_2$ system demonstrated the capability of removing

APAP. After 100 min irradiation, about 95% of APAP decomposed in the $1.0 \, g \, L^{-1}$ TiO_2 aqueous solution with an initial concentration of $100 \, \mu mol \, L^{-1}$. Initial APAP concentration and TiO_2 dosage had effects on degradation efficiency of APAP, which increased with increasing catalyzer concentration, and decreased with increasing initial APAP concentration. Kinetic study and adsorption was analyzed at three different pH value and it has been conducted that pH 3.5, at which APAP was readily adsorbed also degraded at a faster rate. The Langmuir equilibrium constant was slightly greater at pH 9.5 than that of 6.9, reaction rate at pH 6.9 and pH 9.5 was 2.84 and $2.96 \, \mu M \, min^{-1}$, respectively.

Quantum calculation and GC/MS analysis allowed the identification of intermediates and products. The GC/MS analysis indicated that the *ipso*-substitution should be the main channel for the initial reaction of APAP with hydroxyl radical. The direct hole oxidation of APAP will result in the formation of hydroquinone. On the other hand, quantum calculation of frontier electron density is a reasonable method for predicting the electron extraction and hydroxyl radical addition site. The obtained results indicate that TiO_2 photocatalytic degradation is a highly effective way to remove APAP from wastewater and drinking water without any generation of more toxic products.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.12.098.

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