Enhanced photocatalytic degradation of atrazine by platinized titanium dioxide under 352 nm irradiation

Shen-Ming Chen, Norman Lu, Jun-Yu Chen, Cheng-Yu Yang, Yun-Peng Yeh, Tsung-Yao Feng, Yang-hsin Shih, Thangavelu Kokulnathan and Dong Chen

ABSTRACT

Simply coating 1 wt.% of platinum on titanium dioxide (TiO2) surface resulted in simple preparation of platinized TiO2 (Pt-TiO2). This study demonstrated the photodegradation of atrazine (ATZ) using either Pt-TiO2 or TiO2 as a photocatalyst under 352 nm light irradiation. The Pt-TiO2-catalyzed ATZ degradation reached 76% in 3 hours without adding H2O2 solution or aeration, which was more than 10% higher than the TiO2-catalyzed reaction. The decomposition product of Pt-TiO2-catalyzed ATZ degradation was mainly cyanuric acid. Thus, Pt-TiO2 as an effective photocatalyst has three main advantages in the photodegradation of ATZ under 352 nm irradiation. First, the coated Pt can facilitate the generation of appropriate amounts of OH radicals, so it can prevent the formation of over-oxidized TiO2. Second, aeration was not needed. Third, the excited electrons were mainly uni-directionally transferred to the catalyst surface to avoid recombination of electron-hole pairs.

Key words | 352 nm, atrazine, hydroxyl radical, platinized TiO2, Schottky barrier effect

INTRODUCTION

Titanium dioxide (TiO2) is a well-known and effective photocatalyst (Linsebigler et al. 1995; Fujishima et al. 2000) that is widely used in many applications (Hoffmann et al. 1995; Habibi et al. 2001; Esswein & Nocera 2007). The oxidation-reduction (redox) reaction occurs on its surface under UV illumination. The TiO2-catalyzed degradation of organic pollutants in water and air has been extensively investigated under UV and visible light irradiation during the last two decades (Mills et al. 1993; Domínguez et al. 1998). After light illumination, excited electrons migrate from the valence band to the conduction band of TiO2, where the redox reaction takes place, and the targeted organic compounds are degraded. However, the application of UV-driven TiO2 photocatalysis has some limitations because UV light must be used, and the recombination of photoexcited electrons and holes on the surface also leads to reduced efficiency (Yu et al. 2010). Hence, several methods have been used to modify the band gap of TiO2 to enable the excitation under visible light and to prevent recombination (Zang et al. 2000; Asahi et al. 2001; Zhao et al. 2004), including doping TiO2 with nitrogen atoms using a pure phase of TiO2, the formation of simple TiO2 complexes, and the addition of an adsorption sensitizer on the TiO2 surface (Lu et al. 2016). Various metals have been applied to the surface modification of TiO2. Platinum (Pt) is the most widely used metal because it acts as an active site on the TiO2 surface, which not only increases the binding of organic compounds in water to the TiO2 surface, but also increases the electron transfer rate to the surface, and thus accelerates the oxidation of organic compounds (Tanaka et al. 2015). Previous studies have demonstrated that platinum-coated TiO2 (Pt-TiO2) increases the photodegradation activity because the rate of the oxidation reaction at Pt sites is relatively high, and the degradation
rate can be enhanced by up to 30–40% (Papp et al. 1993; Kozlova & Vorontsov 2006). Pt sites on the TiO₂ surface attract and hold the electrons, which reduce the rate of electron-hole pair recombination under UV illumination (Kraeutler & Bard 1978; Yamakata et al. 2001). However, the rate of decomposition of organic compounds on Pt-TiO₂ could also be hindered by the presence of oxidized Pt owing to its lower electron conductivity, which leads to a decrease in the degradation efficiency (Yamakata et al. 2001).

Atrazine (ATZ) is used worldwide for the control of broadleaf and grassy weeds on both agricultural and non-agricultural land (Martin-Neto et al. 2001; Chan & Chu 2005). However, environmental concerns have been raised because it is considered to be a common soil and water pollutant today, especially due to its relatively slow degradation rate and low biodegradability. The photocatalytic degradation of ATZ has been performed under UV light irradiation, and typically cyanuric acid has been found as the final degraded product (Héquet et al. 2001; McMurray et al. 2006). The degradation mechanism of ATZ is complicated, but it is believed that degradation proceeds via several intermediates. For example, Granados-Oliveros et al. (Oliveros et al. 2009) identified desethyl/desisopropyl ATZ as the final product, while Horikoshi and Hidaka (Horikoshi & Hidaka 2003) and Maurino et al. (Maurino et al. 1999) reported that the final product was cyanuric acid. Nevertheless, it is fair to state that the degraded compounds obtained after photo irradiation depend on the degradation conditions. Figure 1 shows the structure of ATZ (C₈H₁₄ClN₅, molecular weight 215, 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and cyanuric acid (C₃H₃N₃O₃, molecular weight 129, 1,3,5-triazine-2,4,6-triol). ATZ has a central carbon/nitrogen-containing triazine ring with three different functional groups, which are Cl⁻, acetamido, and isopropylamino groups.

Two main mechanisms have been proposed for the detoxification of ATZ. One involves complete degradation of the triazine ring, whereas the other proceeds via cleavage of the side chains of ATZ (and replacement of them with OH groups that were generated catalytically). The resulting side chain-cleaved derivative is considered to be non-toxic (e.g., cyanuric acid (Nguyen et al. 2013)). Several methods have been used for the degradation/detoxification of ATZ, such as biodegradation, ozonation, high energy UV irradiation (λmax < 300 nm), and Fenton oxidation. However, many of these methods were time consuming (up to 60 days) and energy intensive. Consequently, there is a need to increase the degradation efficiency and reduce the energy consumption required by exploring novel photocatalysts (Mkhalid 2016). Some studies have investigated the photodegradation efficiency of ATZ under 300 nm UV illumination (Héquet et al. 2001; Azenha et al. 2003; Choi et al. 2013), and decomposition of ATZ has been achieved within 60 min. Héquet et al. (Héquet et al. 2001) and Parra et al. (Parra et al. 2004) used a simulated solar light source with emitted wavelengths >290 nm, including the UV region, and achieved 78% and 100% degradation of ATZ in 60 and 90 minutes, respectively. Pelizzetti et al. (Pelizzetti et al. 1990) obtained an even higher degradation efficiency (100% in 20 minutes) using a 1500 W Xenon light source (>340 nm), but the power was much higher and the energy consumption was much greater. Nevertheless, a shorter wavelength and higher energy were required. However, to our knowledge, almost no studies of ATZ degradation in aqueous solution using Pt-TiO₂ under 352 nm irradiation have been reported.

MATERIALS AND METHODS

Reagents

ATZ (purity >97%) was obtained from Tokyo Chemical Industry (TCI, Japan) and used as purchased. Aerioxide TiO₂ (80% anatase, 20% rutile) P25 was purchased from Degussa (Evonik), Germany. The average particle size was 30 nm. Potassium hexachloroplatinate (IV) (K₂PtCl₆) was purchased from Sigma-Aldrich, and the purity is >99.0%.

Preparation of platinized TiO₂ (Pt-TiO₂)

The modified Pt-TiO₂ was prepared by dissolving K₂PtCl₆ (66 mg) in a 2 M aqueous methanol solution (1 L) and then adding TiO₂ (1 g). The mixture was degassed by bubbling N₂ for 30 min and irradiated with 352 nm UV light for 3 hours. This special Pt-TiO₂, in which the amount of Pt is only about 1 wt. % in the resulting photocatalyst, has been prepared following the literature method (Bae et al. 2004). The mixture was then filtered, and the dark grey precipitate was washed with water and ether to yield 1.06 g of the desired product after drying at 100 °C for 90 minutes.

Photodegradation

Photodegradation of ATZ was performed in a photochemical reactor (PR-2000, Panchum Scientific Corp.) with an
installed mercury lamp (λ = 352 nm, 128 W; see Figure S7 in the Supporting Information (SI) (available with the online version of this paper) for the relative energy distribution of the 352 nm light source). The photocatalyst (10 mg) was added to a 20 ppm aqueous ATZ solution (20 mL) in a 50 mL Pyrex tube. Either bubbling O₂ was carried out, or not, during irradiation. The mixture was sampled (0.6 mL) at certain time intervals. Each sample was diluted accordingly, centrifuged at 3,000 rpm for 30 min, and filtered using an Advantac filter (pore size 0.22 μm) in order to remove the nanoparticles of the photocatalyst.

Analysis

UV-visible spectrum

The filtered samples were subsequently analyzed in a 1.0 cm quartz cuvette cell using a Hitachi U-3010 UV-Visible Scanning Spectrophotometer, and the spectrum of ATZ was recorded between 200 and 350 nm at a scan rate of 120 nm/s. The characteristic absorption peaks for ATZ appear at 222 and 262 nm. The absorbance data for an ATZ calibration curve were fitted using Beer’s law, as shown in Figure 3. The concentration of ATZ was quantified by the absorbance at the 262 nm peak using the established calibration curve between ATZ concentration and absorbance. The fitting line is shown in Figure S1 in the Supporting Information (available with the online version of this paper). The molar extinction coefficient of ATZ is 3.5 × 10⁵ and 3.5 × 10² M⁻¹ cm⁻¹ at 222 and 262 nm, respectively.

Transmission electron microscopy

Additionally, transmission electron microscopy (TEM) samples were prepared by dropping a dilute DMSO solution of Pt-TiO₂ onto copper grids coated with a thin Formvar carbon film with subsequent evaporation of the solvent in air at room temperature. TEM images including high resolution TEM were carried out on a Philips Tecnai G2 F20 microscope (Philips, Holland).

Gas chromatography–mass spectrometry

The gas chromatography–mass spectrometry (GC/MS) results were obtained by an Agilent 6890 series GC system with a 5973 mass selective detector. The sample was monitored with an HP 6890 GC using a 30 m × 0.250 mm HP-1 capillary column with a 0.25 μm stationary phase film thickness. The flow rate was 1 mL/min and splitless. A 1-mL aqueous solution of ATZ before irradiation (20 ppm) and a sample of the reaction mixture after a 3-hour irradiation were added to 1 mL dichloromethane, and the ATZ was extracted from the water for GC analysis. The initial temperature of the GC oven was set at 50 °C for 5 minutes. The ramp was set at 10 °C/minute for 20 minutes, and the temperature was held at 260 °C for 11 minutes.

RESULTS AND DISCUSSION

Platinized TiO₂

Figure 2(a) shows a high resolution TEM image of the synthesized Pt-TiO₂ catalyst. The particles are roughly spherical in shape, with diameters of about 5 nm. The white arrows indicate the locations of deposited Pt nanoparticles, whose size is about 5 nm. One of the deposited Pt nanoparticles was analyzed by EDX, shown in the SI (available with the online version of this paper).

A typical X-ray diffraction (XRD) pattern of TiO₂ and Pt-TiO₂ is shown in Figure 2(b). The XRD result of the bare TiO₂ P25 in rutile and anatase phases shows the characteristic planes at two theta equal to 25.3°, 27.4°, 37.5° and 48.3°. After coating with Pt, the characteristic planes of Pt (111) and Pt (200) can be seen at (2θ =) 40° and 46° on the treated TiO₂, which indicates the incorporation of Pt.
Degradation results of ATZ

The UV-Vis spectra of ATZ before and after photodegradation using the Pt-TiO₂ catalyst are shown in Figure 3. It can be seen that the characteristic peaks for ATZ at 222 and 262 nm were either shifted or decreased in intensity at different time intervals during photo irradiation. These changes in the spectrum of ATZ were thought to be as a result of the replacement or removal of functional groups in ATZ through the TiO₂ or Pt-TiO₂-catalyzed photodegradation under 352 nm irradiation. Therefore, the decrease in intensity and shift of the absorption peaks in the UV-Vis spectrum of ATZ can be used to determine the photocatalytic activity of the photocatalysts. In the introduction, the mechanism of ATZ degradation was proposed for the oxidation process of hydroxyl radicals generated in the photolytic reaction in an aqueous ATZ solution (Maurino et al. 1999). In Figure 3, the spectra were obtained using an initial solution containing 20 ppm ATZ. After photo irradiation, the absorbance of the characteristic peaks decreased with irradiation time, and several intermediate peaks appeared during illumination. These peaks agree with those peaks reported in the literature (McMurray et al. 2006; Choi et al. 2015). The decreased peak at 222 nm indicates the degradation of ATZ after irradiation for a certain time; however, this peak is easily interfered with by other absorption bands for different intermediates, as can also be seen in Figure 3. On the other hand, the molar absorption peaks of the intermediates that occurred at a wavelength longer than 260 nm, were very small compared with those of the intermediates with peaks near 222 nm. Therefore it was feasible to follow the decay of ATZ by monitoring the absorbance at 262 nm, because at this wavelength any interference from the intermediates was negligible.

Figure 4 shows the decomposition results of ATZ at different irradiation times under different conditions. Without the use of any photocatalyst, the ATZ was not significantly degraded after 180 minutes of photo irradiation under 352 nm. Therefore, the photocatalyst was critical to enhance degradation of ATZ. As a control test, adsorption removal of ATZ by Pt-TiO₂ (without photo irradiation) was about 8% after 120 minutes (see Figure S2, available with the online version of this paper), suggesting photodecomposition of ATZ was the major removal mechanism. For the photodegradation of ATZ, with or without TiO₂, the results reported here are consistent with Chan et al. (Chan et al. 2004), although Pt-TiO₂ made the degradation of ATZ faster than TiO₂ (see Figure 4 and Figure S6; Figure S6 is available with the online version of this paper). According to Chan et al. (Chan et al. 2004), the
reaction mixtures were usually the dealkylation product(s) without the use of H2O2. The degradation rate could be greatly enhanced when ATZ photodegradation was catalyzed by TiO2 in the presence of the appropriate amount of H2O2 which is, however, known to easily cause the over-oxidation of TiO2.

As shown in Figure 4 and Table 1, TiO2-catalyzed ATZ degradation reactions without adding H2O2 under the 352 nm irradiation for 3 hours yielded a degradation rate of 66%. The resulting intermediates were mainly analyzed and rationalized by UV-Vis spectrometer. The GC/MS was used to follow the change of the amount of ATZ with time (shown in the SI). Our results were in agreement with those reported by Chan et al. (Chan et al. 2004), in which the TiO2-catalyzed ATZ degradation reactions with the addition of H2O2, but no aeration under the 365 nm irradiation for 3 hours gave a 65.6% degradation rate, and the resulting products were mainly cyanuric acid, and a few less substituted triazine. As shown in Figure 3, Pt-TiO2-catalyzed ATZ degradation reactions without adding H2O2 or bubbling air under the 352 nm irradiation for 3 hours gave rise to the main degraded product, cyanuric acid, with a higher degradation rate of 76%, which is better than the 65.5% from Chan’s study (see Table 1) in similar condition. In other words, simply coating 1wt % of Pt on TiO2 can result in at least a 10% increase in degradation rate without even adding any H2O2 or aeration during the process. Adding appropriate amounts of H2O2 was reported to assist the TiO2-catalyzed reactions by providing additional OH·

![Figure 4](image)

**Figure 4** Degradation results of TiO2 and Pt-TiO2-catalyzed ATZ photodegradation under 352 nm irradiation for different irradiation times under various conditions. Pt-TiO2 condition: when the degassed ATZ solution was irradiated with 352 nm light, no aeration was needed during the process. The initial concentration of ATZ was 20 mg/L. The catalyst dosage was 10 mg/L.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Photodegradation of ATZ under UV irradiation with wavelengths greater than 300 nm</th>
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<tbody>
<tr>
<td>Item</td>
<td>Catalyst</td>
</tr>
<tr>
<td>1. This work</td>
<td>TiO2</td>
</tr>
<tr>
<td>2. This work</td>
<td>Pt-TiO2</td>
</tr>
<tr>
<td>3. This work</td>
<td>Pt-TiO2</td>
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<tr>
<td>4. Chan et al. (2004)</td>
<td>TiO2</td>
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<tr>
<td>5. Campanella et al. (2007)</td>
<td>TiO2</td>
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</table>

*The solution was degassed for several hours by bubbling nitrogen through before the UV irradiation.

*The reaction was carried out without aeration; and it was difficult to know what the appropriate amount of H2O2 was, and excess H2O2 usually caused the over-oxidation of TiO2.
H2O2 and O2 (as electron acceptor or to prevent the recombination of excited electrons), as described by Equations (1)–(3) (Ince 1999; Cornish et al. 2000)

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^+ + \text{OH}^- \quad (1) \]

\[ \text{H}_2\text{O}_2 + \cdot\text{O}_2 \rightarrow \text{OH}^+ + \cdot\text{OH}^- + \text{O}_2 \quad (2) \]

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}^+ \quad (3) \]

It is Pt-TiO2 that was found to have both these favorable effects, as shown below:

1. Schottky barrier effect

\[ \text{Pt-TiO}_2 \]

2. Pt-catalyzed the fast formation of OH radicals.

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow \text{Pt in Pt-TiO}_2 2\text{OH}^+ \]

Thus, Pt-TiO2 can also prevent the drawbacks from adding too much H2O2 (Tay et al. 2001). Equations (4) and (5) (Chan et al. 2004) describe H2O2 scavenging hydroxyl radicals and the formation of Ti(OOH)(OH)3 and other Ti derivatives that inhibit the photocatalytic efficiency of TiO2. In practice, it is typically difficult to control the optimized dosage of H2O2, and adding too much H2O2 is not rare.

\[ \text{H}_2\text{O}_2 + \text{OH}^+ \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (4) \]

\[ \text{HO}_2^- + \text{OH}^+ \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (5) \]

This result can be attributed to the Schottky barrier effect, which increases transfer of electrons to the surface in the conduction band and prevents electron-hole recombination between the conduction and valence bands. Reportedly, Pt-TiO2 forms a Schottky barrier effect between the Pt and TiO2 that prevents the electrons from recombining with the holes (Kirner et al. 1991). The electrons are attracted to the TiO2 surface and participate in additional oxidation and reduction reactions at the TiO2 surface. Several studies have achieved significant degradation of ATZ using TiO2 and irradiation at 352 nm with a high light power in 3–6 hours (Pelizzetti et al. 1990; Héquet et al. 2001; Chan et al. 2004; Parra et al. 2004; McMurray et al. 2006; Oliveros et al. 2009), suggesting the Pt-TiO2 catalyst improved the energy efficiency of photodegradation.

Hydroxyl and superoxide radicals have also been reported to assist ATZ degradation. It can be seen in Figure 4 that the degradation rate of ATZ with TiO2 and Pt-TiO2 varied under different reaction conditions. The different ATZ degradation efficiencies were likely owing to the differences in the hydroxyl radicals and superoxide anions, with different surface occupation generated under different conditions. Granados-Oliveros et al. (Oliveros et al. 2009) also suggested that the degradation of ATZ is initiated by the attack of ·OH radicals on the aminoalkyl groups of the side chains, generating free organic radicals and organic intermediates. Note that, in the present study, the photolysis of the chlorine atom in ATZ and the further displacement of amino groups by hydroxyl groups led to the formation of organic intermediates that were observed in the UV-Vis spectra of ATZ during degradation.

**UV-Vis spectrum**

The percentage of ATZ remaining after photo irradiation for different periods of time in the presence and absence of TiO2 and Pt-TiO2 were listed in Table S1 (available with the online version of this paper). As mentioned above, in Figure 5, the characteristic absorption peaks for ATZ before photo irradiation can be clearly seen at 222 and 262 nm and result from Cl−, acetamido, and isopropylamino groups on a single 1,3,5-triazine ring. The absorption peaks were proposed to represent different energy bands (π to π* transitions). After photo irradiation, the intensity of the characteristic peaks decreased with irradiation time because of the decomposition of ATZ and its side chains. New peaks were quite different from those in the original ATZ spectra, which were attributed to an intermediate with an unsubstituted 1,3,5-triazine ring structure in water. In addition, it can be clearly seen in Figure 5 that both the characteristic peaks at 222 and 262 nm became blue shifted and decreased in intensity (Yadav 2005) with longer irradiation time using both TiO2/H2O2 and Pt-TiO2. These changes in the absorption spectrum were due to the loss of Cl−, acetamido, and isopropylamino groups, which results in an antiauxochromic effect (blue shift). In the present study, the intermediates containing different functional groups were characterized by UV-Vis spectrometer and the observed absorption bands, which result from different π to π* transitions, show in the range of 200–270 nm. As mentioned previously, the
TiO$_2$-catalyzed photodegradation of ATZ in the presence of H$_2$O$_2$ under circa 350 nm was carried out in this research. The UV-Vis spectrum of the end product of this TiO$_2$-catalyzed reaction is shown as a dash trace in Figure 5. Cyanuric acid, the major final product of ATZ photodegradation reported by Horikoshi and Hidaka (Horikoshi & Hidaka 2003), has a characteristic absorption peak in water around 204 nm (red-shifted in Sc H$_2$O).

Campanella and Vitaliano (Campanella & Vitaliano 2007) reported that in degradation of ATZ, after 14 hours of photo irradiation (320 W, 210–400 nm, max at 310 nm) with TiO$_2$ and H$_2$O$_2$, the maximum absorption peak shifted from 222 to 214 nm and the toxicity was reduced to 28% of the original level due to the remaining ATZ, as shown in Table 1. In the present study, the 222 nm absorption peak for the photo irradiation product shifted to 214 nm after 30 minutes, which was much faster (Table S1), suggesting great effectiveness of Pt-TiO$_2$. In addition, the shoulder of this peak, shown in Figure 6, was thought to indicate the replacement of the side chain groups with -OH. Furthermore, the UV-Vis spectrum of the final products obtained in this study had absorption peaks at 204 and 254 nm, which likely were peaks of cyanuric acid (Campanella & Vitaliano 2007).

In addition, numerous absorption peaks for several possible ATZ degradation intermediates can be seen in Figure 5. Photo-assisted catalysis has a remarkable influence on the degradation of ATZ, because the redox process initiated by TiO$_2$ can eventually affect the substitution at the ring, yielding one or several dealkylated intermediates. The radical species may also attack the carbon bonded to the amine groups. The amino groups exhibit low reactivity (Chan et al. 2004), while the chlorine was likely to be replaced by a hydroxyl group. Thus, it was possible that substitution of the chlorine atom by a hydroxyl group was the initial step in the degradation process, followed by destruction of the amine groups via charge transfer and oxidation of the alkyl groups.

In the UV-Vis spectra of intermediate/final products of ATZ degradation that lost -Cl, -CH$_3$, acetamido, and/or isopropylamino groups, the characteristic ATZ peaks would be either decreased or shifted toward the shorter wavelength region. Therefore, in addition to decomposition of ATZ via free radical attack, substitution of the chlorine atom by a hydroxyl group may occur as an initial step in the degradation process.
The photodegradation of ATZ was presumed to follow pseudo-first-order kinetics by using the GC/MS method. The ATZ concentration after photo irradiation was monitored by GC/MS and is shown in Figure S3 (available with the online version of this paper). It can be seen that the ATZ peak appeared between 10.5 to 11.5 minutes before 352 nm light irradiation, and the peak was decreased to around 20% of its original content after 180 minutes of irradiation. Thus, the degradation of ATZ could be affirmed by using the GC/MS method.

**Kinetics**

The photodegradation of ATZ was presumed to follow pseudo-first-order kinetics in the presence of the TiO2/Pt-TiO2 photocatalysts used in this study. The Langmuir–Hinshelwood kinetic model can be used to describe heterogeneous photocatalytic reactions. The regression curve for the natural logarithm of the ATZ concentration versus the irradiation time was approximately a straight line when using Equation (6). The apparent degradation rate (r) can thus be expressed as a first order with respect to the concentration of ATZ:

\[
\ln \frac{C}{C_0} = -kt, \tag{6}
\]

where \(k\) denotes the apparent first-order reaction rate constant \((\text{min}^{-1})\) for ATZ degradation, \(C_0\) was the initial ATZ concentration \((\text{ppm})\), and \(C\) was the concentration of ATZ at time \(t\). The apparent degradation rate constant \((k)\) can be determined from the slope of the regression line. The first-order rate constants are quantitatively presented in Table 2. The degradation rate constant obtained for the photo irradiation \((352 \text{ nm})\) of ATZ for 180 minutes without a photocatalyst was \(3.14 \times 10^{-6} \text{ min}^{-1}\), and only 1.61 ppm \((8\%)\) of the ATZ was decomposed. On the other hand, the degradation rate constant with TiO2 and Pt-TiO2 was \(3.772 \times 10^{-5} \text{ min}^{-1}\) and \(4.556 \times 10^{-5} \text{ min}^{-1}\), respectively (shown in Figure 6).

**UV-Vis spectrum interference from excess H2O2**

On the basis of ATZ photodegradation results using Pt-TiO2 and pure TiO2, two pathways for ATZ degradation catalyzed by TiO2 excited under UV \((352 \text{ nm})\) illumination have been proposed, as mentioned earlier. The main pathway involves the generation of electron and hole pairs (Equation (7)), and hence decomposition of ATZ that was adsorbed directly on the surface of the excited TiO2. The second pathway involves decomposition of ATZ via the attack of hydroxyl radicals formed from oxygen in the aqueous solution. In the literature, the proposed mechanisms for ATZ decomposition largely involve superoxide anion and hydroxyl radicals (Equations (8)–(10)). Hydrogen peroxide under visible light irradiation has been found to be effective for the degradation of ATZ owing to the generation of large quantities of hydroxyl radicals in solution. However, the synergistic effect of H2O2 was not clearly observed in this study because Pt-TiO2 directly decomposed 76% of the ATZ within 3 hours. The decomposition of H2O2 to O2 and H2O was faster than the formation of a Schottky barrier at the Pt-TiO2 interface, therefore no H2O2 absorbance was detected in the UV-Vis spectrum under the Pt-TiO2-catalyzed reaction. Conversely, the redox reaction of excess H2O2 may cause oxidation of Pt at Pt-TiO2, which would also increase the electron-hole pair recombination, and hence decrease the degradation efficiency of ATZ. In addition, a great H2O2 concentration can scavenge photocatalytically produced hydroxyl radicals as shown in Equations (4) and (5).

\[
\text{TiO}_2 + hv \rightarrow e^-_b + h^+_b \tag{7}
\]

\[
\text{O}_2 + e^-_b \rightarrow \text{O}_2^- \tag{8}
\]

\[
2\text{O}_2^- + 2\text{H}^+ \rightarrow 2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{9}
\]

\[
\text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH} + \text{O}_2 \tag{10}
\]

The absorbance of 0.05 M \((30 \text{ wt%})\) H2O2 occurred at a wavelength below 300 nm; hence, after illumination, the residual H2O2 may still interfere with the analysis of the absorbance of 20 ppm ATZ using UV-Vis scanning spectroscopy, as shown in Figure S4 (available with the online version of this paper). Although H2O2 can facilitate the generation of OH radicals, its UV-Vis spectrum

| Concentrations before and after 180 minutes' photodegradation of ATZ and the apparent degradation rate constants \((k)\) |
|---|---|---|
| C0 \((\text{ppm})\) | 20 | 20 | 20 |
| C \((\text{ppm})\) | 18.39 | 8.44 | 6.78 |
| \(k\) \((\text{min}^{-1}) \times 10^{-6}\) | 3.14 | 37.72 | 45.56 |
strongly interferes with the absorbance of ATZ in the UV region. Therefore, manganese dioxide (MnO₂) was used to catalyze the decomposition of excess H₂O₂ into water, oxygen, and heat, as shown in Equation (11).

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + \text{heat} \quad (11)
\]

5 mg of MnO₂ was added into each H₂O₂ solution, which contained 20 mL of ATZ aqueous solution to decompose H₂O₂ for 50 minutes. Without the treatment of the MnO₂ catalyst, the decomposition of H₂O₂ does not occur at an appreciable rate.

After removal of the excess H₂O₂ using MnO₂, the peaks for ATZ were observable, and the degradation of ATZ could be followed, as shown in Figure S5 (photodegradation of ATZ with H₂O₂ only). The degradation effect of the hydroxyl radicals generated by H₂O₂ can be clearly seen, and 28% of the ATZ was degraded after 3 h photo irradiation. Figure S6 shows ATZ degradation using both the TiO₂ photocatalyst and 0.05 M (30 wt%) H₂O₂. Again, it can be seen that the presence of H₂O₂ affected observation of the ATZ absorption peak using the UV-Vis spectrometer. After removing the absorbance of H₂O₂ by MnO₂, it was clear to see the ATZ degradation efficiency using TiO₂ reached 66% only. MnO₂ did not decompose ATZ in this study because the amount of MnO₂ was small and removed after 50 minutes reaction immediately, so the decomposition of ATZ by MnO₂ can be neglected (shown in Figure S7). (Figures S5–S7 are available with the online version of this paper.)

**CONCLUSIONS**

Photodegradation of ATZ under UV (352 nm) irradiation was shown to be assisted by the photocatalyst of either TiO₂ or Pt-TiO₂. The surface modification of TiO₂ by only 1 wt % Pt (i.e. Pt-TiO₂) could effectively enhance the photodegradation of ATZ under UV (352 nm) irradiation without adding H₂O₂ or aeration, and all the process could be effectively monitored and studied by UV-Vis spectroscopy. The degradation efficiency of ATZ reached 76% without aeration in 3 hours using Pt-TiO₂, which was at least 10% higher than that obtained using catalyst TiO₂ in the presence of H₂O₂. Adding H₂O₂ (or bubbling O₂) on the photocatalyst surface leads to the formation of hydroxyl radicals that facilitate ATZ degradation. However, any residual H₂O₂ whose UV-Vis spectrum absorbs strongly at a wavelength below 500 nm heavily interferes with the analysis of ATZ by UV-Vis spectroscopy. When H₂O₂ needs to be added, it was found that by treating the solution with small amounts of MnO₂, the H₂O₂ interference in the UV-Vis spectrum can then be resolved. In summary, Pt-TiO₂ as an effective photocatalyst has three main advantages: (i) the coated Pt can facilitate the generation of appropriate amounts of OH radicals, so it can also prevent the formation of over-oxidized TiO₂ [e.g. Ti (OOH)(OH)₃]; (ii) aeration was not needed; and (iii) the excited electrons were mainly uni-directionally transferred to the catalyst surface to avoid recombination of electron-hole pairs.

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