

Visible Light-Induced Photodegradation of Simazine in Aqueous TiO₂ Suspension

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ABSTRACT: The degradation of simazine (SMZ) in TiO₂ suspension with the presence of H₂O₂ was investigated under the irradiation of 420 nm lamps. This process could be optimized by adjusting TiO₂ dosage, initial concentration of H₂O₂, and the initial pH of the solution. The optimum TiO₂ dosage was found to be 0.1 g/L, and the highest SMZ decay rate was achieved with the initial H₂O₂ concentration at 4 mM. Overdose of H₂O₂ is found to be more critical in jeopardizing the SMZ decay than the overdose of TiO₂. A neutral initial pH level at 6.5 was found to be favorable for SMZ degradation. The presence of Cr(VI) significantly accelerated SMZ degradation in the TiO₂/H₂O₂/vis (visible light) process. In addition, 10 simazine derivatives were identified by liquid chromatography–mass spectrometry/mass spectrometry. It was suggested that dealkylation is the major pathway of SMZ photodecay in the TiO₂/H₂O₂/vis process. The final product was found to be ammeline.

1. INTRODUCTION

The extensive application of herbicides and pesticides as a routine practice to control weed growth has resulted in increasing public concerns in the past decades. A major concern with herbicides is the potential to leach into surface and groundwater systems that are used as drinking water sources. According to Hoffmann et al., groundwater contamination is the primary source of human contact with toxic or harmful chemicals which are coming out from more than 70% of the hazardous waste sites in the United States.¹ In Europe, as groundwater is one of the most important sources for drinking water, the protection of groundwater resources against contamination by surface-applied herbicides receives considerable attention in European legislation.² Simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine, SMZ) is a member of the triazine family of herbicides. Persistence of SMZ in soil and widespread use have led to its detection in rivers,³ groundwaters,⁴ soils,⁵ and even rainfall.⁶ It was reported that SMZ posed an adverse effect on aquatic macrophytes,⁷ and it also exerted a significant influence on pubertal development in female rats.⁸ SMZ is one of the five pesticides which needed to be controlled due to the frequency of their occurrence and the potential to pollute groundwater by the State Management Program (SMP) proposed by the U.S. Environmental Protection Agency (EPA).⁹ The use of SMZ has been banned in European Union states (EU directive 91/414/EEC).

Therefore, there is an urgent need to develop an effective and efficient treatment method for SMZ's removal from waters and soils of concern. TiO₂-based photocatalysis has been proven to be a promising technology for water treatment. However, the practical application of TiO₂ has been restrained by its optical properties in that TiO₂ is only sensitive to UV light.¹⁰ The sun can provide an abundance of photons; in which UV light only accounts for a small portion (~5%) of the sun spectrum in comparison to the visible region (~45%). Therefore, great efforts including photosensitization by dye, transition metal, and nonmetal doping have been dedicated to improving the

utility of TiO₂ by shifting its optical response from the UV to the visible spectral range.^{11–13} However, the process in preparing these photocatalysts is time-consuming and expensive, which may hamper the use of these technologies in practical applications. Therefore, H₂O₂-assisted and TiO₂-based photocatalysis has been proposed to work with the irradiation of visible light,^{14,15} while some studies have investigated the degradation of SMZ by ozonation,^{16,17} photocatalysis,¹⁸ Fenton's oxidation,^{9,17} UV photolysis,¹⁹ and biological methods.^{20,21} Until now, the information regarding the photocatalytic decay of SMZ under visible light, however, is still limited.

This study aims to investigate the photocatalytic decomposition of SMZ under visible range irradiation with the presence of H₂O₂. The performance of the TiO₂/H₂O₂/vis (visible light) process was evaluated in terms of SMZ degradation under different conditions, such as TiO₂ dosage, concentration of H₂O₂, initial pH levels, and the coexistence of different metal ions. The decay pathways of SMZ in TiO₂ suspension under the irradiation of visible light with the assistance of H₂O₂ were proposed as well.

2. METHODOLOGY

2.1. Chemicals. The probe simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine; ≥97%) was obtained from Supelco. The TiO₂ catalyst used was Degussa P25 (80% anatase and 20% rutile) with a Brunauer–Emmett–Teller (BET) surface area of 50 m²/g and a density of 3.85 g/cm³. H₂O₂ and K₂Cr₂O₇ were purchased from Riedel–deHaën Laboratory and Sigma–Aldrich, respectively. All of the chemicals and solvents were of analytical and HPLC grade, respectively, and used without further purification. For pH adjustment, 0.1 M sulfuric

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acid and 0.1 M sodium hydroxide were used. The water used in the preparation of solution was obtained from a Millipore Waters Milli-Q water purification system.

2.2. Photocatalytic Reaction. The photodegradation of SMZ was conducted in a Luzchem CCP-4 V photochemical reactor controlled by a computer. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination. Twelve low-pressure mercury lamps at 420 nm were installed in the photoreactor. The experimental installation and the emission spectra of the lamps were stated elsewhere.¹⁵ For the experiments involved with Cr^{6+} , $\text{K}_2\text{Cr}_2\text{O}_7$ was added into the suspension of TiO_2 before the photocatalytic reaction. Samples were withdrawn at a predetermined interval and filtered through a 0.2 μm poly(tetrafluoroethylene) (PTFE) membrane to keep the particles free from the solution prior to quantification. All experiments were carried out at room temperature (air-conditioned) at 23 °C in duplicate.

2.3. Chemical Analysis. Remaining SMZ after photo-reaction was determined by high-performance liquid chromatography (HPLC), which was comprised of a Waters 515 HPLC pump, Waters 2487 dual λ absorbance detector, and an Agilent Hypersil ODS column (5 μm , 0.46 cm \times 25 cm). The maximum adsorption wavelength (λ_{max}) was selected as 222 nm for SMZ. A mixture of 50% acetonitrile and 50% water was used as the mobile phase running at a flow rate of 1 mL/min. A five-point calibration curve was run for SMZ with the limit of quantification (LOQ) at 0.5 ng/L.

Identification of intermediates and end products was conducted by liquid chromatography–electrospray ionization–mass spectrometry (LC–ESI–MS) at positive modes with MS/MS analysis by ion traps (Finnigan ThermoQuest LCQ Duo) equipped with an ESI interface. The eluent (0.8 mL/min) was delivered by a gradient system from a Spectra SYSTEM P4000, coupled to a Spectra SYSTEM AS3000 Autosampler with a 20 mL injection loop, an Alltech (Alltech Associates Inc.) Hypersil ODS column (C18, 5 μm , 250 mm \times 4.6 mm), and a Spectra SYSTEM UV6000LP photodiode array UV detector. The gradient elution was carried out with a gradient of ammonia acetate (5 mM, pH 4.6) and acetonitrile from 95 to 15%, and from 5 to 85%, in 30 min, respectively. The MS capillary temperature was set at 250 °C with a voltage of 46 V and a spray voltage of 4.5 kV. The MS/MS tests were carried out using helium as the collision gas.

3. RESULTS AND DISCUSSION

3.1. SMZ Degradation in Various Systems. The degradation of SMZ was investigated under various conditions including the presence or absence of TiO_2 and/or H_2O_2 . As shown in Figure 1, no decay of SMZ was observed under visible light irradiation (420 nm) in the absence of TiO_2 either with or without the addition of H_2O_2 . This is because the combination of H_2O_2 and visible light generally cannot directly dissociate H_2O_2 into $\cdot\text{OH}$. The UV–visible light from twelve 420 nm lamps could not provide enough energy to break down the O–O bond of H_2O_2 . Such a dissociation can be obtained through absorption of UV light ($\lambda < 320$ nm). The adsorption of SMZ on the TiO_2 surface is less than 2% (data not shown). It was interesting to note that a small fraction (around 8%) of SMZ was decayed in 2 h by the TiO_2/vis process (420 nm). The slight SMZ removal in the TiO_2/vis (420 nm lamps) system is likely due to the production of a trace amount of e^- and h^+ (on the TiO_2 surface). The upper threshold wavelength that P25

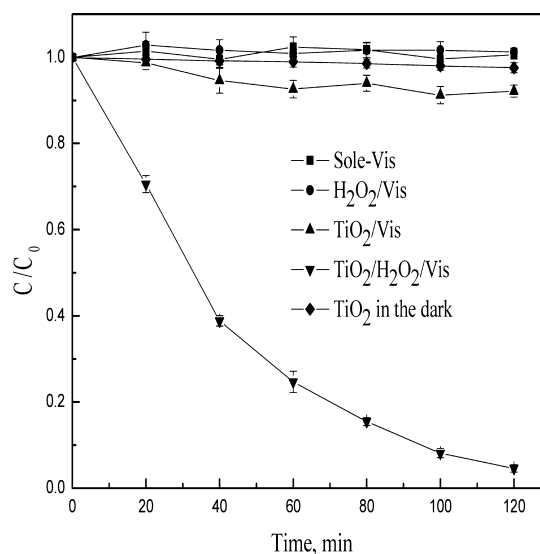


Figure 1. SMZ degradation under different reaction conditions: $[\text{SMZ}]_0 = 0.6$ mg/L, $[\text{H}_2\text{O}_2]_0 = 4$ mM, TiO_2 dosage is 0.2g/L, and initial pH is 6.5.

can absorb is 410 nm (data not shown), which is slightly overlapped with the emission spectra of the 420 nm lamps (a narrow-band monochromic lamp with a tailing down to 380 nm). The formation of an oxidizing agent on the surface of TiO_2 , i.e., a titanium peroxide complex due to the interaction between H_2O_2 and valence-unfilled Ti(IV) on the TiO_2 surface, was also reported previously.²² In the dark, no SMZ degradation was observed in an aqueous dispersion of TiO_2 and H_2O_2 (data not shown), indicating the presence of light is critical in such a process.

As also shown in Figure 1, the addition of 4 mM H_2O_2 to the TiO_2/vis process significantly improves the removal efficiency of SMZ from 8 to 95.4%. According to our previous studies,^{14,15} $\cdot\text{OH}$ plays a dominating role in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. In this process, it is believed that hydroxyl radicals originate from three sources: (1) The titanium peroxide complex formed on the TiO_2 surface extends the photo-response of TiO_2 from UV to the visible region, leading to the generation of visible-light-induced surface electrons which can be transferred from the surficial complexes to the conduction band of TiO_2 and the electrons on the conduction band of TiO_2 can then initiate the decomposition of H_2O_2 to produce hydroxyl radicals; (2) trace electrons generated on the conduction band of TiO_2 under the irradiation of 420 nm lamps initiate the decomposition of H_2O_2 to produce hydroxyl radicals; and (3) trace holes generated on the value band of TiO_2 under the irradiation of 420 nm lamps react with H_2O or OH^- to yield hydroxyl radicals. In general, the first one is likely the major source in generating $\cdot\text{OH}$ in this process.

3.2. Effect of TiO_2 Dosage. Proper dosage of TiO_2 as a photocatalyst is an important parameter for the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. In this study, photodecay rates of SMZ at different TiO_2 dosages (ranging from 0.05 to 0.80 g/L) were examined with an initial concentration of H_2O_2 at 4 mM and initial pH level at 6.5. The initial concentration of SMZ was kept at 0.06 mg/L. SMZ degradation was found to follow the pseudo-first-order kinetics with an R^2 value of 0.96 (see Figure 2). When TiO_2 dosage was below 0.1 g/L, SMZ decay accelerated remarkably with the increment of TiO_2 dosage. Above 0.1 g/L, however, the degradation rate of SMZ decreased gradually. This

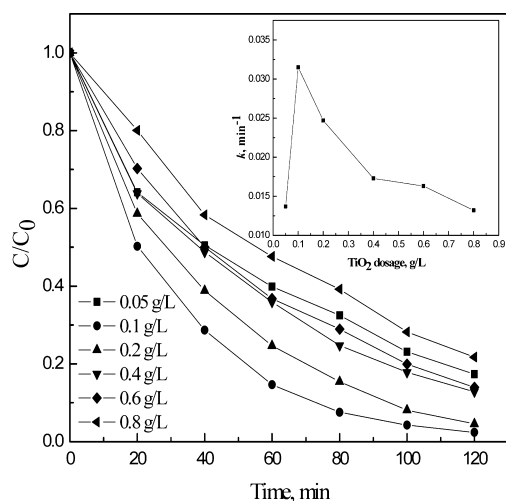


Figure 2. Effect of TiO_2 dosage on SMZ decay rate: $[\text{SMZ}]_0 = 0.6$ mg/L, $[\text{H}_2\text{O}_2]_0 = 4$ mM, and initial pH value is 6.5.

is possibly due to the increase in the opacity of the solution with the excessive amount of TiO_2 in the reaction, leading to light attenuation.²³ In practice, TiO_2 particles may act as a light filter that reduces the light penetration if overdosed. They reduce the incident light intensity by absorbing most of the photons and then giving out energy in other forms such as heat energy.²⁴ Therefore, an optimum dosage of TiO_2 was determined to be 0.1 g/L, which is a critical design parameter for a light-dependent process in real applications.

3.3. Effect of H_2O_2 Concentration. It is believed that hydroxyl radicals play a key role in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. The determination of an optimal concentration of H_2O_2 , the major source of hydroxyl radicals, thus is critical for practical application. The SMZ degradation at 0.2 g/L TiO_2 with H_2O_2 concentration varying from 0.5 to 6.0 mM was investigated as indicated in Figure 3.

At low H_2O_2 concentrations (below 4 mM), the pseudo-first-order degradation rate constant increased linearly with the $[\text{H}_2\text{O}_2]$, as shown in the inset of Figure 3. The increase of H_2O_2 concentration results in the generation of more titanium peroxide complex which is capable of absorbing visible light and

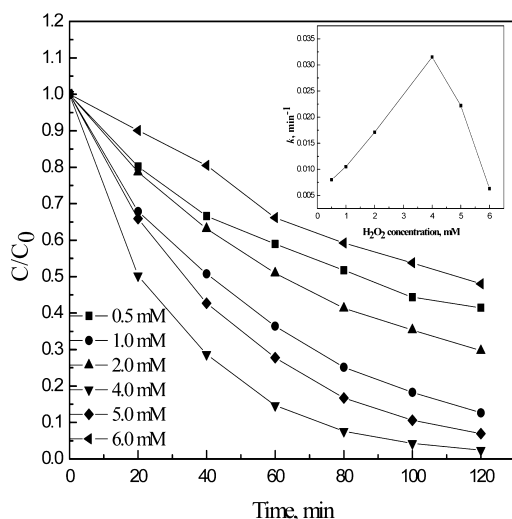
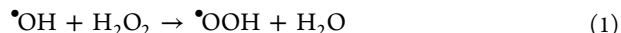


Figure 3. Effect of H_2O_2 concentration on SMZ decay rate: $[\text{SMZ}]_0 = 0.6$ mg/L, TiO_2 dosage is 0.1 g/L, and initial pH is 6.5.

subsequently produces more hydroxyl radicals. When the concentration of H_2O_2 was further increased, however, the rate constant decreased significantly likely due to the reaction between extra H_2O_2 and $\cdot\text{OH}$ (eq 1), leading to a negative effect on SMZ decay (the $\cdot\text{OOH}$ is a much weaker oxidant than that of $\cdot\text{OH}$). Therefore, the optimum concentration of H_2O_2 in the process was found to be 4 mM.



By comparing the marginal effect of the two parameters via normalizing the TiO_2 dosage and H_2O_2 concentration, the process can be divided into two sections, i.e., the ratio of $[\text{dosage}]/[\text{optimum dosage}]$ smaller and larger than unity (see Figure 4). It was interesting to note that the increment of

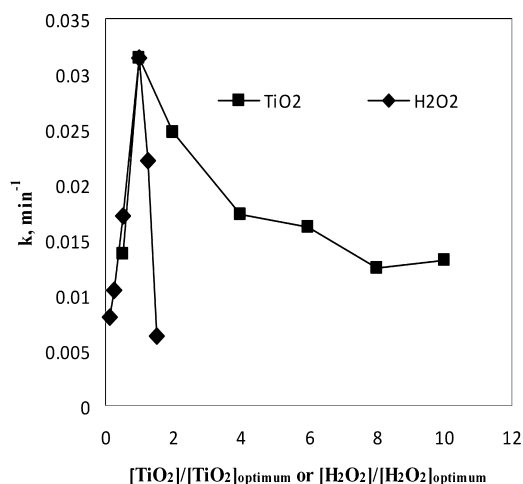


Figure 4. Comparison of the effects between TiO_2 dosage and H_2O_2 concentration on the SMZ decay rate.

$[\text{H}_2\text{O}_2]$ and TiO_2 dosage showed a similar influence on the SMZ decay rate when $[\text{dosage}]/[\text{optimum dosage}] < 1$, while $[\text{H}_2\text{O}_2]$ exhibited more negative effects on the performance of SMZ decay than that of TiO_2 dosage when $[\text{dosage}]/[\text{optimum dosage}] > 1$. This suggests the selection/design of the $[\text{H}_2\text{O}_2]$ in the process is more critical than that of the TiO_2 dosage, especially if the process is expected to be operated under an overdosed condition.

3.4. Effect of the Initial pH Level. Due to the amphoteric behavior of most semiconductor oxides, the pH level is believed to play an important role in reactions which take place on the surface of the semiconductor particle since it influences the surface charge properties of the photocatalyst. Tests have been conducted by varying the initial pH level from 2.5 to 10.5 on 0.06 mg/L SMZ degradation at 4 mM H_2O_2 and 0.1 g/L TiO_2 . The degradation of SMZ can be described by a pseudo-first-order kinetics at different pH levels, and the observed rate constants are summarized in Figure 5b. As demonstrated in Figure 5, the SMZ degradation rate was inhibited under acidic conditions ($\text{pH} = 2.5$ and 4), while at alkaline conditions ($\text{pH} \geq 8.0$), the degradation process was significantly retarded. The best SMZ degradation efficiency was obtained at initial pH level around 6.5.

In an alkaline medium, it was well-known that H_2O_2 is unstable and easily breaks down into water and oxygen, indicating less H_2O_2 molecules are available for the reactions that can produce hydroxyl radicals. In addition, the point of zero charge (PZC) of TiO_2 dispersion was reported to be

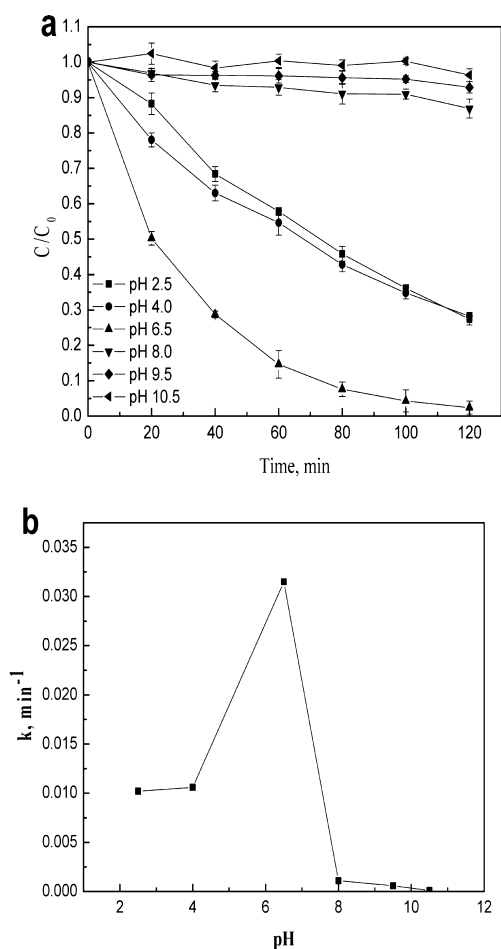


Figure 5. Effect of the initial pH level on the SMZ decay rate: $[SMZ]_0 = 0.6$ mg/L, $[H_2O_2]_0 = 4$ mM, and TiO_2 dosage is 0.1g/L.

around 6 and the pK_a of SMZ was reported to be 1.6.²⁵ SMZ carried a negative charge at the tested range of pH levels. Under basic conditions, repulsive forces between the negatively charged TiO_2 molecules and SMZ molecules retard the adsorption of SMZ on the surface of TiO_2 . This further inhibited the degradation of SMZ under basic conditions. Another minor reason is the dissolution of CO_2 from the air during mixing and the formation of the end product of SMZ decay (i.e., mineralization). The first and second pK_a of H_2CO_3 are 6.4 and 10.3, respectively; when the initial pH level is higher than 6.4, the predominant species in a carbonate system will either be bicarbonate or carbonate ions. These ions may compete with SMZ for hydroxyl radicals as radical scavengers.

Under acidic conditions, H_2O_2 exists in the form of $H_3O_2^+$ (eq 2) and TiO_2 carries positive charges since the PZC of TiO_2 is around 6. The positive charges on the surface of TiO_2 may hamper the adsorption of $H_3O_2^+$ on the surface of TiO_2 due to electrostatic repulsion, leading to the retardation of the formation of titanium peroxide complex and hence the decomposition of H_2O_2 on the surface of TiO_2 , which is essential for generating hydroxyl radicals. Another rationale is that the adsorbed protons could accelerate the degradation of titanium peroxide.^{26,27} Under acidic conditions, protons may be adsorbed by titanium peroxide. In theory, the decomposition of titanium peroxide by breaking the O–O bond will be facilitated by the adsorbed protons via the protonation of peroxide.²⁶



It is interesting to note that the pH level exerted more negative influence on SMZ degradation than that of linuron (LNR) under basic conditions.¹⁵ In our previous study, the removal efficiency of LNR was more than 60% after 2 h of reaction in the $TiO_2/H_2O_2/vis$ process at pH 9.0, while SMZ degradation almost stopped at pH 8.0 in the same process. On the other hand, it was observed that LNR decay was extremely inhibited (around 10% removal after 2 h) at pH 2.0 in the previous study. In this study, around 70% removal of SMZ was achieved after 2 h of reaction at pH 2.5. This can be rationalized by the different pK_a values of these two compounds. The pK_a of SMZ was reported to be 1.6,²⁵ and the pK_a of LNR is between 4.3 and 5.5.³ Under basic conditions, the lower pK_a of SMZ led to SMZ carrying more negative charges than LNR. Therefore, repulsive forces between the negatively charged TiO_2 and SMZ molecules are stronger than that of the negatively charged TiO_2 and LNR molecules. At acidic pH level (around 2), both LNR and TiO_2 were positively charged while the latter was slightly (negatively) charged. Thus, SMZ can be easily adsorbed on the surface of TiO_2 while repulsive forces between positively charged LNR and TiO_2 hamper the adsorption of LNR on the surface of TiO_2 .

3.5. Effect of Chromium(VI). Chromium(VI) is a common toxic metal frequently detected in wastewater from industrial effluents. It has been reported that the coexistence of TiO_2 , Cr(VI), and 4-chlorophenol (4-CP) in water allows efficient Cr(VI) reduction and 4-chlorophenol oxidation simultaneously under the irradiation of visible light.^{28–30} The possible mechanism was proposed as follows: Cr(VI) takes the electrons that are generated inside the TiO_2 (oxygen vacancies or trapping sites) and pass them on to the TiO_2 surface under visible light irradiation, while 4-CP is oxidized by holes with continuous reduction of Cr(VI). In addition, the adsorption of Cr(VI) ions on the surface of TiO_2 makes the TiO_2 more photosensitive to visible light, which is believed to play an important role in the degradation of 4-CP.²⁹ Therefore, the simultaneous eradication of both Cr(VI) and SMZ was also investigated in TiO_2 suspension under visible light. It was interesting to note that the degradation of SMZ was not observed in the presence of both Cr(VI) and TiO_2 under visible light irradiation as compared to that from previous studies. This is likely because SMZ (without having the acid and/or phenolic groups in its molecule) cannot adsorb easily on TiO_2 , which weakens SMZ's adsorption competition with Cr(VI) to the adsorption site on TiO_2 . Similar phenomenon was observed with diethyl phosphoramidate.²⁸ The presence of Cr(VI), however, remarkably accelerated the degradation of SMZ in the $TiO_2/H_2O_2/vis$ process (Figure 6). The removal efficiency of SMZ was nearly 100% after 20 min in the presence of 0.5 mM Cr(VI), while it took 120 min to achieve a similar efficiency without the Cr(VI). It was also observed that the removal of Cr(VI) was insignificant in this case (data not shown), implying the role of Cr(VI) is a photosensitizer for TiO_2 instead of an electron acceptor. At pH 6, $Cr_2O_7^{2-}$ can be more easily adsorbed on the surface of TiO_2 than H_2O_2 (positively charged), leading to a TiO_2 surface mainly sensitized by Cr(VI) instead of titanium peroxide ($TiOOH$). Thus, Cr(VI) ions adsorbed on the surface of TiO_2 allowing TiO_2 to become more photosensitive to visible light and then generating more electrons. The electrons, then, induce H_2O_2 decomposition to produce hydroxyl radicals. The result

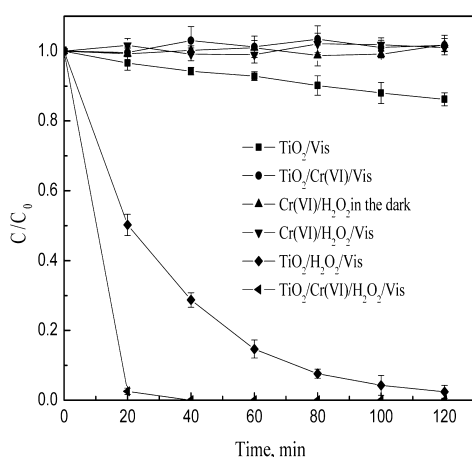


Figure 6. Effect of Cr(VI) on SMZ degradation: $[\text{SMZ}]_0 = 0.6 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$, $[\text{Cr(VI)}]_0 = 0.5 \text{ mM}$, TiO_2 dosage is 0.1 g/L , and initial pH is 6.5.

suggests that the accelerating effect of the Cr(VI)-sensitized TiO_2 surface can absorb more photons than a TiO_2 surface complexed with titanium peroxide (TiOOH) under the irradiation of 420 nm lamps, which allows the former to generate more electrons for the initiation of H_2O_2 decomposition.

3.6. Decay Pathways of SMZ in $\text{TiO}_2/\text{H}_2\text{O}_2/\text{Vis}$ System.

During SMZ degradation by the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process, 10 intermediates were identified by LC-MS/MS (see Table 1), among which the identity of compounds 5 and 7 was confirmed by comparing their retention time and mass fragmentation patterns to that of the authentic compounds (2-chloro-4-(ethylamino)-6-amino-s-triazine and 2-hydroxy-4-(ethylamino)-6-amino-s-triazine). The formation/degradation profiles of intermediates/products were organized and shown in Figure 7. In the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process, the dominating oxidant is hydroxyl radicals ($\cdot\text{OH}$) as reported in our previous study.¹⁵ Hydroxyl radicals initiate the decay of SMZ through alkyl oxidation (alkylamino side chain oxidation), dealkylation (alkyl side chain cleavage), and/or dechlorination (hydroxylation at the chlorine site), leading to the generation of the corresponding intermediates. Dealkylation might occur by the abstraction of H from the secondary C of the ethylamino side chain producing a free radical, which subsequently produces various intermediates. Dechlorination–hydroxylation could be initiated by the nucleophilic attack of $\cdot\text{OH}$ on the s-triazine ring at the C–Cl position, resulting in an oxidation of the aromatic heterocyclic ring of SMZ, while hydroxylation occurred simultaneously, so that the chlorine atom was substituted by a hydroxyl group. Hence, the generation of various hydroxylated s-triazines was also observed in the solution.

As indicated in Figure 7, compounds 1 and 3 were first detected and quickly reached their peak concentrations, indicating that alkyl oxidation first occurred during the reaction. At the same time, compound 2 was also detected but at a much lower concentration than compounds 1 and 3, suggesting dechlorination–hydroxylation is a minor decay pathway which also occurred at the initial stage of the reaction.

On the basis of the results of the profile analysis, the possible decay pathways of SMZ by the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process were proposed as shown in Figure 8. At the initial stage, the attack of $\cdot\text{OH}$ on the secondary C of one ethylamino side chain resulted in the generation of compound 3. The attack on the secondary

Table 1. Intermediates and Products Detected by LC-MS/MS during SMZ Degradation by the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{Vis}$ Process

Product ID	ESI(+)/MS m/z	ESI(+)/MS ² m/z	Retention Time (min)	Proposed Structure
1	234, 236	234, 156	13.75	
2	184	184, 155, 126	4.06	
3	216, 218	216, 188, 174, 146, 132, 110	11.90	
4	198	198, 180, 154, 134, 128, 110	7.36	
5	174, 176	174, 146, 132, 110, 104	8.73	
6	212	212, 170, 128, 86	7.51	
7	156	156, 128, 114, 96, 86	5.78	
8	170	170, 128, 86	6.72	
9	146, 148	146, 110, 104, 79, 68	6.26	
10	128	128, 86	7.85	

C of both ethylamino side chains produced compound 1. At the same time, dechlorination–hydroxylation of SMZ gave compound 2. As shown in Figure 7, the yields of compounds 1 and 3 are much higher than that of compound 2. The electron-rich positions are more susceptible to the attack of hydroxyl radicals as an electrophilic reagent, leading to alkyl oxidation and subsequent dealkylation being the major decay pathways due to electron-donating properties of the alkyl substituent group. The attack of hydroxyl radicals on the secondary C of the ethylamino side chain of compound 2 generated compound 4. Compound 4 may also originate from the dechlorination–hydroxylation of compound 3. Compound 6 is also believed to come from two sources. One is the further attack of hydroxyl radicals on the secondary C of the ethylamino side chain of compound 4, and another is the further oxidation of compound 1. The dealkylation of compound 3 yielded compound 5. Compound 5 also has two

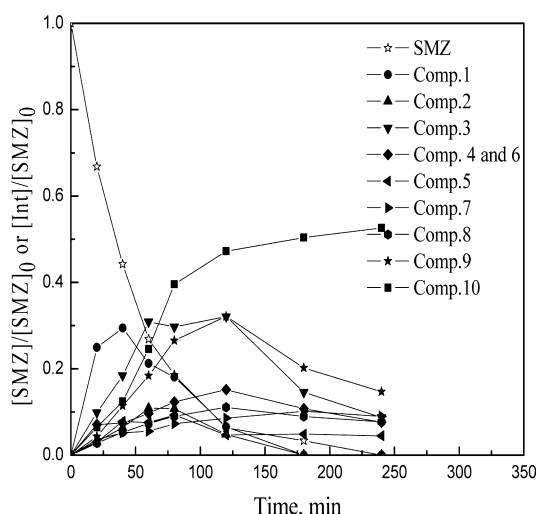


Figure 7. Evolution profile of SMZ and intermediates in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ system: $[\text{SMZ}]_0 = 5 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 4 \text{ mM}$, TiO_2 dosage is 0.1 g/L , and initial pH is 6.5.

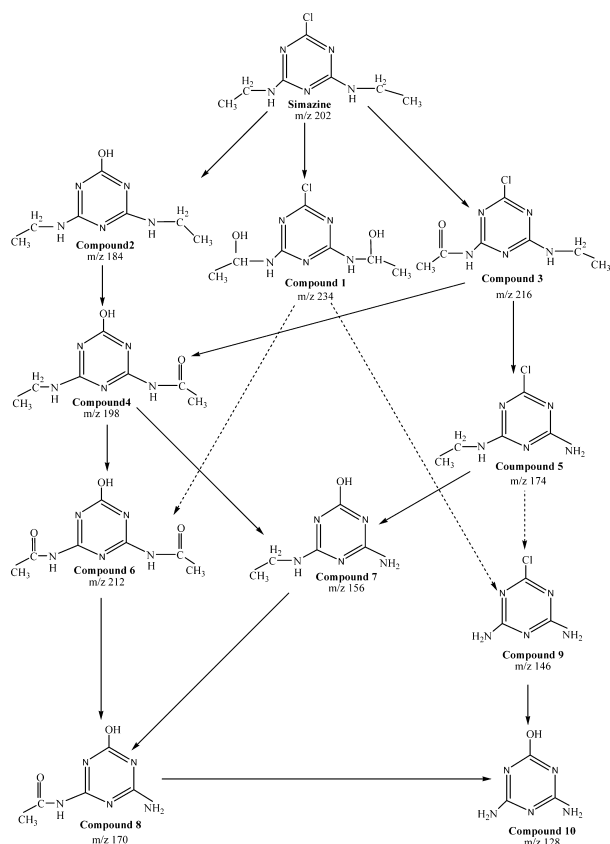


Figure 8. Proposed decay pathways of SMZ by the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process.

decay pathways; one is dechlorination–hydroxylation producing compound 7, and the other is dealkylation generating compound 9. They were confirmed by conducting an individual test on the decomposition of compound 5 in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. However, it is interesting to note that a specific intermediate (2-chloro-4-acetamido-6-amino-s-triazine, CAAT) was detected during the direct degradation of compound 5 but escaped from being detected in SMZ decay in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. This is likely because CAAT can quickly be

transformed into compound 9 and cannot accumulate to a detectable level in the solution. Another possible source of compound 9 is coming from compound 1. The lack of the detailed pathway from compound 1 to 9 in this process was due to low (undetectable) intermediate concentrations, where the chance to have a direct transformation from compound 1 to 9 (i.e., double dealkylation occurring simultaneously on both amino side chains) is believed to be low. Compound 7 may also derive from the dealkylation of compound 4. The dealkylation of compound 6 and oxidation of compound 7 gave rise to compound 8. A high level of compound 10 was observed and accumulated at the end of the process, as indicated in Figure 7, which originated from the dechlorination–hydroxylation of compound 9 and the dealkylation of compound 8. Compound 10 (ammeline) is believed to be the final product during SMZ degradation by the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. Compound 10 was generated from dechlorination–hydroxylation. From a remediation point of view, the dechlorination is considered to be the critical step for detoxification since the chlorinated products are generally considered as toxic as SMZ itself.³¹ Ammeline can be further transformed to cyanuric acid, which was not observed in this study. It has been reported that mineralization of triazine compounds can be achieved by the hydrolysis of cyanuric acid over Al_2O_3 at the temperature ranging from 240 to 450 °C³² and in supercritical water.³³ The biologically based degradation of cyanuric acid using *Pseudomonas* sp. bacteria has also been reported.³⁴ In addition, total organic carbon (TOC) removal was found to be insignificant after 4 h of degradation reaction since the cleavage of the heterocycle ring of SMZ was not achieved.

4. CONCLUSION

The photodegradation of SMZ under different conditions was investigated. No SMZ decay was observed under visible light irradiation (420 nm) in the absence of TiO_2 with and without the addition of H_2O_2 . In the process of TiO_2/vis (420 nm), SMZ removal efficiency is around 8% in 2 h. The addition of 2 mM H_2O_2 to the above process however significantly improved its rate to more than 95%.

The process is optimized by examining the reaction rate under various reaction conditions. The decay rate of SMZ, generally, increased with the increment of TiO_2 dosage. However, the SMZ degradation could be gradually retarded when TiO_2 was overdosed (above 0.1 g/L) due to the reduction of light penetration. The optimum concentration of H_2O_2 in the system was found to be 4 mM. The highest SMZ degradation efficiency was obtained at the initial pH level around 6.5. The degradation rates of SMZ were reduced at acidic conditions and extremely retarded under alkaline conditions. The presence of Cr(VI) drastically accelerated SMZ degradation in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process. More than 97% removal of SMZ was achieved in 20 min in the presence of 0.5 mM Cr(VI) ; otherwise, it would take 120 min to achieve the same.

The decay pathways of SMZ in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process were also proposed. Chlorinated intermediates were quantified at much higher concentrations than dechlorinated intermediates, suggesting that dealkylation was the major decay pathway in the process. Since there was no ring cleavage observed and compound 10 (2-hydroxy-4,6-diamino-s-triazine, ammeline) was found to accumulate in the solution, it was suggested that compound 10 should be the final product of SMZ degradation in the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{vis}$ process.

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Notes

The authors declare no competing financial interest.

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