

Removal of Simazine in a UV/TiO₂ Heterogeneous System

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The degradation of simazine by photocatalytic oxidation in a TiO₂ suspension was studied. The influence of various parameters such as wavelength sources, light intensity, TiO₂ dosage, and initial pH has been investigated, and the optimum conditions for the degradation of simazine have been identified. The photocatalytic degradation of simazine was observed to follow a pseudo-first-order reaction. The overdose of light intensity and photocatalyst does not always guarantee a beneficial effect on the photocatalytic reaction, and the optimum TiO₂ dosage was found to be 0.1 g/L in this study. The optimum pH value is 9.0 for the photocatalytic degradation of simazine, whereas extremely acidic and alkaline conditions inhibit photocatalytic efficiency. Simazine can be fully destroyed, but ring-opening and mineralization are not observed in this system. In addition, seven simazine derivatives (CEAT, OEET, CAAT, ODET, OEAT, OAAT, OOOT) were detected by LC-ESI/MS. It is suggested that dealkylation is the major pathway of simazine photodecay in UV/TiO₂ systems. The final product was found to be cyanuric acid.

KEYWORDS: Simazine; TiO₂ suspension; photocatalytic oxidation; light intensity mechanism

INTRODUCTION

Simazine (6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine, SIM), a chloro-*s*-triazine herbicide, is widely used to control broad-leaf and grassy weeds in crop fields and on noncrop areas such as farm ponds and fish hatcheries by inhibiting the normal photosynthesis of plants (1). This herbicide is moderately persistent (up to 149 days) in the soil, and its extensive use has led to traces of simazine in rivers (2), groundwaters (3), soils (4), and even rainfall (5). Simazine is suspected as a possible endocrine disrupter and human carcinogen (6) and is believed to have adverse effects on algal flora in soil and water (7). It is one of five pesticides that were controlled due to the frequency of their occurrence and the potential to contaminate groundwater by the State Management Program (SMP) proposed by the U.S. EPA (8). In Europe, the maximum contaminant level (MCL) for simazine has been set at 0.1 µg/L in drinking water. Furthermore, simazine is totally banned in some European countries such as Norway (9).

Therefore, there is a need to develop effective treatment methods for removing and detoxifying this herbicide from the waters of concern. Some investigations have been conducted using absorption by granular activated carbon (GAC) (10), ozonation (11–13), Fenton's oxidation (9) UV photolysis, UV/H₂O₂ (14), photocatalytic oxidation (15, 16), and biological methods (17–19).

The use of TiO₂ as a medium for environmental cleanup of organic pollutants through the activation of the photo-oxidation has received much attention in the past decade due to its low cost, photostability, and low toxicity to humans and the

environment (20). The phototransformation of organic compounds by UV/TiO₂ is presumably initiated by the hydroxyl radical (*OH), which is formed by reacting electron holes on the excited TiO₂ surface and OH[−] (or H₂O) from the surrounding water (21). Until now the investigation of the photocatalytic oxidation of simazine has been focused on reaction kinetics. Detailed information related to the parameters involved in this process and reaction mechanism is yet limited.

In this study, the photodegradation of simazine (SIM) was examined in TiO₂ suspension activated by UV at different wavelengths. In addition, the effects of light intensity, TiO₂ dosage, and pH level on the decay rate of SIM were also investigated. Furthermore, the intermediates and end products in the studied process were identified, and a systematic decay pathway was proposed accordingly.

MATERIALS AND METHODS

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. Simazine (≥97%) was obtained from Supelco. The intermediates 6-chloro-*N*-ethyl[1, 3, 5]triazine-2, 4-diamine (CEAT) and 6-hydroxy-2-amino-4-ethyl-amino-1,3,5-triazine (OEAT) were purchased from RdH Laborchemikalien GmbH & Co. For other intermediates for which standards are unavailable, their concentration was quantified in terms of ion intensity relative to initial simazine concentration for comparison.

All chemicals were of analytical grade, and all solvents were of HPLC grade and used without further purification. The water used in the preparation of all solutions was generated from a Millipore Waters Milli-Q water purification system. For pH adjustment, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used. All experiments were carried out at room temperature

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(air-conditioned) at $23 \pm 2^\circ\text{C}$ in duplicate, and the error was $<1.0\%$.

The photodegradation of SIM was conducted in a Rayonet RPR-200 photochemical reactor manufactured by the Southern New England Ultraviolet Co. To ensure a thorough mixing, 150 mL of reaction solution was dispensed into a 300 mL quartz cylinder with mechanical stirring throughout the illumination. The initial concentration of SIM in experiments was 0.025 mM unless stated otherwise. Samples were withdrawn at a predetermined time interval and were filtered through a $0.45\ \mu\text{m}$ membrane to keep the TiO_2 free from the solution before quantification. Control experiments without photocatalyst and UV illumination were also performed for comparison.

The concentration of a probe compound and the intermediates that remained in the treated samples was analyzed by liquid chromatography (LC). The LC system comprised a 515 HPLC pump, a $20\ \mu\text{L}$ loop injector port, an Econosphere C18 ($5\ \mu\text{m}$, $0.46 \times 25\ \text{cm}$) column, and a UV detector. The maximum absorption wavelength (λ_{max}) of SIM was determined and selected as 222 nm. A mixture of 50% acetonitrile and 50% water was used as the mobile phase running at a flow rate of 1 mL/min. In addition, a five-point calibration curve was run for SIM with the limit of quantification (LOQ) at 0.5 ng/L. Total organic carbon was determined by a Total Organic Carbon Analyzer (TOC-5000A, Shimadzu).

Identification of intermediates and end products was conducted by LC-ESI/MS at positive modes and MS/MS analysis, utilizing an ion trap (Finnigan ThermoQuest LCQ Duo) equipped with an ESI interface. The eluent (1 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, $5\ \mu\text{m}$, $250\ \text{mm} \times 4.6\ \text{mm}$), 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), acetonitrile, and water from 95 to 0%, from 5 to 89%, and from 0 to 11% in 15 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 (30 and 100% collision energy corresponding to 5 V from peak to peak).

RESULTS AND DISCUSSION

Comparison of Quantum Yields for both Direct Photolysis and Photocatalysis. The degradation efficiency of SIM by both direct photolysis and photocatalysis was investigated at three selected wavelengths (254, 300, and 350 nm), and their corresponding reaction rates are shown in Figure 1.

Using eight lamps throughout, the difference in reaction rates showed that photodecay of SIM was most effective by sole UV at 254 nm, whereas the use of longer wavelengths caused a slower decay in both sole UV and UV/ TiO_2 systems. The decay rate of SIM in UV/ TiO_2 system is much faster than that in a sole UV system at wavelengths of 300 and 350 nm (Figure 1). However, it was interesting to note that, under 254 nm UV illumination, better degradation performance of SIM was achieved by using direct photolysis instead of photocatalysis. This was probably due to light attenuation by the fine TiO_2 particles in the solution. As TiO_2 particles act as a light filter (reducing the light penetration), they reduce the incident light intensity by absorbing most of the photons and then giving out energy in other forms such as heat energy, phosphorescence, and fluorescence (22). Because the amounts of photons that can be generated at each specific wavelength are different, quantum yield could be a better and more precise parameter to quantify the photolytic efficiency.

The decay quantum yield of SIM at different wavelengths could be manipulated by eq with the inclusion of rate constants

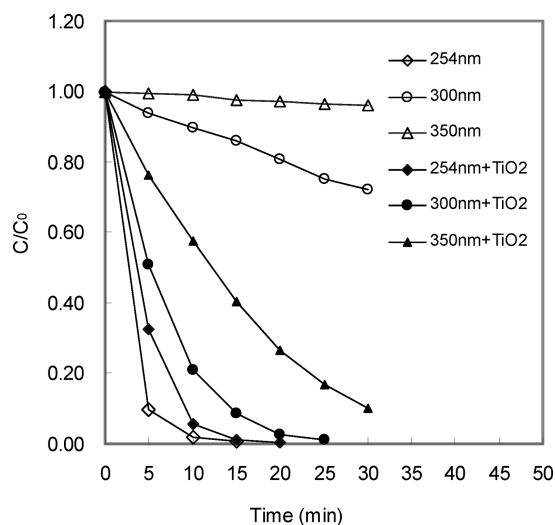


Figure 1. Pseudo-first-order decay reaction of simazine for both direct photolysis and photocatalysis. Eight UV lamps were used, initial simazine concentration was $2.5 \times 10^{-5}\ \text{M}$, TiO_2 dosage was 0.1 g/L, and initial pH was 5.6.

(from Figure 1), molar absorptivity, and light intensities, and the results are summarized in Table 1.

$$\phi = \frac{k}{2.303I_{0,\lambda}\epsilon_{D,\lambda}l} \quad (1)$$

The photocatalysis processes could obtain higher quantum yield than direct photolysis (about 15 times) except for the case of 254 nm (Table 2). For photocatalysis processes, higher quantum yield efficiencies were observed at 300 and 350 nm than at 254 nm, which suggests the electron–hole excitation of TiO_2 is more sensitive at these wavelengths. Furthermore, higher quantum yields were observed at 300 nm than at 350 nm, which is rationalized by the quantum theory that the shorter UV wavelengths result in the stronger radiation energy. Because the highest quantum yield was achieved at 300 nm, it was adopted as the exclusive light source for the remaining study.

Effect of TiO_2 Dosages. The amount of photocatalyst is an important parameter that can affect the photocatalytic degradation rate of organic compounds, so the effect of different TiO_2 dosages on SIM decay rate was also investigated. The initial concentration of simazine was kept at 0.025 mM, and different TiO_2 dosages were added to the solution with continuous mechanical stirring under UV illumination at 300 nm (Figure 2).

A blank test has been conducted in a dark (without UV illumination) TiO_2 system for comparison, in which very little SIM loss (around 5%) was observed after 30 min, implying light source was essential for the reaction. The loss of SIM apparently is due to adsorption on the TiO_2 surface, and no further adsorption was observed after 2 h. Therefore, the absorption effect will be neglected in this study.

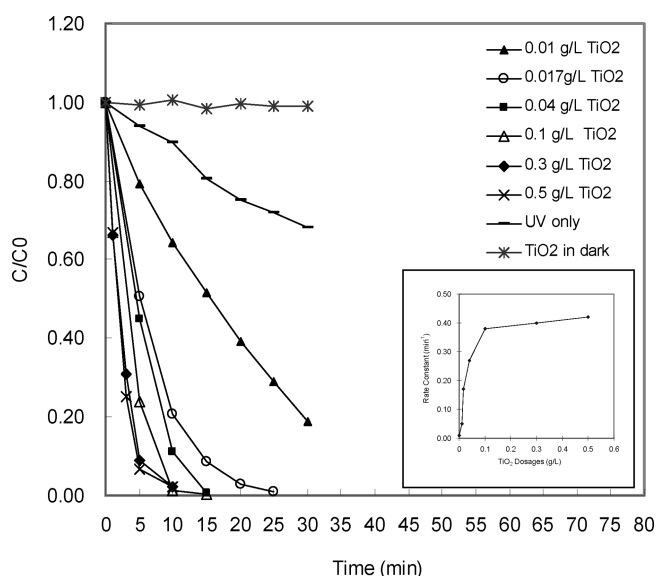
All of the degradations follow the pseudo-first-order decay with an r^2 above 0.98. The photocatalytic degradation rate of SIM was not a simple linear correlation with the $[\text{TiO}_2]$ doses as shown in the inset of Figure 2. At lower TiO_2 dosages, the pseudo-first-order rate constants increased significantly (and linearly) with the increment of TiO_2 doses. As the TiO_2 doses increased above $0.1\ \text{g L}^{-1}$, however, the decay rate constants of SIM increased at a much slower rate, indicating that the process was gradually retarded. This is possibly due to the increase in the opacity of the solution with an excessive amount of TiO_2 in the reaction, causing a reduction in the penetration of light

Table 1. Identification of Degradation Intermediates of Simazine

| abbreviation | compound | RT (min) | [M + H ⁺] | detected |
|--------------|---|----------|-----------------------|----------|
| CEET | 6-chloro- <i>N,N</i> -diethyl-1,3,5-triazine-2,4-diamine | 13.68 | 202 | yes |
| CEAT | 6-chloro- <i>N</i> -ethyl-[1,3,5]triazine-2, 4-diamine | 9.44 | 174 | yes |
| CAAT | 6-chloro-[1,3,5]triazine-2,4-diamine | 5.59 | 146 | yes |
| ODET | 6-hydroxy-2-acetamido-4-(ethylamino)-1,3,5-triazine | 8.03 | 198 | yes |
| OEET | 6-hydroxy- <i>N,N</i> -diethyl-1,3,5-triazine-2,4-diamine | 8.86 | 184 | yes |
| OEAT | 6-hydroxy-2-amino-4-ethylamino-1,3,5-triazine | 6.65 | 156 | yes |
| OAAT | 6-hydroxy-2,4-diamino-1,3,5-triazine | 7.70 | 128 | yes |
| OOAT | 2,6-dihydroxy-4-amino-1,3,5-triazine | | 129 | no |
| OOOT | 2,4,6-trihydroxy-1,3,5-triazine | 11.39 | 130 | yes |

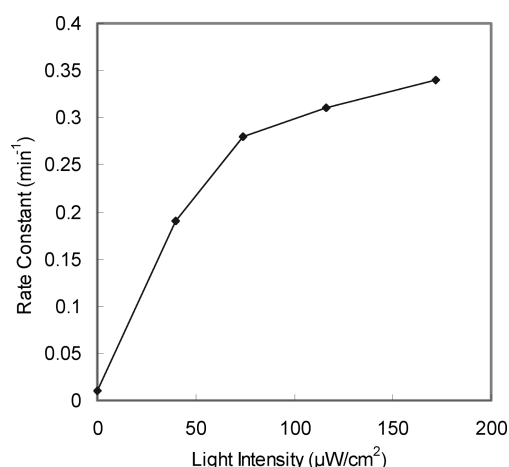
Table 2. Comparison of Quantum Yield for Direct Photolysis and Photocatalysis at Different UV Wavelengths^a

| | UV wavelength, λ_i | | |
|---|----------------------------|-----------------------|------------------------|
| | 254 nm | 300 nm | 350 nm |
| photointensity, I (einstein L ⁻¹ s ⁻¹) | 1.2×10^{-5} | 5.6×10^{-6} | 2.488×10^{-5} |
| molar absorptivity, $\epsilon\lambda_i$ (cm ⁻¹ M ⁻¹) | 2760 | 43.96 | 20.17 |
| direct photolysis rate constant, k_1 (s ⁻¹) | 6.06×10^{-3} | 1.83×10^{-4} | 2.33×10^{-5} |
| direct photolysis quantum yield, ϕ_1 | 0.013 | 0.053 | 0.0033 |
| photocatalysis rate constant, k_2 (s ⁻¹) | 4.55×10^{-3} | 2.96×10^{-3} | 1.17×10^{-3} |
| photocatalysis quantum yield, ϕ_2 | 0.010 | 0.87 | 0.16 |

^a TiO₂ dosage is 0.1 g/L, and initial pH is 5.6.**Figure 2.** Comparison of photodecay rate of simazine at various TiO₂ dosages. (Inset) Kinetic constants of simazine photodegradation at various TiO₂ in UV/TiO₂ system. Eight UV lamps were used at 300 nm, initial simazine concentration was 2.5×10^{-5} M, and initial pH was 5.6.

and a slowing of further rate increments (23). In summary, an unlimited increase in photocatalyst is not always favorable to the photoreaction. An optimum dose of photocatalyst (e.g., 0.1 g L⁻¹ in this case) is surely one of the critical design parameters for such a slurry system in any practical application.

Effect of Light Intensity. A series of tests by increasing the light intensity from 40 to 172 μ W/cm² (i.e., from two to eight lamps) were carried out (Figure 3). In general, the photocatalytic degradation rate was found to depend on the light intensity. At higher light intensity, more photons enter the reaction solution, leading to the production of more positive holes (h⁺) and then more hydroxyl radicals, resulting in faster photocatalytic oxidation rates of SIM. Similar results were reported by Zhang et al. (24).

**Figure 3.** Effect of light intensity on the photodecay rate constant. Initial simazine concentration was 2.5×10^{-5} M, initial pH was 5.6, and TiO₂ dosage was 0.06 g/L.

However, the photocatalytic degradation rate of simazine did not show a linear correlation with the light intensity. As the light intensity increased above 60 μ W/cm², the increase of reaction rate declined gradually. This is likely due to the change of photon/SIM (and photon/TiO₂) ratios from an optical dilute to an optical dense system. In the former system (with lower ratios), most of the photons are absorbed by SIM/TiO₂, whereas in the latter system photons can be overdosed (due to higher ratios) and some of them may escape from reacting with SIM molecules or TiO₂, so that the light performance (i.e., the reaction rate) cannot increase linearly with the increment of light intensity. In addition, intermediate competition in the reaction solution might partly contribute to such an observation. Under higher light intensity, the generation rate of intermediates was faster, so that more intermediates were produced within the same period of reaction time. These intermediates are organic compounds that may possess a photon absorption nature similar to that of simazine, so they would compete with simazine for the photons and/or hydroxyl radicals, resulting in a retardation of the simazine degradation. An optimal light intensity of 60 μ W/cm² was therefore chosen in the study for its better cost-effectiveness.

Effect of Initial pH. The pH levels of the solution could be another critical factor affecting the UV-catalytic process. A study on the effect of initial pH levels on the decay rate of SIM was therefore conducted at a range from 2.78 to 11.65 (Figure 4). It was observed that the decay rate largely increased with pH levels. This was likely due to the increase of hydroxide ions (OH⁻) in the solution, which induce the generation of more hydroxyl free radicals (OH) in the electron-hole pairs of TiO₂. Because the hydroxyl free radical is the major oxidizing species in the

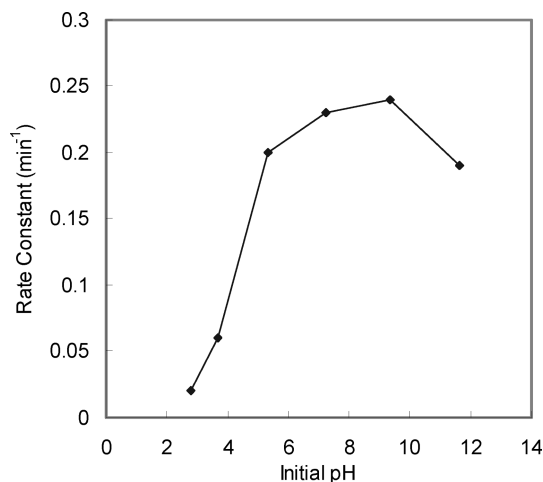


Figure 4. Effect of pH values on the photodecay rate of simazine. Eight UV lamps at 300 nm were used, initial simazine concentration was 2.5×10^{-5} M, and TiO_2 dosage was 0.06 g/L.

photocatalytic process, the decay rate of SIM tends to be accelerated in the alkaline environment.

The best SIM degradation efficiency was obtained at initial pH around 9, whereas the photocatalytic reaction was retarded under strong acidic and extreme basic (pH > 11) conditions.

The point of zero charge (amphoteric) of TiO_2 dispersion was reported to be around 6.8 (25), so TiO_2 is negatively or positively charged when the pH level is above or below this level. The optimum initial pH was found in the slightly basic environment at pH around 9. Under these circumstances, TiO_2 would become negatively charged on the surface, which enhances the transportation of holes to the surface, which react with OH^- and/or H_2O to generate more hydroxyl free radicals and then enhance the photocatalytic degradation reaction (26).

The performance of the photocatalytic degradation was retarded when the initial pH was at extreme base environment (initial pH ~11). This can possibly be due to the accumulation of surface negative charges on TiO_2 surfaces at high pH value, leading to a supplementary repulsive phenomenon between TiO_2 particles and SIM molecules and then a lower photocatalytic degradation rate (27, 28) because the $\text{p}K_a$ of SIM was reported to be 1.6 (9).

Reaction Mechanism. Upon the degradation of SIM by UV/ TiO_2 , eight intermediates were identified by LC-MS (see Table 1) and their formation/degradation profiles were organized and are shown in Figure 5. In the UV/ TiO_2 system, the major oxidant is the $\cdot\text{OH}$ because $\text{HOO}\cdot$ and its conjugate base $\text{O}_2^{\cdot-}$ are much less reactive than hydroxyl radicals. The presence of $\cdot\text{OH}$ initiates the decay of simazine through alkyl oxidation (alkylamino side chain oxidation), dealkylation (alkylic side chain cleavage), and/or dechlorination (hydroxylation at the chlorine site) and generates 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 $\cdot\text{OH}$ attack of the *s*-triazine ring at the C–Cl position, resulting in an oxidation of the aromatic heterocyclic ring of simazine, whereas hydroxylation occurred simultaneously, so that the chlorine atom was substituted by a hydroxyl group. Hence, various hydroxylated *s*-triazines also formed in the solution.

CEAT and CAAT were first detected and quickly reached their peak concentrations, indicating that dealkylation first occurred in the reaction (Figure 5). At the same time, OEET and OEAT were also detected but at much lower concentration than CEAT and

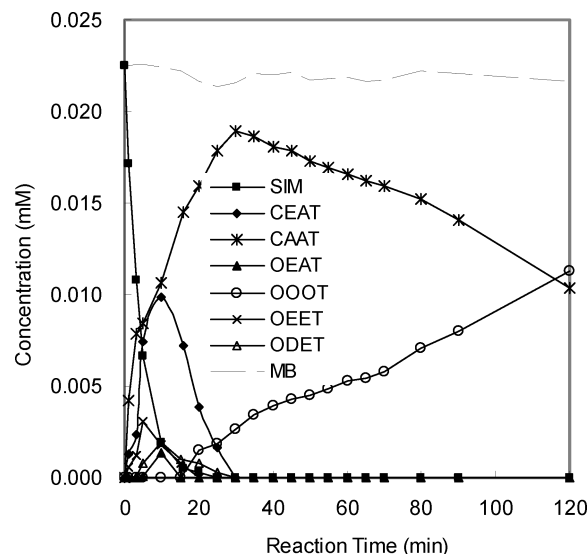


Figure 5. Evolution profile of simazine (SIM) and intermediates in the UV/ TiO_2 system.

CAAT, suggesting that dechlorination–hydroxylation is a minor decay pathway which also occurred at the initial stage of the reaction as dealkylation. After that, a trace level of OEAT was detected after the decay of CEAT and ODET, indicating dechlorination continued to occur at the secondary stage. Chloride ion was not detectable in this process, which confirms our observation that dealkylation is the major decay pathway at the initial stage of UV/ TiO_2 process. It was found that the concentration of CAAT was much higher than that of OEAT, which validated the domination of dealkylation in the process again.

Next, only a trace level of OAAT was detected by LC-MS, and no OOAAT was detected in the reaction. This was likely due to the decay rate differences between the intermediates. The kinetic rate of k_1 ($\text{CEAT} \rightarrow \text{CAAT}$) was much faster than k_2 ($\text{CAAT} \rightarrow \text{OAAT}$), and the kinetic rate of k_4 ($\text{OOAT} \rightarrow \text{OOOT}$) was much faster than k_3 ($\text{OAAT} \rightarrow \text{OOAT}$), which made the intermediates OAAT and OOAT difficult to accumulate to perceptible levels (Figure 6). As a result, CAAT presents at a higher concentration, as also reported by other studies (29, 30).

As demonstrated in Figure 5, cyanuric acid (OOOT) was detected after 15 min of the reaction and starts to accumulate in the solution afterward (no degradation within the tested period of 120 min), whereas [CAAT] dropped after 30 min. It is obvious that OOOT is the final product of the SIM oxidation by UV/ TiO_2 process. Furthermore, total organic carbon (TOC, the initial and final TOC are 2.01 and 1.98 mg/L, respectively) and mass balance (MB) remain unchanged throughout the process, indicating no ring cleavage or mineralization of the SIM within 120 min.

On the basis of the results of the profile analysis, the possible decay pathways of simazine by using UV/ TiO_2 were proposed as shown in Figure 6. The reactions mainly involve (1) dealkylation, (2) dechlorination–hydroxylation, (3) alkyl oxidation, and (4) substitution of amino groups by OH. Route a was based on the dechlorination process, whereas route b involved the dealkylation process. Because the electron-rich positions are more susceptible to the attack of hydroxyl radicals as an electrophilic reagent, route b (dealkylation) was believed to be the major decay pathway due to the electron-donating properties of the alkyl substituent group, which was substantiated by the accumulation of CAAT. Identification of low concentrations of OEET, ODET, and OEAT indicated that a minor decay pathway of dechlorination–hydroxylation also occurred in this process. CAAT was

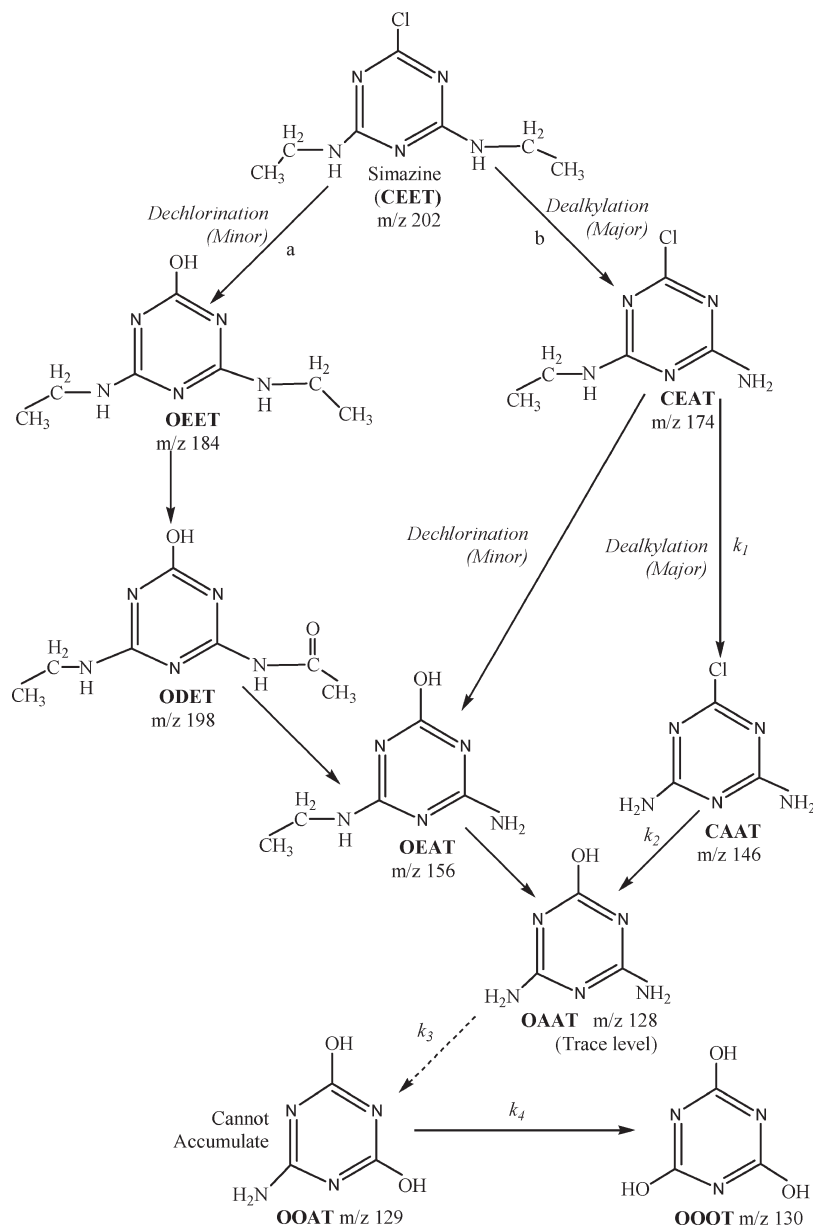


Figure 6. Proposed reaction mechanism of simazine degradation in the UV/TiO₂ system. The dashed arrow indicates a possible pathway because OOAT was not detected in this study.

further transformed to OAAT by dechlorination–hydroxylation; however, the reaction rate k_2 (CAAT → OAAT) was much slower than the kinetic rate of k_1 (CEAT → CAAT) due to the electron-withdrawing properties of chlorine. However, OAAT cannot accumulate in the solution due to the quick transformation of OAAT to OOOT via OOAT through the substitution of amino groups by hydroxyl groups. OOOT was believed to be the final product in this study.

The product OOOT (cyanuric acid) is known as a stable end product of oxidative decomposition of atrazine/simazine and irritates the respiratory tract and eyes. For the further treatment of cyanuric acid, conventional water treatment processes such as precipitation/adsorption may not be efficient due to the lower level in water. Nevertheless, some advanced oxidation processes such as UV/ZnO (oxygen-saturated or ozone-saturated) (31), UV/TiO₂/O₃ with the assistance of H₂O₂ at pH 12, UV/O₃/H₂O₂ at pH 12 (32), sulfate radical (33), and Fenton-enhanced radiolysis (34) were suggested for further downgrading of cyanuric acid.

This examination of intermediates and end-products has provided valuable information on the feasibility and optimization of the photocatalytic process in terms of the degradation of simazine. It is believed that cyanuric acid (OOOT) is the end-product in this process. However, the recalcitrant nature of the triazine ring of cyanuric acid may lead to its accumulation in natural waters; thus, the removal of cyanuric acid in aqueous phase will be studied at the next stage.

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