Pergamon

Tetrahedron 55 (1999) 3401–3412

TETRAHEDRON

Study of the Mechanisms of the Photodegradation of Atrazine in the Presence of Two Photocatalysts : TiO_2 and $Na_4W_{10}O_{32}$

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Received 27 July 1998; revised 25 September 1998; accepted 2 October 1998

Abstract : The mechanisms of the photodegradation of atrazine under direct photolysis and in the presence of two different photocatalysts, TiO_2 and $Na_4W_{10}O_{32}$, are investigated by the means of GC/MS, total radioactivity counting, HPLC and TLC analysis on ^{14}C ring-labelled atrazine solutions. Integration of photo- and biodegradation processes is studied.

INTRODUCTION

Atrazine **1** (2-chloro-4,6-bis(ethylamino)-s-triazine) is a widely used pesticide, especially in corn cultures. Its intensive use and persistence in soils[1,2] makes it a possible contaminant of water. This pollutant has already been detected in ground and wells waters of some American states[3,4] at levels higher than the recommended values.[5,6] Atrazine is classified as a possible human carcinogen.[7,8] In water, the presence of the pollutant affects algaes,[9] plankton[10] and fishes.[11-13]

Several studies have already been made on the degradation of this pollutant in water, either by thermal or microbial degradation. Atrazine is slightly and partly degradated by micro-organisms.[14] The reactions observed are mainly dealkylations leading to deethylatrazine DEAT **2** (structures on Scheme 1) and deisopropylatrazine DIAT **3**.[14] Only few strains are able to cleave the C-Cl bound of **1**, **2** or **3** to the corresponding dehalogenated derivatives.[14-17] The differences of reactivity between atrazine and its possible metabolites are even greater when the mineralisation of the triazine ring of the pollutant is considered. For example, the same strain can mineralise 0.6% of atrazine **1** in 375 days, 22% of deethyldeisopropylatrazine DEDIAT **5** in 192 days and 83 % of cyanuric acid **9** in 66 days.[18]

Chemical degradation of atrazine has been extensively studied : Fenton's reaction,[19,20] UV irradiation combined with photosensitizers,[21] H_2O_2,[22] ozonation,[23,24] and titanium dioxide as a photocatalyst,[25] have been explored. Pelizzetti et al[26] have shown that the photodecomposition of atrazine and other triazines in the presence of TiO_2 leads to cyanuric acid **9**, chloride and nitrate ions, and that only the alkyl side chains are mineralised. Ozonation also leads to cyanuric acid **9**[24] whereas Fenton's reaction ends at DEDIAT **5** and amide 4-acetamido-6-amino-2-chloro-s-triazine.[19,20]

Two points have to be taken into account when considering the efficiency of a decomposition method of atrazine: the dechlorination of the pollutant and the mineralisation of the triazine ring. The dechlorination of the molecule is a key step in its degradation mechanism since the dechlorinated metabolites of atrazine loose the phytotoxicity of their parent molecules.[18,27] However, total mineralisation of the pollutant has to be achieved in an efficient degradation process. Our work has two main objectives. The first objective is to identify and compare the degradation products of atrazine at the early times of photodegradation in the presence of two different photocatalysts, TiO_2 and sodium decatungstate $Na_4W_{10}O_{32}$. Photodecomposition of pollutants using photocatalysis on TiO_2 has been widely studied.[28-30] The possibilities offered by polyoxometalates for the depollution of water have been pointed out recently.[31-33] Among the different polyoxometalates available, sodium decatungstate is interesting in view of applications since its absorption

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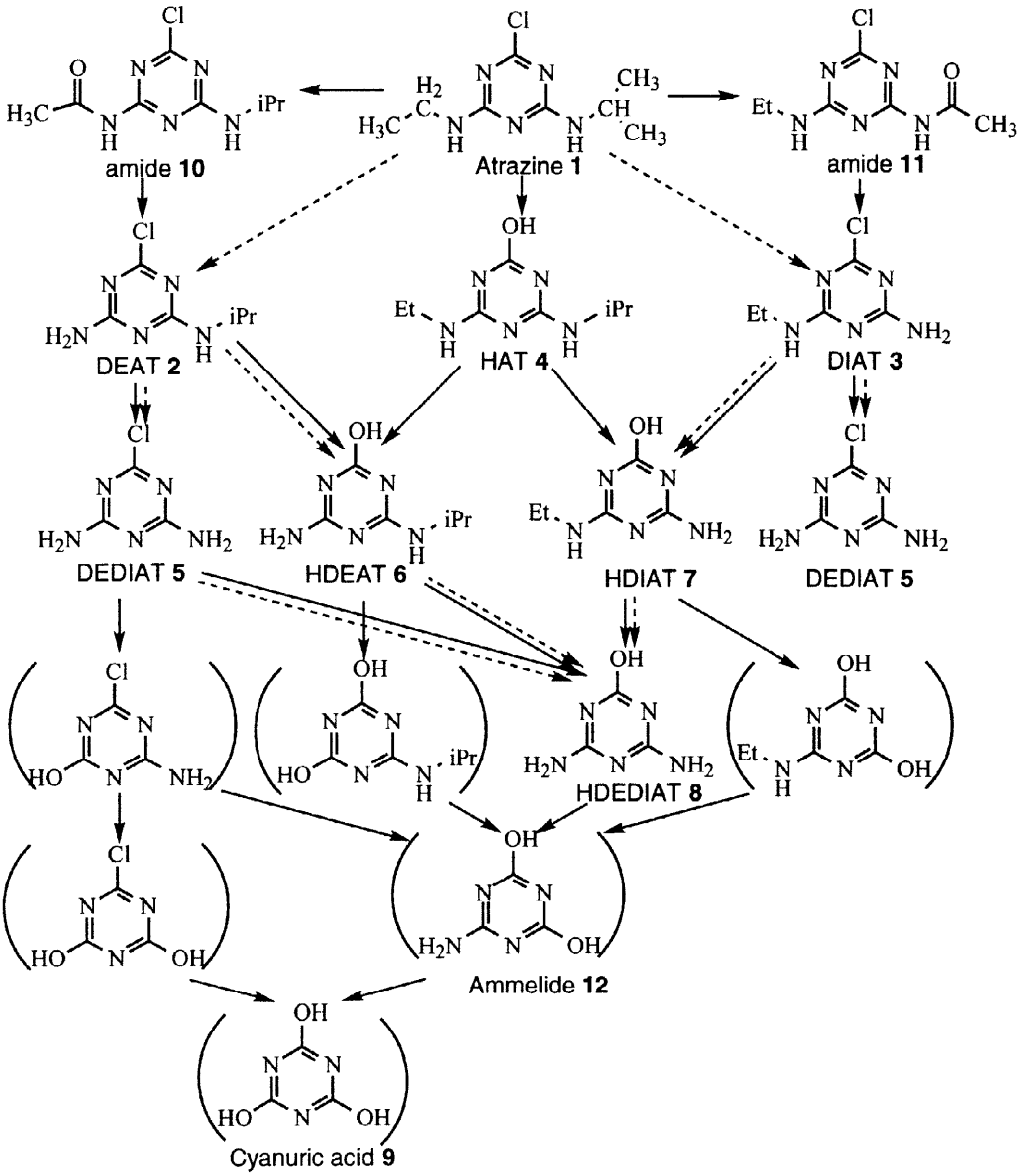
PII: S0040-4020(98)01150-8

spectrum overlaps the far UV solar emission spectrum. The second objective is to couple photodegradation and biodegradation processes in order to lead efficiently to the total mineralisation of the substrate. Photodecomposition appears as a promising process for the dechlorination of the pollutant but inefficient for its total mineralisation, whereas some micro-organisms could be able to mineralise the dechlorinated metabolites of atrazine.

^{14}C ring-labelled atrazine solutions are used to follow the mineralisation and the formation of the decomposition products. The use of radioactive solutions allows a quantification of the products detected by HPLC and TLC analysis.



Scheme 1: Proposed mechanisms for the photodecomposition of atrazine in the presence of TiO_2 (full-lined arrows ⟶) or $Na_4W_{10}O_{32}$ (dashed-lined arrows- - - -⟶).
Products inside brackets are not detected in our experimental conditions, but are observed by other groups,[25] or postulated.

EXPERIMENTAL

Products

^{14}C ring-labelled atrazine is purchased from Sigma, TiO_2 P25 from Degussa. Atrazine **1** and standards of the degradation metabolites of the pollutant (deethylatrazine DEAT **2**, deisopropylatrazine DIAT **3**, hydroxyatrazine HAT **4**, deethyldeisopropylatrazine DEDIAT **5**, hydroxydeethylatrazine HDEAT **6**, hydroxydeisopropylatrazine HDIAT **7**, hydroxydeethyldeisopropylatrazine HDEDIAT **8**) are obtained from Cluzeau Info Labo (purity > 99%). Sodium decatungstate $Na_4W_{10}O_{32}$ is synthesised[34] and characterised[35] according to literature methods (Anal. Calcd. for $Na_4W_{10}O_{32}.7H_2O$: W, 71.49; H, 0.55. Found: W, 71.50; H, 0.55; C, < 0. 01; IR (KBr, cm^{-1}): 1004 w; 962 s; 912 s; 800 vs; 580 w; 420 s; UV (CH_3CN): $\varepsilon_{323\ nm}$ = 14,700 ± 300 L mol^{-1} cm^{-1}).

Irradiations

For HPLC and TLC analysis and to follow the total mineralisation of the pollutant, 25 mL of acidic aqueous solution of atrazine 20 ppm (9.2 10^{-5} mol L^{-1}) containing ^{14}C ring-labelled atrazine (2 µCi / 25 mL), and eventually added either with TiO_2 (0.2 g L^{-1}) or $Na_4W_{10}O_{32}$ (1.5 10^{-3} mol L^{-1}), are irradiated in a Rayonet type external reactor with a medium pressure 125 W mercury lamp. The stirred solutions are set in the middle of the reactor, in a Pyrex tube equipped with a water-cooling Pyrex envelope. The solutions of atrazine are acidified with $HClO_4$ to pH 2.4 since $W_{10}O_{32}^{4-}$ isomerizes above pH 3 to form the metatungstate anion which absorbs UV light only below 260 nm.[36] For GC/MS analysis, 100 mL of non radioactive acidic aqueous solution of atrazine 20 ppm (9.2 10^{-5} mol L^{-1}), eventually added either with TiO_2 (0.2 g L^{-1}) or $Na_4W_{10}O_{32}$ (1.5 10^{-3} mol L^{-1}) are irradiated in a photochemical reactor composed of an immersed Pyrex envelope containing a medium pressure 125 W mercury lamp. The aqueous solutions are centrifuged, extracted twice with 25 mL of dichloromethane and concentrated 100 times before injection.

Total radioactivity counting

400 µL of the solution is added to 10 mL of scintillant Aquasafe 300 Zinsser Analytic, and counted by a LKB 1214 Rackbeta counter.

GC/MS analysis

GC/MS analysis are performed on a Varian 3400 chromatograph equipped with a DB5 capillary column, and coupled with an Incos 50 Finningan Mat mass spectrometer, using electronic impact or chemical ionisation detection. The temperature program used is 180°C isothermal for 2 min, then temperature gradient of 8°C min^{-1} until 270°. Only low polarity products can be detected by this method: atrazine **1**, DEAT **2**, DIAT **3**, and 2 new products which we identify as the amide 4-acetamido-2-chloro-6-isopropylamino-s-triazine **10** (MS(EI): 229 ($M^{\cdot+}$, 40.5); 214 (M-CH_3, 26.6); 172 (M-CH_3-CH_2CO, 100); 68 (NCN-C-NH_2^+, 38.0); 58 (25.3); 43 (H_2NC-NH^+, 91.1)) and amide 4-acetamido-2-chloro-6-ethylamino-s-triazine **11** (MS(EI): 215 ($M^{\cdot+}$, 27.1); 200 (M-CH_3, 49.3); 187 (M-C_2H_4, 65.7); 172 (M-CH_3-CO, 100); 68 (NCN-C-NH_2^+, 55.1); 58 (20.3); 43 (H_2NC-NH^+, 50.2)). The mass spectra of **10** and **11** are similar to those published in the literature for the synthesised products.[24] GC/MS allows a qualitative analysis of the products of degradation, but is not quantitative due to the extraction procedure. Moreover, polar products cannot be detected by this technique.

HPLC analysis

150 µL of centrifuged samples are analysed by HPLC (Waters 717 injector, Waters 600 E pump), equipped with an Hypersil ODS 5 µm column and a Berthold LB 506 C-1 radioactivity detector using a 3 mL min^{-1} flow of Quickzint scintillant. 1 mL min^{-1} flow of a gradient of A (95% KH_2PO_4 0.01 mol L^{-1}, H_3PO_4 pH = 2.1, 5% CH_3CN) and B (30% KH_2PO_4 0.01 mol L^{-1}, H_3PO_4 pH = 2.1, 70% CH_3CN) elutes atrazine **1**, DIAT **3**, DEDIAT **5**, HDEDIAT **8**. DEAT **2** and HAT **4** are eluted together under these conditions of

analysis, whereas HDEAT **6** and HDIAT **7** are eluted with other more polar products. Then, to complete the identification and quantification of the photodecomposition products, we performed some quantitative TLC analysis.

TLC analysis

20 µL of centrifuged aliquots of solutions were applied on a silica plate and eluted by either eluant C (90% $CHCl_3$, 9% acetone, 1% CH_3CO_2H) or eluant D (84% $CHCl_3$, 8% EtOH, 8% CH_3CO_2H). Eluant C separates atrazine **1**, DEAT **2**, DIAT **3**, DEDIAT **5**. Eluant D separates HAT **4**, HDEAT **6**, HDIAT **7**. The analysis and quantification is performed by a Tracemaster 20, Berthold, plates reading scanner. Combining the HPLC and TLC analysis, compounds **1-8** can be identified and quantified. The self-consistency between HPLC and TLC measurements has been checked.

Incubations and preparation of solutions for integrating photochemical and biological degradation

Acidic aqueous solutions of ^{14}C-ring labelled atrazine are irradiated 33 hours in the presence of either TiO_2 or $Na_4W_{10}O_{32}$ as described above. *Penicillium chrysogenum, Phanerochaete chrysosporium* and *Bacillus licheniformis* are isolated from aqueous industrial waste containing explosives. The micro-organisms are grown at 27°C on a rotary shaker (200 rpm) in a liquid medium containing (per litre): 0.5 g KH_2PO_4, 1 g K_2HPO_4, 30 g D-glucose, 10 g corn steep, 0.5 g $MgSO_4$, 2 g $NaNO_3$, 0.5 g KCl, 0.02 g $FeSO_4$. Biomass from 3 day-old cultures is recovered and placed directly in the filtered photolysis medium brought to pH 7 by addition of 2N NaOH. The mixture is then incubated at 27°C and shaken at 200 rpm. Samples of the medium are removed and analysed by TLC, as described previously. The experiments are repeated in order to check their reproducibility.

RESULTS

GC/MS analysis of photodegradated solutions

After 90 % of photodecomposition of atrazine under direct photolysis or in the presence of TiO_2, four photodegradation products are detected and identified by GC/MS : the dealkylated metabolites DEAT **2** and DIAT **3**, and the amides **10** and **11**. Two minor non identified peaks were also evidenced, accounting for less than 5% of the total detected products. In the presence of $Na_4W_{10}O_{32}$, only the dealkylated metabolites DEAT **2** and DIAT **3** were formed.

HPLC and TLC analysis: kinetics of atrazine photodegradation

The steps involved in the time evolution of atrazine and some of its metabolites can be established from the results obtained in HPLC and TLC. The products are identified by comparison with the available standards. Figure 1 shows the decay of 20 ppm atrazine in aqueous acidic solutions, versus the irradiation time, under direct photolysis and in the presence of either TiO_2 or $Na_4W_{10}O_{32}$. Figures 2, 3 and 4 report the time evolutions of some metabolites of atrazine under direct photolysis (Figure 2), in the presence of either TiO_2 (Figure 3) or $Na_4W_{10}O_{32}$ (Figure 4).

Total radioactivity countings and biodegradation of previously photodegradated solutions of atrazine

Whenever the solutions are heterogeneous (in the presence of TiO_2 or biomass), the counting is performed on the total and centrifuged solutions. No difference is observed for TiO_2 solutions, which means that no products are quantitatively adsorbed on TiO_2. Concerning solutions of atrazine irradiated in the absence or in the presence of one of the photocatalysts TiO_2 or $Na_4W_{10}O_{32}$, in all the cases the radioactivity of the samples remains the same. We conclude therefore that no mineralisation of the aromatic ring occurs during the photodegradation processes, as was already observed by Pelizzetti et al in the case of TiO_2.[25,26]

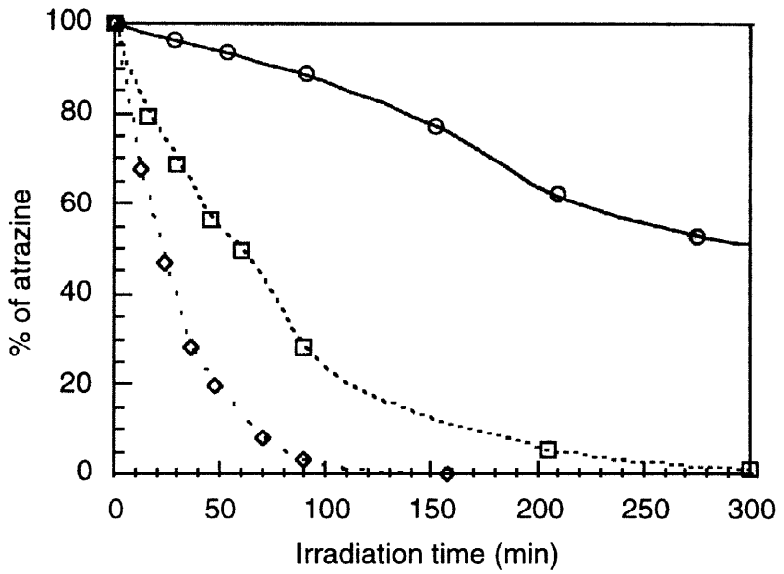


Figure 1 : Decays of 20 ppm ($9.2\ 10^{-5}$ mol L^{-1}) atrazine in aqueous acidic solutions ($HClO_4$, pH = 2.2) under direct photolysis, or in the presence of TiO_2 (0.2 g L^{-1}) or $Na_4W_{10}O_{32}$ ($1.5\ 10^{-3}$ mol L^{-1}). - · ◆ · - with TiO_2 0.2 g L^{-1}; ···□··· with $Na_4W_{10}O_{32}$ $1.5\ 10^{-3}$ mol L^{-1}; —○— under direct photolysis.

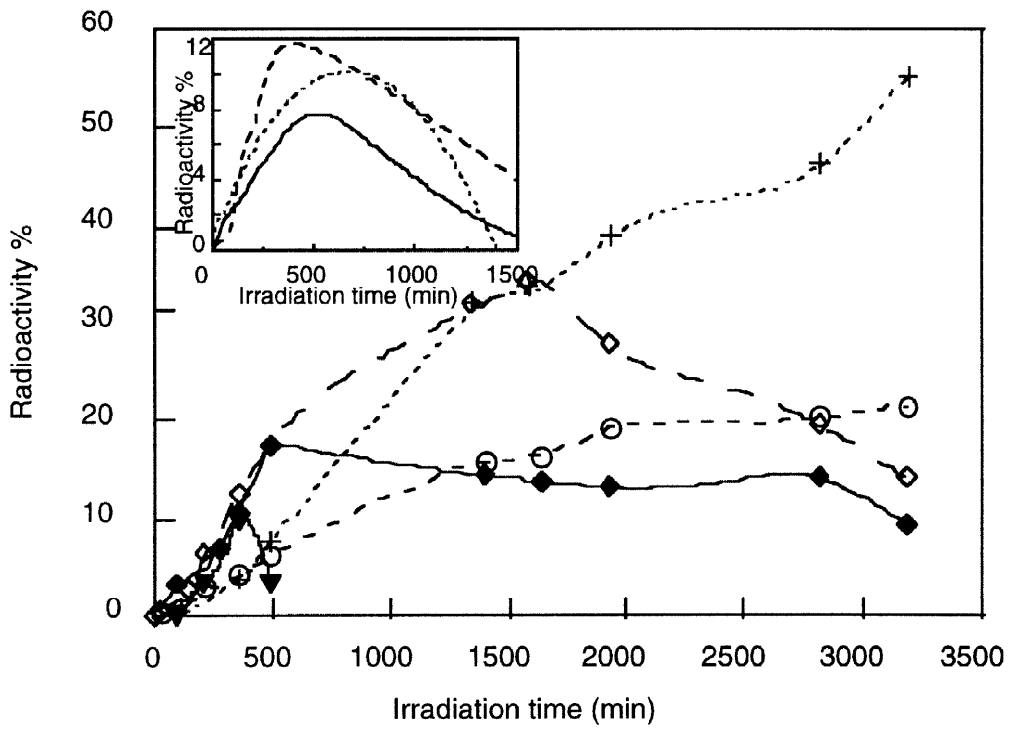


Figure 2 : Time evolutions of some metabolites during the photodegradation of an aqueous acidic solution ($HClO_4$, pH=2.2) of 20 ppm atrazine, under direct photolysis, determined by HPLC and TLC.
Main graph: — ◆ - DEDIAT **5**; —◆— HDEAT **6**; —▼— HDIAT **7**; - -⊖- - HDEDIAT **8**; - -+- - other products. *Insert (short irradiation times) :* — — DEAT **2**; —— DIAT **3**; - - - - HAT **4**.

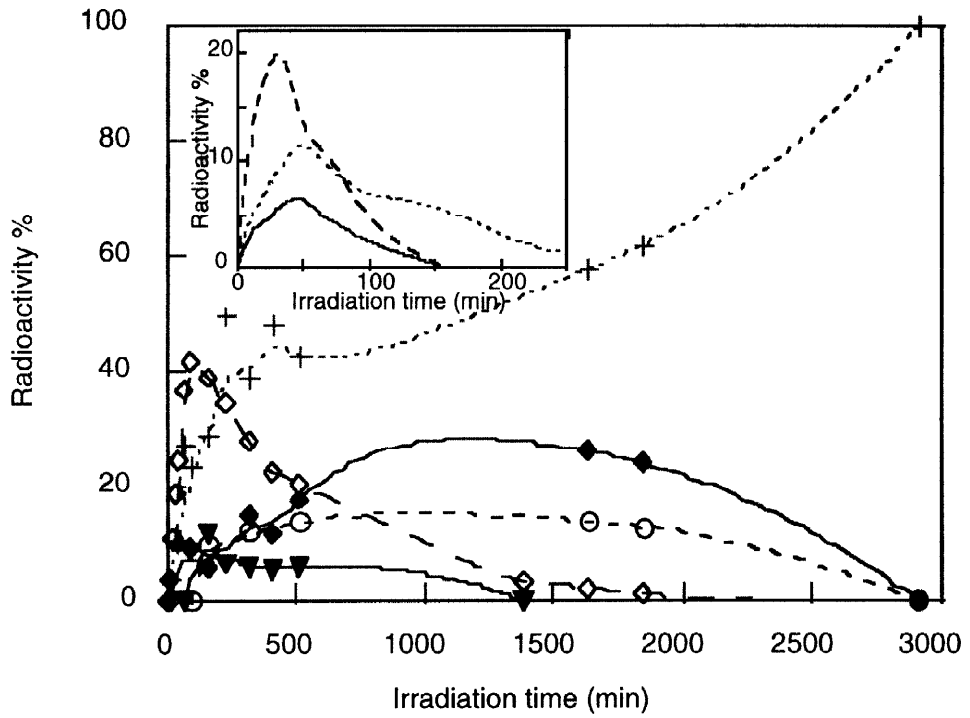


Figure 3 : Time evolutions of some metabolites during the photodegradation of an aqueous acidic solution ($HClO_4$, pH=2.2) of 20 ppm atrazine, in the presence of TiO_2 (0.2 g L^{-1}), determined by HPLC and TLC. *Main graph*: — ◇ - DEDIAT **5**; —◆— HDEAT **6**; —▼— HDIAT **7**; - -⊖- - HDEDIAT **8**; - -+- - other products. *Insert (short irradiation times) :* — — DEAT **2**; —— DIAT **3**; - - - - HAT **4**.

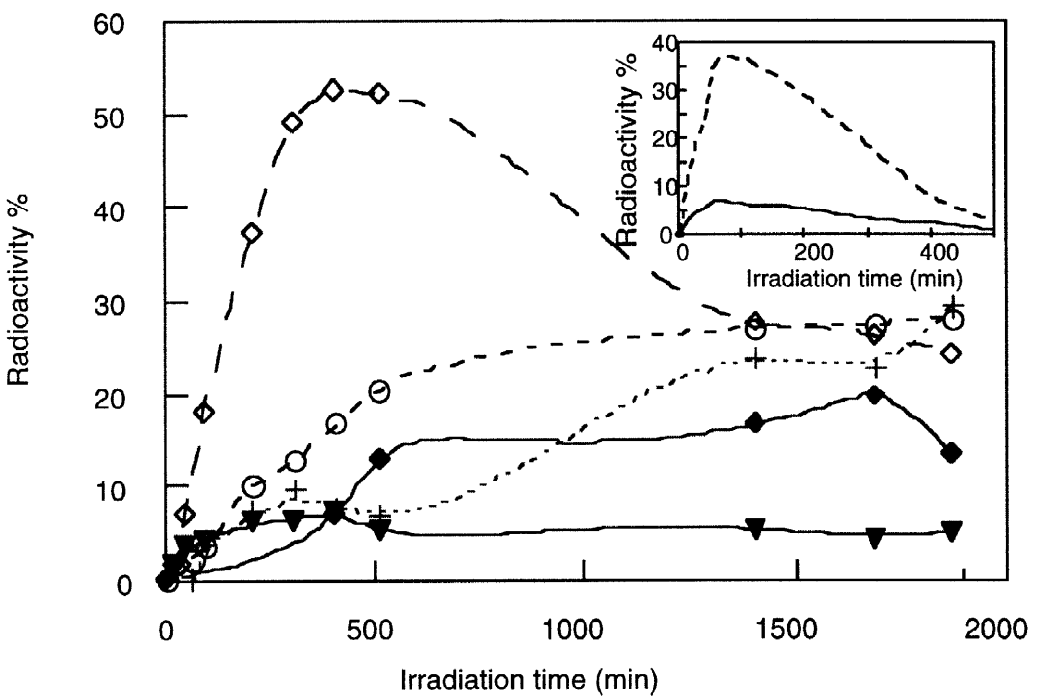


Figure 4 : Time evolutions of some metabolites during the photodegradation of an aqueous acidic solution ($HClO_4$, pH=2.2) of 20 ppm atrazine, in the presence of $Na_4W_{10}O_{32}$ ($1.5\ 10^{-3}$ mol L^{-1}), determined by HPLC and TLC. *Main graph*:— ◇ - DEDIAT **5**; —◆— HDEAT **6**; —▼— HDIAT **7**; - -⊖- - HDEDIAT **8**; - -+- - other products. *Insert (short irradiation times) :* — — DEAT **2**; —— DIAT **3**.

Biodegradations are then started after 33 hours (2000 minutes) of irradiation in the presence of TiO_2 or $Na_4W_{10}O_{32}$. According to Figure 3 (TiO_2) and Figure 4 ($Na_4W_{10}O_{32}$), the composition of the irradiated solutions reaches a steady state around this irradiation time. The HPLC and TLC analysis (Figure 5A) of a solution of atrazine irradiated 33 hours in the presence of $Na_4W_{10}O_{32}$ gives the following composition for the solution: 25% of DEDIAT **5** (Rf=0.80), 15% of HDEAT **6** (Rf=0.13), 5% of HDIAT **7** (Rf=0.12), 30% of HDEDIAT **8** (Rf=0.06), 25% of unidentified products (Rf=0; Rf=0.30 and Rf=0.55). The HPLC and TLC analysis (Figure 5D) of a solution of atrazine irradiated 33 hours in the presence of TiO_2 gives the following composition for the solution: 5% of DEDIAT **5** (Rf=0.80), 20% of HDEAT **6** (Rf=0.13), 15% of HDEDIAT **8** (Rf=0.06), 60% of unidentified products (Rf=0; Rf=0.30 and Rf=0.55).

Incubations with *Phanerochaete chrysosporium* of atrazine solutions irradiated in the presence of either TiO_2 or $Na_4W_{10}O_{32}$ do not lead to the biotransformation or biomineralisation of the solutions after 1 week of incubation. In the presence of *Bacillus licheniformis*, practically no biotransformation occurs for TiO_2 photodegradated solutions, whereas the products distribution of $Na_4W_{10}O_{32}$ photodegradated solutions change dramatically, as demonstrated by the TLC analysis shown on Figure 5B. After 1 week of incubation, only very few polar products remain, but the total radioactivity of the solutions has not decreased (Figure 5C). In the presence of *Penicillium chrysogenum*, we observe the biotransformation and the partial mineralisation of the $Na_4W_{10}O_{32}$ photodegradated solutions (27 % of mineralisation) and the TiO_2 photodegradated solutions. In this last case, 20 % of mineralisation is obtained after 1 week of incubation (Figure 5F), and the biotransformation leads to the formation of an unidentified product (Rf=0.30, Figure 5E), which is also observed in the case of $Na_4W_{10}O_{32}$ solutions.

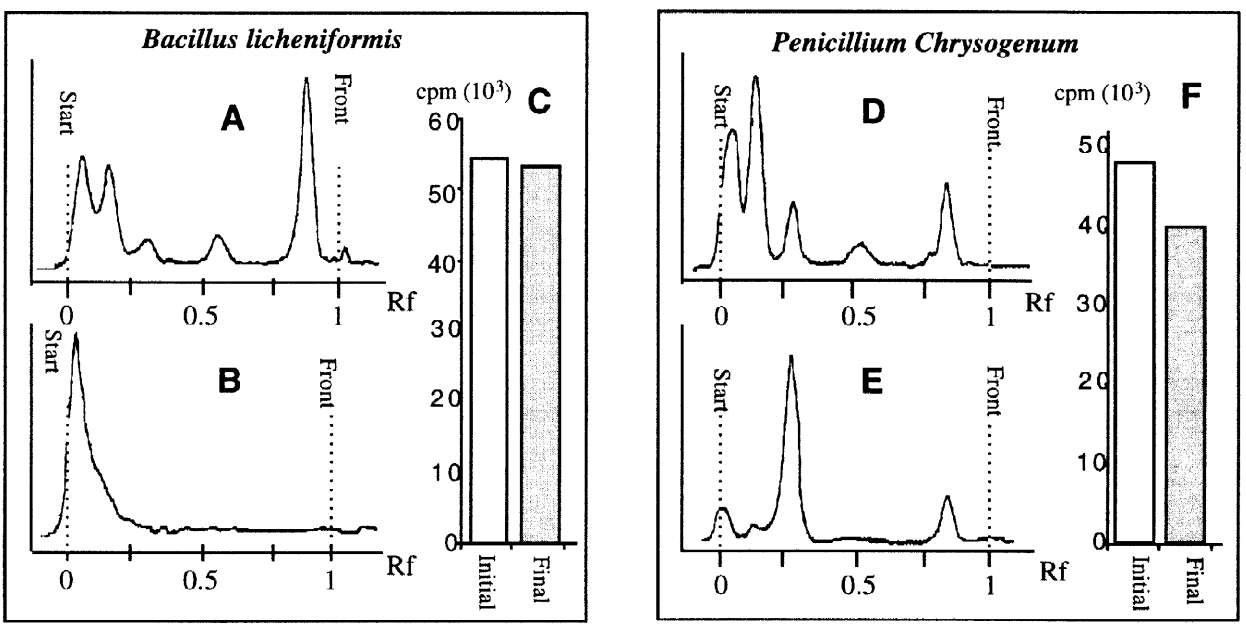


Figure 5: TLC analysis (eluent D) and total radioactivity countings before and after biodegradation of previously photodegradated solutions of atrazine. *Left*: : biodegradation by *Bacillus licheniformis* of $Na_4W_{10}O_{32}$ 33 hours photodegradated solution of atrazine; **A** TLC analysis before biodegradation, **B** TLC analysis after 1 week of incubation, **C** Total radioactivity counting. *Right* : biodegradation by *Penicillium chrysogenum* of TiO_2 33 hours photodegradated solution of atrazine; **D** TLC analysis before biodegradation, **E** TLC analysis after 1 week of incubation, **F** Total radioactivity counting.

DISCUSSION

Photodecomposition of atrazine under direct photolysis and kinetics of photodecomposition

Under direct photolysis, the degradation of atrazine is quite slow (Figure 1), since the Pyrex envelope cuts the wavelengths below 290 nm and atrazine absorption peaks around 280 nm. In respect to the products formed, the degradation scheme we propose includes similar intermediates to those reported earlier[25] (Scheme 1). Under direct photolysis of atrazine, TLC analysis also shows the formation of a large variety of unidentified products, the concentration of which remains very low (below 3 or 4 %). The existence of other degradation pathways, which may include photolysis of primary products, is then possible.

Figure 1 shows clearly that the presence of TiO_2 or $Na_4W_{10}O_{32}$ increases the rate of the photodecomposition of the pollutant. It is difficult to quantify the relative efficiencies of both photocatalysts since sodium decatungstate is homogeneous, whereas TiO_2 is heterogeneous. In heterogeneous photocatalysis, estimation of the absorbed photonic energy is not easy due to the important light scattering,[37] and quantum yields are therefore difficult to measure. Up to now, Fenton's reaction seems the quicker chemical degradation process[20] for atrazine degradation. However, this process leads to the formation of DEDIAT **5** and amide 4-acetamido-6-amino-2-chloro-s-triazine as final products,[19,20] whereas TiO_2 and $Na_4W_{10}O_{32}$ photocatalysis processes lead to more advanced degradation compounds (HDEAT **6**, HDIAT **7**, HDEDIAT **8**, cyanuric acid **9**).[25]

Comparison between photocatalysis in the presence of TiO_2 and $Na_4W_{10}O_{32}$

Besides TiO_2 being slightly more efficient than $Na_4W_{10}O_{32}$, both photocatalysts differ by the nature of the degradation intermediates. In the presence of TiO_2, HAT **4** represents up to 11 % of the total radioactivity during the course of the photodegradation (Figure 3), whereas no formation of this product is detected in the presence of $Na_4W_{10}O_{32}$ (Figure 4). 10 % of the initial atrazine is converted to HAT **4** under direct photolysis (Figure 2). Both amides **10** and **11** have not been detected in the presence of $Na_4W_{10}O_{32}$. However, ketones are quite reactive towards the excited states of polyoxometalates.[38] If amides follow a similar reactivity, the steady state concentrations of amides **10** and **11** during the photodegradation of atrazine by photocatalysis with $Na_4W_{10}O_{32}$ could be too low to be detected by GC/MS. Both photodegradation processes (in presence of $Na_4W_{10}O_{32}$ and TiO_2) thus appear to be different in their mechanism.

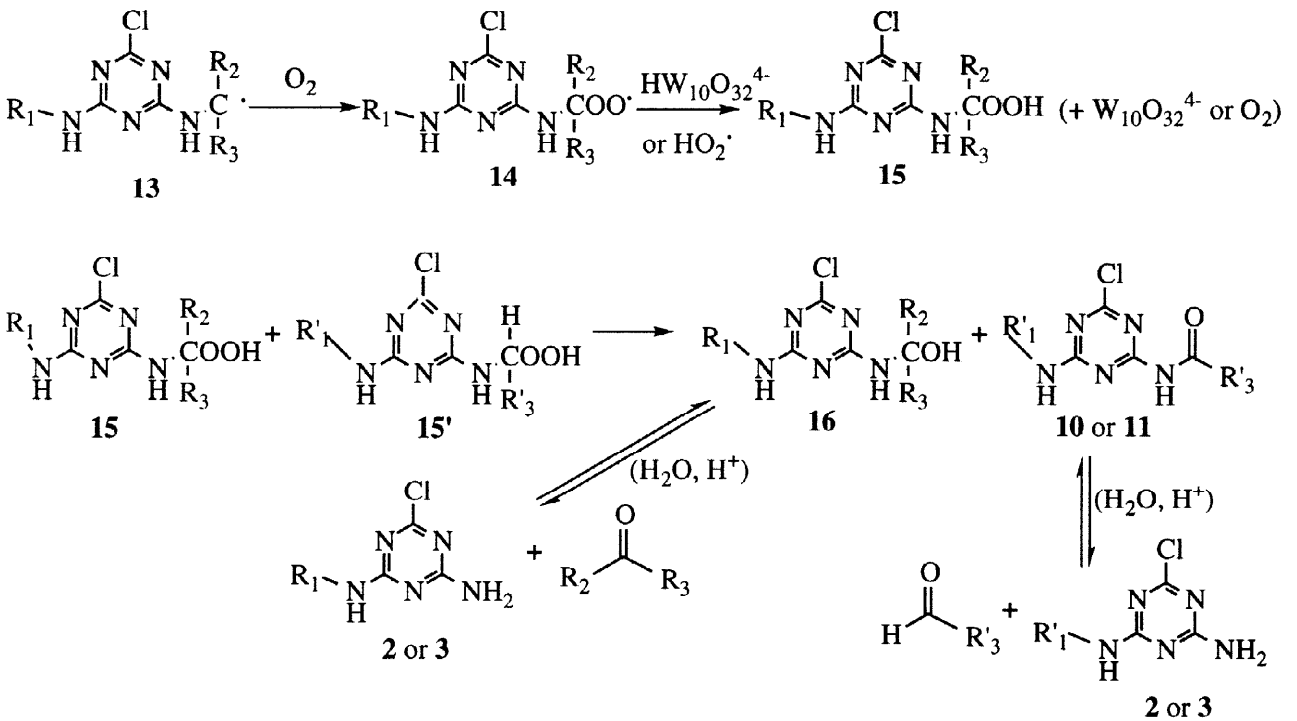
Mechanism of the photodecomposition of atrazine by photocatalysis in the presence of TiO_2

Primary steps of the photodecomposition. The primary steps of the decomposition of pollutants by photocatalysis on TiO_2, and on semi-conductor particles in general, are now well established.[29] In water and under oxygen, the different steps finally lead to the formation of the electrophilic hydroxyl radicals $OH^{\cdot}$[29] (very oxidant) and nucleophilic radicals $O_2^{-\cdot}$.[29,39,40] In acidic medium, $O_2^{-\cdot}$ is under its acidic form $HO_2^{\cdot}$ ($pKa = 4.8$).[31]

Products and scheme of photodecomposition. The identified decomposition products lead us to propose the degradation Scheme 1, full-lined arrows. Two major pathways induced by $OH^{\cdot}$ are possible for the first steps of the photodegradation of atrazine in the presence of TiO_2: dealkylation and dehalogenation. For dealkylation, H abstraction by $OH^{\cdot}$ on the alkane side-chains of the pollutant will lead to the formation of an organic radical $R^{\cdot}$ **13**. Oxidation of that radical produces peroxy radical **14** and the hydroperoxide ROOH **15**, which decomposes into the amides **10** and **11**, and DEAT **2** or DIAT **3**, as described on Scheme 2. A mechanism involving $OH^{\cdot}$ and Fe^{II} species for the formation of amides **10** and **11** has already been proposed by Scott et al in the case of the degradation of atrazine by the Fenton's reaction.[20]

The second degradation pathway, dehalogenation, would occur following attack of the hydroxyl radicals $OH^{\cdot}$ on the Cl position of the s-triazine ring. It has to be noticed that most of the time, a reaction of the mechanism described on Scheme 1, represented by an arrow, includes itself several elementary steps. For example, the intermediate amide 4-acetamido-6-amino-2-chloro-s-triazine, observed during the course of the Fenton's reaction,[19,20] can be formed from DEAT **2** or DIAT **3** in the pathway for DEDIAT **5**. Scheme 1 can

be compared to the one proposed by Pelizzetti et al.[25] In their work, Pelizzetti et al, who used a more powerful irradiation lamp in the presence of TiO_2 particles, observed the formation of more advanced decomposition products, such as ammelide **12** and cyanuric acid **9**, all the way to 1 mol of cyanuric acid **9**, 1 mol of Cl^-, 2 mol of NO_3^- and 5 mol of CO_2 for initially 1 mol of atrazine. In addition to the products that Pelizzetti et al[25] detected, we observed in our work the formation of amides **10** and **11**, and the formation and decay of HDEAT **6** and HDIAT **7**.



Scheme 2 : Proposed mechanism for the reaction of the radical R· to form the dealkylated intermediates of atrazine in aqueous acidic solutions, in the presence of molecular oxygen.

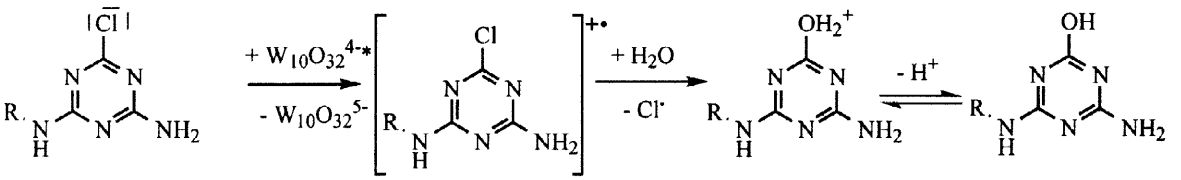
Mechanism of the photodecomposition of atrazine by photocatalysis in the presence of $Na_4W_{10}O_{32}$

Primary steps of the photodecomposition. The formation of hydroxyl radicals OH· upon irradiation of aqueous solutions of sodium decatungstate has been suggested by Papaconstantinou et al[31,32] for the photocatalysed degradation of phenols in the presence of $Na_4W_{10}O_{32}$. However, up to now, in the absence of any organic substrates (organic solvents and organic counter ions of the decatungstate anion can act as substrates[41]), no photoreaction has been detected,[42,43] whereas generation of H_2O_2 would be expected if OH· radicals were formed. The formation of these radicals then seems to be ruled out.

Another mechanism has been proposed, consecutive to nanosecond and picosecond flash-photolysis experiments.[34,44] Hill et al[34] established that a transient X, the nature of which is still poorly known, is formed in less than 30 picoseconds after the excitation of the ligand-to-metal charge transfer band of $W_{10}O_{32}^{4-}$. In the absence of any organic substrate, X has a lifetime of 56 nanoseconds in water.[34,44,45] In the presence of an organic substrate RH, this lifetime is shorter, due to the reaction between X and the substrate.[34,44-46] We determined a bimolecular kinetics rate constant of $(1.0 \pm 0.1)\ 10^8$ L mol^{-1} s^{-1} for the reaction between X and atrazine in acetonitrile.[47] This reaction can be either an electron transfer or an H atom abstraction.[34,44-46] H atom abstraction occurs during the reaction between X and alcohols[45,46] or alkanes.[34,44,46] The reaction then leads to the formation of an R· radical and the acidic reduced form of the polyoxometalate $HW_{10}O_{32}^{4-}$. In the presence of oxygen, the radical R· is oxidised into the superoxide radical ROO· in the solvent cage. By

subsequent H atom transfer between $HW_{10}O_{32}^{4-}$ and ROO$^{\cdot}$, hydroperoxides are formed and the decatungstate anion is regenerated, closing the catalytic cycle.[44] An alternate pathway for the regeneration of the photocatalyst is the following:[45] the reduced form of the polyoxometalate is reoxidised by O_2 to form the initial catalyst and $HO_2^{\cdot}$, which subsequently reacts with the peroxy radical to form the hydroperoxide and O_2. Both mechanisms can explain the observed stoechiometric consumption of oxygen. Electron transfer is another possible pathway for the reaction between X and the organic substrate RH,[34,44-46] especially in the case of aromatic amines.[46] It leads to the formation of the unprotoned reduced decatungstate $W_{10}O_{32}^{5-}$ and to the oxidised radical $RH^{\cdot+}$.

Products and scheme of photodecomposition. The identified degradation products lead us to propose the decomposition scheme represented on Scheme 1 by the dashed-lined arrows. The major pathway of degradation is dealkylation. Dehalogenation can occur, but only on the dealkylated products. Concerning the dealkylation reactions, the primary steps of the photocatalysed reactions, as described above, form the hydroperoxide ROOH. The mechanism of its formation is different in the presence of TiO_2 and $Na_4W_{10}O_{32}$, but its subsequent evolution is the same, and was described on Scheme 2. It is difficult to assess the cleavage of the C-Cl bound by H atom abstraction. Electron transfer reaction, as described on Scheme 3, seems to be the most reliable pathway. The cation radical formed is stabilised by delocalisation of the charge on the aromatic ring and the amino group. There is a competition between electron transfer and H atom abstraction from the N-alkyl groups of atrazine. Since hydrogen abstraction is kinetically favoured,[46] electron transfer can occur efficiently only after dealkylation of at least one amino group, that is when there are less labile hydrogen atoms.



Scheme 3: Proposed mechanism for the dechlorination of the metabolites of atrazine, consecutive to an electron transfer during photocatalysis in the presence of $Na_4W_{10}O_{32}$.

Integrating photocatalytic and microbial degradation of atrazine

Integration of chemical or photochemical and biodegradation processes in order to reach a better depollution efficiency has not yet been extensively studied up to now. In the case of atrazine, one study by Arnold et al,[48] coupling Fenton's reaction to biodegradation with *Rhodococcus corallinus* and *Pseudomonas sp.* leads to 70 % of mineralisation after ten days incubation. Another attempt for coupling ozonation and biodegradation by *Klebsiella terragena* leads to 80 % mineralisation of atrazine in nine days.[49]

In our study, two strains (*Penicillium chrysogenum* and *Bacillus licheniformis*) out of the three tested show a biodegradation activity on the $Na_4W_{10}O_{32}$ photodegradated solutions and one (*Penicillium chrysogenum*) on the TiO_2 photodegradated solutions. The products formed by these biodegradation processes are still to be identified. The significant mineralisation observed for photodegradated solutions incubed 1 week with *Penicillium Chrysogenum* (27 % for $Na_4W_{10}O_{32}$ photodegradated solutions and 20 % for TiO_2 photodegradated solutions) makes the integration of the two degradation processes appear as very promising. New strains and optimisation of the incubations conditions are still to be investigated.

CONCLUSIONS

We have shown that TiO_2 and $Na_4W_{10}O_{32}$ are efficient photocatalysts for the decomposition of atrazine, since both increase the photodegradation rate of the pollutant. The degradations can even be performed under solar irradiation.[50,51]

The mechanisms of the photodegradation in the presence of TiO_2 and $Na_4W_{10}O_{32}$ are different. In the presence of TiO_2, hydroxyl radicals are the reactive oxidant species, whereas in the presence of $Na_4W_{10}O_{32}$, H atom abstraction on the alkyl side-chains of the pollutant, and in a minor pathway, dehalogenation by electron transfer on the dealkylated metabolites, occur.

However, none of these photocatalysts are able to mineralise the aromatic ring of the pollutant, which lead us to investigate coupling of bio and photodegradation processes. The preliminary results obtained in this direction are promising, since up to 27 % of mineralisation of the aromatic ring was obtained during biodegradation by *Penicillium Chrysogenum* of $Na_4W_{10}O_{32}$ photodegradated solutions. Investigations with new strains will be developed more extensively.

Acknowledgements : We greatly appreciate A. Billion's help for GC/MS analysis and S. Roux for fruitful discussion.

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