

Degradation of metsulfuron methyl by heterogeneous photocatalysis on TiO₂ in aqueous suspensions: Kinetic and analytical studies

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Abstract

The photocatalytic degradation of metsulfuron methyl (MTSM) on TiO₂ in aqueous solutions is described in detail. Irradiation of the mixture TiO₂/MTSM (1.0 g L⁻¹/1.0 × 10⁻⁴ mol L⁻¹) within the wavelength range 300–450 nm leads to the complete degradation of the pesticide. Steady state experiments as well as pulse radiolysis of MTSM aqueous solutions clearly show the involvement of hydroxyl radicals. The rate constant of the reaction of MTSM with such reactive species leading to the adduct MTSM-•OH was evaluated to 2.7 × 10⁹ mol⁻¹ L s⁻¹. The disappearance of MTSM is mainly due to three main routes: hydroxylation of the aromatic moiety of the pesticide, cleavage of the sulfonyl urea bridge and the demethylation of the methoxy group within the triazine part. The photoproducts were identified by using HPLC-MS-MS technique and a mechanism for their formation is proposed. The degree of mineralisation estimated by the difference between the initial total organic carbon amount and that obtained after prolonged irradiation was evaluated to 80%. The observed non-complete mineralisation is more likely owing to the formation of cyanuric acid product from the oxidation of the triazine part of the pesticide. Efficient photocatalytic disappearance of MTSM was also found when natural water and solar irradiation were used.

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1. Introduction

In the last two decades, research on new methods for water decontamination is attracting interest and is developing in different ways. Among these various methods, photochemical treatment using solar light appears to be a promising technique, which has been the subject of intensive studies [1–5]. It has emerged as an important tool of decontamination because of its low cost and its large scale of use. Heterogeneous photocatalysis by using semi conductors has proved to be among the most powerful techniques for complete degradation of refractory pollutants [6–13]. Absorption of light by semi conductors, such as TiO₂ and ZnO promotes an electron from the valence band to the conduction band [14–16]. Such process

leads to the formation of a positive hole (h⁺) in the valence band. In aerated solutions, oxygen plays the very important role of electron trap, which permits the increase of the catalytic efficiency by avoiding the hole—electron annihilation [17,18]. Positive holes oxidize water molecules or ⁻OH with the formation of hydroxyl radicals. These latter species have shown an efficient ability in the oxidation and degradation of a broad scale of organic pollutants [19–22]. If adsorption is present, the direct oxidation of the substrate by the positive holes may also occur and play an important role. The TiO₂ and ZnO semi conductors have been efficiently used for the degradation of various organic pollutants [23,24].

In the present work, we focused on the degradation of metsulfuron methyl by heterogeneous photocatalysis using TiO₂, Degussa P25 and Millennium P500. Such compound belongs to the sulfonyl urea family, which presents an important role in modern agriculture because of its significant action in plant protection [25,26]. It presents a high selectivity

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against a wide range of plants. As has already been reported for most sulfonyl urea compounds, hydrolysis was shown to be a significant pathway for their degradation [26–28]. This is obviously owing to the presence in the molecular structure of many functional groups that are subject to hydrolytic reactions. Such hydrolysis process is effective only for acid solutions and in a lesser extent for basic solutions. At neutral pH, hydrolysis was shown to be negligible. Previous studies on the photodegradation by UV light of metsulfuron methyl in aqueous solutions showed the primary formation of two products: *s*-triazine amine and phenyl sulfonyl carbamic acid [29]. The latter product leads to the corresponding sulfonamide and to a cyclization compound. In the case of triasulfuron and cinosulfuron, the sunlight-induced photodegradation proceeds via various reaction pathways: cleavage of the sulfonyl urea bridge, desulfonation, demethylation of the methoxy group on the triazine moiety and dealkylation of the substituted benzene group [30]. The kinetic studies clearly showed that at pH 7 the photodegradation becomes an important pathway when compared to chemical transformations. Similar cleavage of the sulfonyl urea bridge was also obtained when the herbicides tribenuron methyl and chlorsulfuron were irradiated in different solvents [31,32]. Recently, we reported on the induced degradation of metsulfuron methyl by excitation of iron(III) aquacomplexes [33]. The process involved the formation of hydroxyl radicals via the excitation of the most photoactive monomeric species of iron(III), namely $\text{Fe}(\text{OH})^{2+}$.

The work presented herein describes the heterogeneous photocatalytic degradation of metsulfuron methyl (MTSM) in the presence of titanium dioxide. Our main interest was the kinetic disappearance of the pesticide as a function of various parameters, such as the amount of the photocatalyst, pH, oxygen concentration and also the elucidation of the structures of the intermediate photoproducts in order to have a better insight into the pesticide degradation mechanism. Data concerning the rate constants were obtained by using pulse radiolysis. Besides the products and the transient species intermediates, we also investigated the possibility of total degradation as well as the mineralisation of metsulfuron methyl in pure as well as in natural waters.

2. Experimental

Metsulfuron methyl was from Riedel-de Haën and was used as received. 2-Amino-4-methoxy-6-methyl-1,3,5-triazine and 2-(carbomethoxy) benzenesulfonamide (Scheme 1) were obtained from Aldrich as the purest grade available. They were used as received.

Titanium dioxide TiO_2 Degussa P25 was 80:30 anatase:rutile with a surface area of $55 \text{ m}^2 \text{ g}^{-1}$. Titanium PC 500 was provided by millenium Inorganic Chemicals. It is 100% anatase with a surface area higher than $250 \text{ m}^2 \text{ g}^{-1}$.

The irradiation device consists of a vertical Pyrex tube (20 mm i.d.) with a water-cooling jacket. It is located along

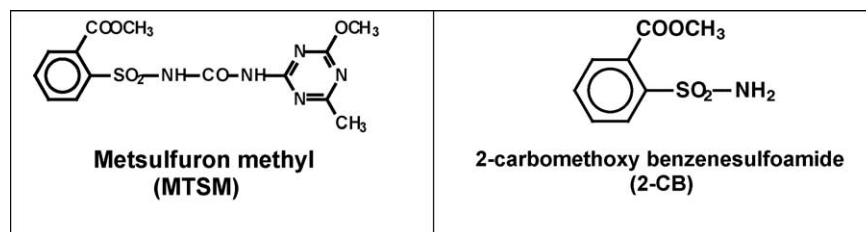
one of the focal axes of a cylindrical mirror with an elliptic base. A fluorescent lamp TLD15 W/05 emitting within the range 300–450 nm is located along the other focal axis. TiO_2 is maintained in suspension by magnetic stirring. The irradiation conditions remain almost constant during sampling. Under our experimental conditions, the number of photons received by the suspension is almost proportional to the irradiated volume. It is worth to note that the evaporation was found to be negligible.

Acetonitrile was from Carlo Erba (HPLC grade). All other reactants were of the highest grade available and were used as received. All solutions were prepared with deionised ultrapure water, which was purified with Milli-Q device (Millipore) and its purity was controlled by its resistivity. The de-oxygenation of the solutions was accomplished by bubbling argon for 30 min at room temperature. For prolonged irradiations, nitrogen bubbling was maintained during the irradiation. pH Measurements were carried out with a JENWAY 3310 pH-meter to ± 0.01 pH unit. The ionic strength was not controlled.

The degradation of metsulfuron methyl and the formation of the photoproducts were followed by high performance liquid chromatography using a Hewlett Packard liquid chromatography system (HP1050) equipped with a mono-channel UV–vis detector and an automatic injector. The experiments were performed by UV detection at 250 nm and by using a reverse phase Merck column (Spherisorb ODS-2 $5 \mu\text{m}$; 250–4.6 mm). The flow rate was 1.0 mL min^{-1} and the injected volume was 50 μL . The elution was accomplished with water with acetic acid (0.1%) and acetonitrile (6/4, v/v). A Waters 540 HPLC chromatograph system equipped with a Waters 996 photodiode array detector was used for recording the UV–vis spectra of the photoproducts.

LC–MS and LC–MS–MS studies were carried out with a Waters (Alliance 2695) HPLC system coupled to a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ionisation source (ESI). Data acquisition and processing were performed by MassLynx NT 3.5 system. Chromatography was run using a Nucleodur column (250 mm \times 4.6 mm, $5 \mu\text{m}$) and a 6/4 (v/v) mixture of acetonitrile and water with 0.2% acetic acid as mobile phase at 1 mL min^{-1} . The electrospray source parameters were: capillary voltage 3.5 kV (or 3 kV in the negative mode), cone voltage 15 V, source block temperature 120°C , de-solvation gas temperature 400°C . Argon was used for collisional activated dissociation (CAD) at a pressure of $1.5 \cdot 10^{-3}$ Torr and 10–50 eV collision energy.

The progress of the mineralisation of metsulfuron methyl was monitored by measuring the total organic carbon concentration (TOC) via a Shimadzu Model TOC-5050A equipped with an automatic sample injector. The calibration curve within the range $1\text{--}15 \text{ mg L}^{-1}$ was obtained by using potassium hydrogen phthalate and sodium hydrogen carbonate for organic and inorganic carbon, respectively. The evolution of ammonia ions and sulfate ions concentration as a func-



Scheme 1.

tion of irradiation time was obtained by ionic chromatography using a Gilson 305 pump equipped with a Waters 431 conductivity detector and a Hamilton cationic column (PRP-X200). The elution was accomplished by using HNO_3 ($2.0 \times 10^{-3} \text{ mol L}^{-1}$)/methanol (7/3, v/v). The flow was adjusted to 1.0 mL min^{-1} .

UV–vis spectra were recorded with a Cary 3 double beam spectrophotometer.

3. Pulse radiolysis

The pulse radiolysis experiments were carried out with a 12 MeV RDL, 3 GHz electron linear accelerator. We used a single pulse mode with a pulse duration from 0.22 to $2 \mu\text{s}$ and with a peak current of about 30 mA. The accelerator is normally operated at 10 pulses per second but the single pulse mode is achieved by modifying the pulses to the gun [34]. The detection system consisted of a Xe arc lamp and a pulsing unit, high radiance Kratos monochromator and quartz optics. Optical transmissions at various wavelengths selected with the monochromator, bandwidths 10–40 nm, were observed as a function of time before and after the laser flash using photoelectric detection. The output of the photomultiplier (EMI 9558Q) was displayed on a Tektronix TDS 380 digitizing oscilloscope. Data processing were performed on a Dan PC using software developed in house. The sample cell, constructed from Spectrosil quartz, had an optical path length of 25 mm [35].

Absorbed doses were determined from the transient $(\text{SCN})_2^{\bullet-}$ formation in air-saturated 10^{-2} M KSCN as described by Adams et al. [36] but using the updated G_ϵ value of $2.59 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ obtained by Buxton and Stuart [37] G being the radiation chemical yield of $(\text{SCN})_2^{\bullet-}$ and ϵ its molar absorption coefficient at 475 nm. Saturation of such solutions with N_2O results in a doubling of the $(\text{SCN})_2^{\bullet-}$ yield.

4. Results and discussion

4.1. Kinetics of MTSM disappearance

The photocatalytic degradation of metsulfuron methyl ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) was studied in the presence of two different kinds of titanium dioxide: Degussa P25 and Millennium PC500. The former presents the composition

anatase/rutile of 80/20 with a surface area of $55 \text{ m}^2 \text{ g}^{-1}$ while the latter is 100% anatase with a surface area higher than $250 \text{ m}^2 \text{ g}^{-1}$. As shown in Fig. 1, the irradiation within the range $300 < \lambda < 450 \text{ nm}$ of an aqueous suspension of the mixture TiO_2/MTSM ($1.0 \text{ g L}^{-1} / 1.0 \times 10^{-4} \text{ mol L}^{-1}$) at pH 3.9 led to the complete degradation of the organic substrate. The kinetics of disappearance was shown to be faster with Degussa P25 than with PC500 with half-lifetimes of 20 and 80 min, respectively. The total degradation was achieved after 500 and 800 min irradiation time, respectively. It has to be pointed out that TiO_2 Degussa P25 was shown to be more efficient than PC500, whatever the concentration of the photocatalyst within the concentration $0.1\text{--}2.5 \text{ mg L}^{-1}$. No disappearance was observed when the photocatalyst was removed from the solution and no significant adsorption was obtained when the mixture TiO_2/MTSM was left under stirring in the dark for more than 2 h.

Since all the experiments were undertaken in the presence in heterogeneous system, the determination of the quantum yield was then not possible. In order to have a better insight in the photocatalytic process of MTSM, the efficiency was evaluated by using phenol as a reference compound as proposed by Serpone et al. [38]. It is worth to note that both sets of experiments were performed within the same experimental conditions (similar reactor, constant amount of TiO_2 , similar concentration of the substrate...). The respective life-

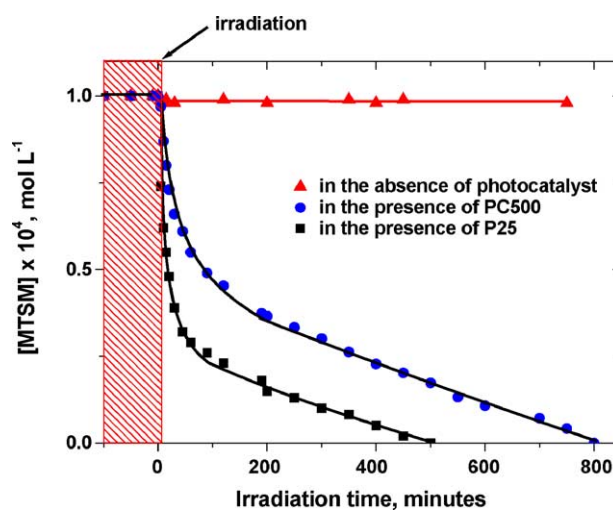


Fig. 1. Kinetics of the photocatalytic transformation of MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) with TiO_2 Degussa P25 and PC500 (1.0 g L^{-1}).

Table 1

The efficiency of the heterogeneous photocatalytic process of metsulfuron methyl (TiO_2 , 1.0 g L^{-1})

| Substrates | Degussa P25, pH 3.9, $t_{1/2}$ (min) | Millennium P500, pH 3.9, $t_{1/2}$ (min) |
|--|--------------------------------------|--|
| Phenol ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) | 16 | 58 |
| MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) | 20 | 80 |
| Efficiency (ξ) | 0.80 | 0.72 |

times and the efficiency given in Table 1 clearly show that the photocatalytic process was important.

4.2. Effect of the amount of titanium dioxide

This effect was studied within a relatively large concentration domain of TiO_2 (Degussa P25): $0.1\text{--}3.0 \text{ g L}^{-1}$. As shown in Fig. 2, even though no linear plot was obtained, the initial rate of MTSM disappearance increased when the amount of the photocatalyst increased. Such rate reached a plateau value for an optimum concentration of about 2.0 g L^{-1} (Fig. 2). This effect can be explained by an increase of the concentration of hydroxyl radical for higher amount of the catalyst. The observed non-linear plot as well as the limit value of the initial rate constant is due to an inner filter effect when the concentration of TiO_2 was higher than 2.0 g L^{-1} .

4.3. Effect of oxygen concentration and 2-propanol

As shown in Fig. 3, the degradation of MTSM was inhibited at more than 95% in de-aerated solution while in oxygen saturated solution it was complete in less than 100 min irradiation time. Such result can be explained by the formation of superoxide anion, which permitted the increase of the efficiency by avoiding the electron–hole annihilation. Moreover, it is worth to note that in aerated solutions containing 2-propanol 0.05 mol L^{-1} , used as hydroxyl radicals scavenger [19,20,33] the degradation of MTSM was completely inhibited. Such effect was observed with concentrations of 2-

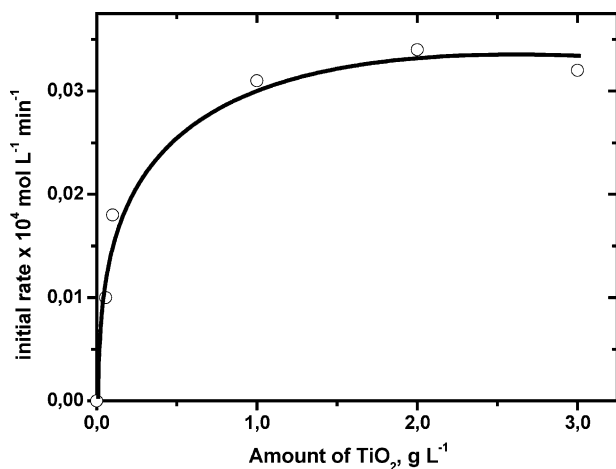


Fig. 2. The initial rate of MTSM disappearance as a function of TiO_2 concentration.

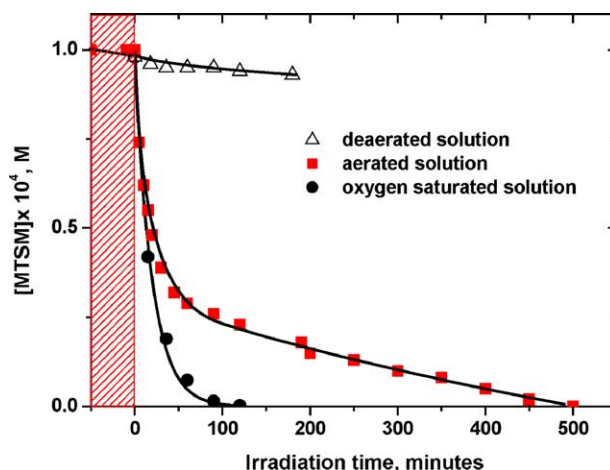


Fig. 3. The photocatalytic degradation of MTSM as a function of oxygen concentration ($[\text{MTSM}] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; TiO_2 , 1.0 g L^{-1}).

propanol as low as $1.0 \times 10^{-2} \text{ mol L}^{-1}$. This leads us to the conclusion that the process involved the intermediate formation of hydroxyl radicals, which appear to be the only species implicated in the process.

The study of the effect of pH showed that the initial rate of MTSM disappearance increased when the pH increased. This could be due to a more efficient formation of hydroxyl radicals from HO^- than from water as already reported in the literature [11].

In order to evaluate the rate constant of the reaction of hydroxyl radical with MTSM, we have undertaken pulse radiolysis experiments.

4.4. Pulse radiolysis

On pulse radiolysis of N_2O -saturated aqueous solution containing MTSM at a concentration of $5.0 \times 10^{-4} \text{ mol L}^{-1}$ the absorption spectrum in Fig. 4A was recorded at $2 \mu\text{s}$ after the pulse. Under our conditions, it is worth to recall that the solvated electron is scavenged by N_2O leading to an additional way for the formation of hydroxyl radicals [39,41]. The obtained spectrum is characterized by two well-defined absorption bands at 360 and 540 nm. The similarity of the decays at these two wavelengths leads to the conclusion that both bands correspond to the formation of the same transient species. Such spectrum has got the same features as that generated by laser flash photolysis while studying the degradation of MTSM induced by excitation of iron(III) aquacomplexes [33].

By comparison with those of aromatic compounds, such as phenol derivatives and aminobenzenesulfonates [40–43], the obtained spectrum can be assigned to the adduct $\text{MTSM}\cdot\text{OH}$ as generally admitted for such substrates. Such assignment was further confirmed by using 2-(carbomethoxy) benzenesulfonamide (2-CB) as a model molecule representing the aromatic moiety of MTSM (Scheme 1).

Aqueous solution of 2-CB ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) saturated with N_2O was pulse irradiated and the absorption spectrum

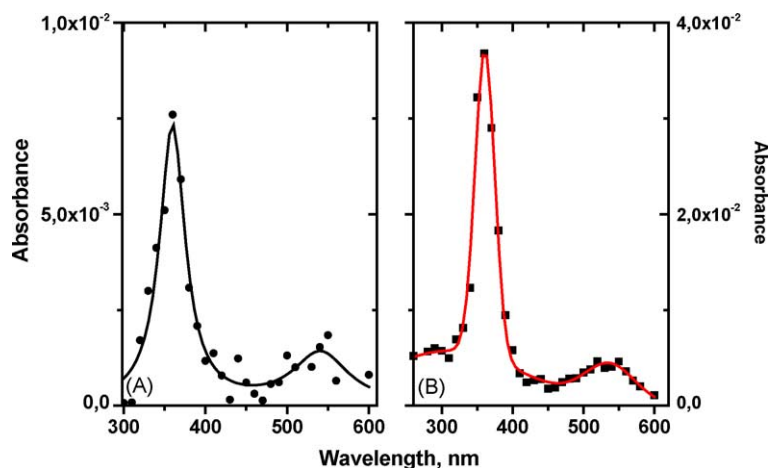


Fig. 4. Transient absorption spectrum from pulse radiolysis of aqueous solution saturated with N_2O and containing MTSM at a concentration of $5.0 \times 10^{-4} \text{ mol L}^{-1}$ (A) and 2-CB (B).

was recorded $2 \mu\text{s}$ after the pulse. As shown in Fig. 4B, the transient absorption spectrum shows two absorption bands at 360 and 540 nm. It presents a 100% similarity with that obtained with MTSM. This leads us to the conclusion that the addition of the hydroxyl radical occurred on the aromatic part of the molecule leading to the formation of the adduct 2-CB- $\bullet\text{OH}$. The bimolecular rate constants for the reaction of $\bullet\text{OH}$ radicals with MTSM and 2-CB were determined by following the growth at 360 nm as a function of substrate concentration within the range 2.0×10^{-5} – $2.5 \times 10^{-4} \text{ mol L}^{-1}$. They were evaluated to 2.7×10^9 and $1.7 \times 10^9 \text{ mol}^{-1} \text{ L s}^{-1}$, respectively.

4.5. Intermediate products

The photocatalytic degradation of MTSM on TiO_2 led to the formation of several photoproducts (Fig. 5). The complete analytical studies were performed with less than 15–20% conversion extent of the pesticide in order to avoid the formation of secondary photoproducts.

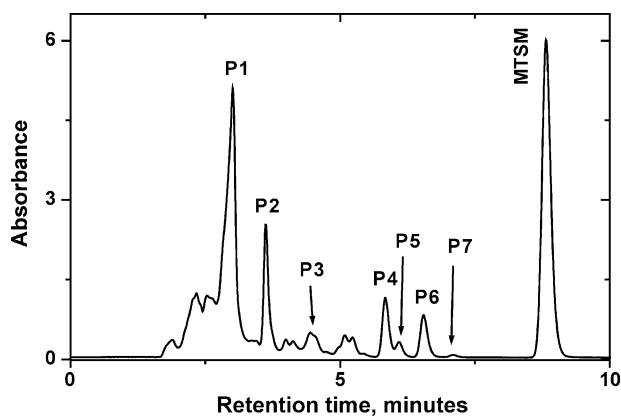


Fig. 5. HPLC chromatogram of an aqueous solution of MTSM after 10% conversion extent ($[\text{MTSM}] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; TiO_2 , 1.0 g L^{-1}).

2-Amino-4-methoxy-6-methyl-1,3-triazine (P1) and 2-(carbomethoxy) benzene-sulfonamide (P3) were easily identified by comparison of HPLC retention times and diode array spectra with those of authentic samples. All other photoproducts were identified by using HPLC–MS–MS technique in ESI+ mode (Table 2). It is important to note that these photoproducts were also formed while studying the degradation of MTSM induced by excitation of iron(III) aquacomplexes [33], which highlights the fact that the process mainly involves the attack of hydroxyl radicals. As shown in Table 2, the four hydroxylated isomers correspond to the reaction of hydroxyl radical on the four free sites on the aromatic ring. We were not able to determine the exact position of the hydroxyl function for each isomer. However, by assuming similar molar absorption coefficient for the four photoproducts, it is clear that P4 and P6 are formed in a relatively large amount. This is more likely owing to the withdrawing effect of the $-\text{SO}_2-\text{NH}-$. It has to be pointed out that all the products are mainly formed in the presence of oxygen.

The evolution of the products concentrations as a function of irradiation time shows that the formation occurs without any induction period (Fig. 6). All the products reached a maximum concentration at roughly 25 min irradiation time. After this period, they disappeared in their turn with a rate that depends on the chemical structure. Those containing an aromatic moiety rapidly disappeared probably by the action of the $\bullet\text{OH}$ radicals while that with a triazine part (P1) accumulated in the solution and slowly disappeared. The main reason for this is that the reaction of hydroxyl radicals with the triazine is not efficient. Such conclusion was further confirmed by pulse radiolysis experiments. On pulse radiolysis of N_2O -saturated aqueous solution containing 2-amino-4-methoxy-6-methyl-1,3-triazine (P1) at a concentration of $5.0 \times 10^{-4} \text{ mol L}^{-1}$, the rate constant was evaluated to $3.8 \times 10^8 \text{ mol}^{-1} \text{ L s}^{-1}$. This value is approximately one order of magnitude lower than that obtained with aromatic compounds [19,33].

Table 2
Intermediate products as obtained by LC–MS–MS analyses

| Product | Retention time (min) | m/z (ESI+) ($[M+H]^+$) | Chemical structure |
|----------------|----------------------|----------------------------|--------------------|
| MTSM | 8.8 | 382 | |
| P1 | 3.0 | 141 | |
| P2 | 3.6 | 368 | |
| P3 | 4.5 | 216 | |
| P4; P5; P6; P7 | 5.8; 6.1; 6.5; 7.1 | 398 | |

4 hydroxylated isomers

4.6. Reaction mechanism

The results obtained by the kinetic studies and the formation of intermediate photoproducts allows the following degradation mechanism to be proposed.

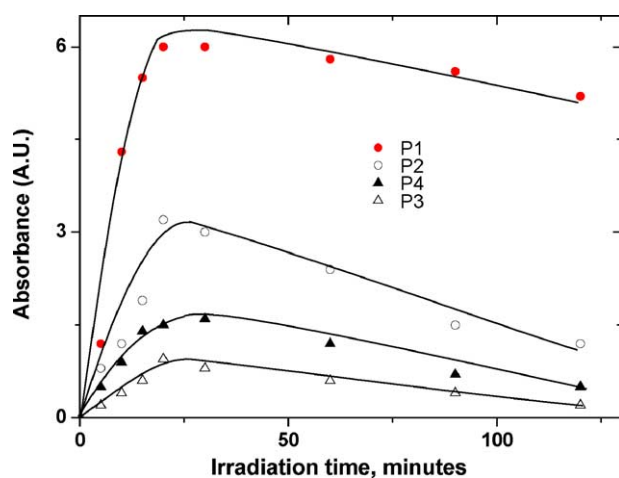
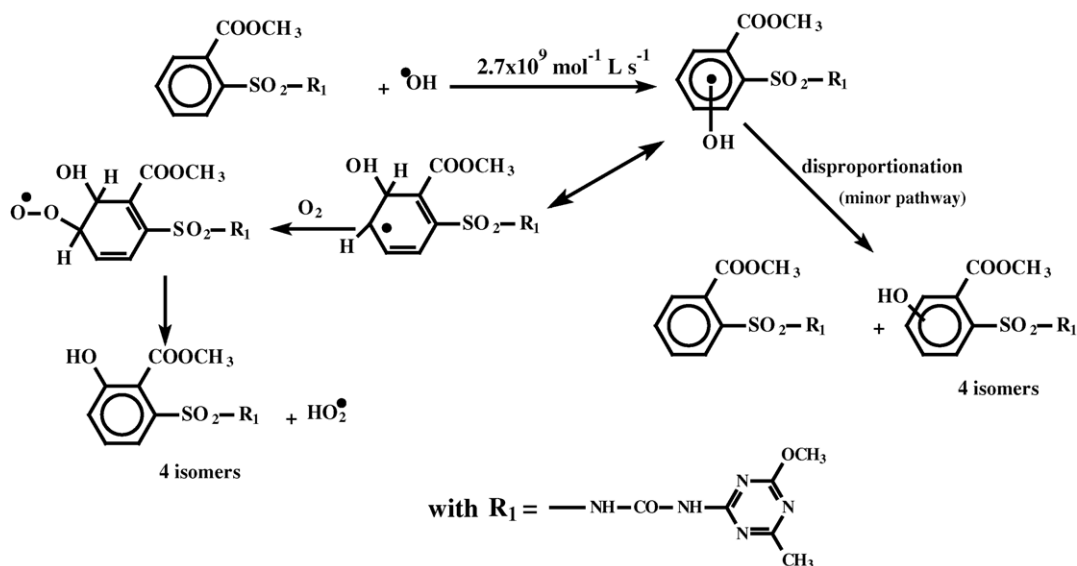


Fig. 6. Evolution of the concentration of the photoproducts as a function of irradiation time ($[MTSM] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; $TiO_2, 1.0 \text{ g L}^{-1}$).

The main pathway in the photocatalytic transformation of MTSM by titanium dioxide involves an oxidation by hydroxyl radicals as evidenced by pulse radiolysis experiments as well as the effect of 2-propanol. The major reaction involves the formation of an intermediate adduct $MTSM \cdot OH$. Such adduct species may disproportionate into MTSM and hydroxylated products as proposed in the literature (Scheme 2) [23]. However, since the photoproducts were only formed in the presence of oxygen, such reaction may represent a minor way. The major process could be that $MTSM \cdot OH$ adduct reacts with oxygen and leads to the formation of the four isomers and hydroperoxy radical via the formation of the short lived peroxy radical (Scheme 2).

The formation of the product P2 involves the attack of the hydroxyl radical on the methoxy group. This reaction leads to the formation of peroxy radicals, which undergoes a β -cleavage process as largely proposed in the literature (Scheme 3) [44,45]. The reduction step may involve the superoxide anion formed by trapping the electron from the conduction band.

The formation of P1 and P3 can be presented as the result of the cleavage within the sulfonyl urea bridge. Such process involves the attack of the hydroxyl radical on the carbonyl group followed by a decarboxylation reaction (Scheme 4).

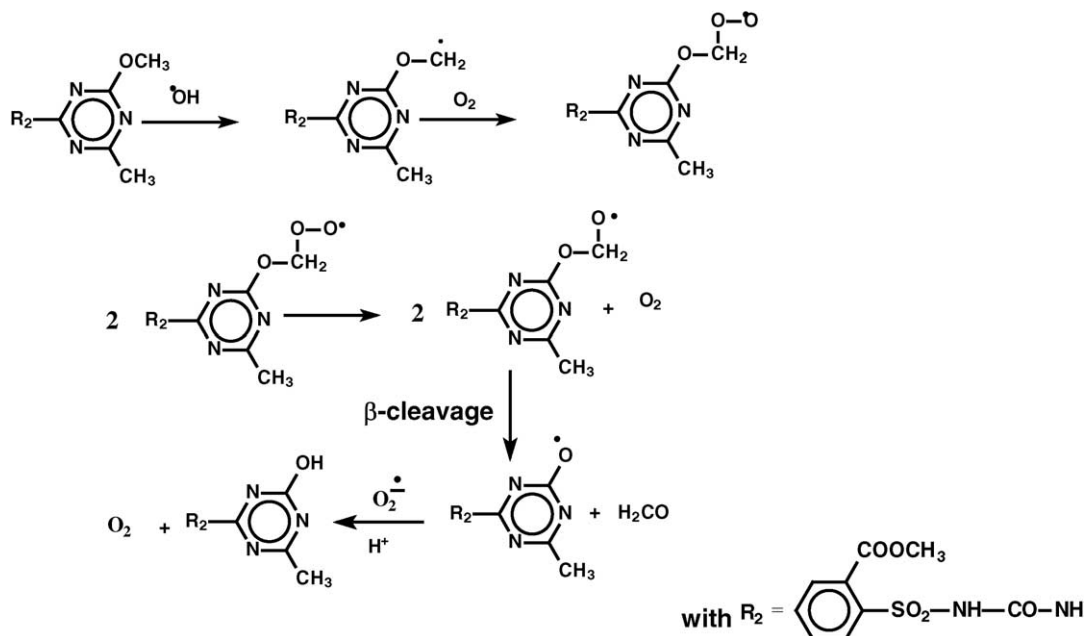


Scheme 2. Mechanism for the formation of the hydroxylated isomers of MTSM.

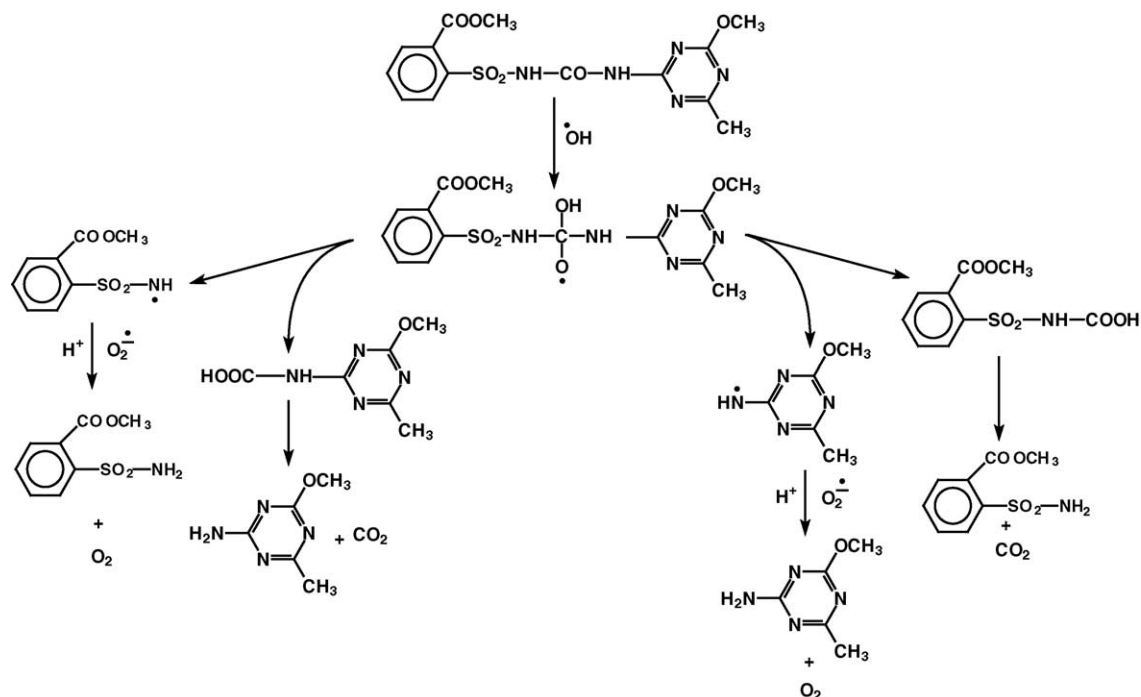
4.7. Mineralisation of MTSM

The mineralisation of MTSM was studied by following the evolution of the total organic carbon. As clearly shown in Fig. 7, the decrease of TOC was effective from the early stages of the irradiation and levelled off at a value of 4.0 mg L^{-1} after about 50 h irradiation time. The absence of the induction period may be explained by the rapid decarboxylation leading to the formation of 2-amino-4-methoxy-6-methyl-1,3-triazine (P1) and 2-(carbomethoxy) benzene-sulfonamide (P3) as

shown in Scheme 4. The incomplete mineralisation of MTSM is more likely owing to the formation of cyanuric acid (three carbon atoms are conserved) involving the triazine moiety. It was largely reported that such product accumulates in the solution and its photoinduced photodegradation is not efficient at all. The mineralisation of MTSM was also demonstrated by following the formation of inorganic ions, such as sulfates ions and ammonia ions (Fig. 7B). Such ions are formed without any induction period and reached a plateau value after 50 h irradiation time.



Scheme 3. Mechanism for demethylation process of MTSM.



Scheme 4. Mechanism for the scission of the sulfonyl urea bridge.

4.8. Degradation of MTSM in natural waters

Two different kind of natural waters were used for this study. They were collected from the rivers Allier (Clermont Ferrand, France) and Rio Mondego (Coimbra, Portugal). After filtration in order to remove solid particles, the composition of these waters in term of the concentration of the total organic carbon and some ions, such as Cl^- , SO_4^{2-} , NO_3^- , appears to be similar. As shown in Fig. 8, the irradiation of MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) in the absence of TiO_2 within the range 300–450 nm in natural water from Rio

Mondego led to a significant disappearance when compared to that in pure water. This is probably due to induced processes from irradiation of humic substances and nitrate ions [46–49]. The former lead to the formation of several reactive species, such as hydroxyl radicals, singlet oxygen, reactive triplet state while the latter leads to the formation of hydroxyl radicals. In the presence of TiO_2 , it is clear that the disappearance of the pesticide is much faster. The half-lifetime was estimated to be 400 min with water from Rio Mondego and 420 min with that from Allier. From these results, it is clear that the degradation of MTSM photoinduced by exci-

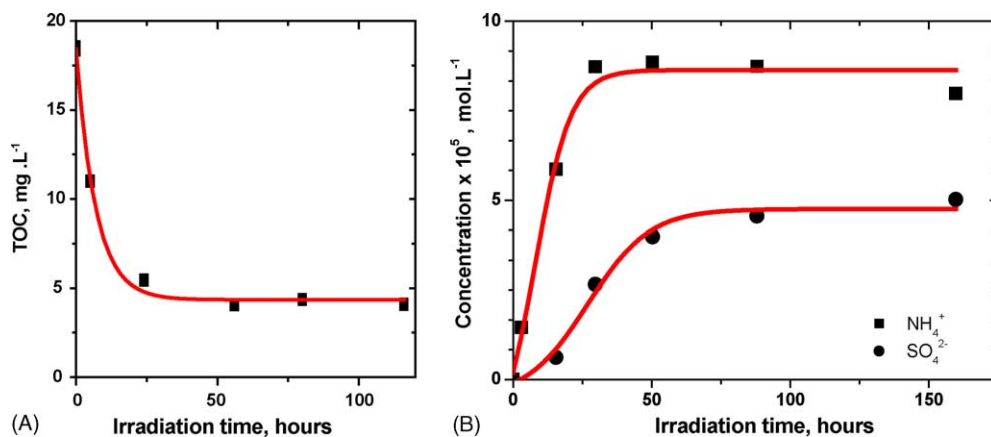


Fig. 7. Evolution of total organic carbon and the concentration of sulfate and ammonia ions as a function of irradiation time ($[\text{MTSM}] = 5.0 \times 10^{-4} \text{ mol L}^{-1}$; TiO_2 , 1.0 g L^{-1}).

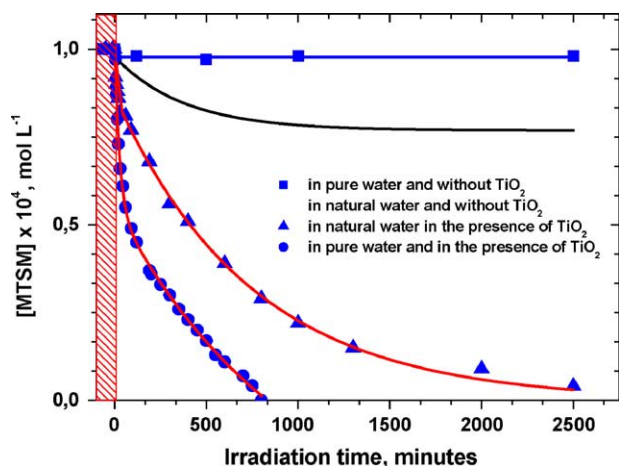


Fig. 8. Kinetics of the photocatalytic transformation of MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) with TiO_2 P25 in natural waters (from Rio Mondego river, Coimbra in Portugal) compared to that obtained in pure waters.

tation of TiO_2 in natural waters is efficient. It is important to note that the degradation was also efficient when the mixture MTSM/TiO_2 ($1.0 \times 10^{-4} \text{ mol L}^{-1}/1.0 \text{ g L}^{-1}$) was exposed to solar light during sunny days in October in Clermont-Ferrand (France, latitude 46°N , altitude 420 m above sea level).

5. Conclusion

The photocatalytic degradation of metsulfuron methyl aqueous solutions has been examined by using TiO_2 as catalyst. The efficiency was higher with Degussa P25 than with Millennium PC500. No significant adsorption was observed and the process involved the photogeneration of hydroxyl radicals. As clearly demonstrated by pulse radiolysis experiments, these reactive species add to the aromatic moiety of the pesticide leading to the formation of hydroxylated photoproducts. Two other processes were also observed: cleavage of the sulfonyl urea bridge and the demethylation of the methoxy group on the triazine part. Photocatalytic degradation of MTSM with TiO_2 by using natural waters as well as solar light was shown to be efficient.

Acknowledgments

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