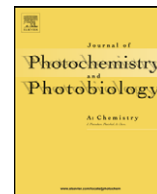




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Photocatalytic degradation of metsulfuron methyl in aqueous solution by decatungstate anions

Salah Rafqah^a, Pascal Wong-Wah Chung^a, Claude Forano^b, Mohamed Sarakha^{a,*}^a Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal, F-63177 Aubière-Cédex, France^b Laboratoire des Matériaux Inorganiques, UMR CNRS 602, Université Blaise Pascal, F-63177 Aubière-Cédex, France

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ABSTRACT

The degradation of the pesticide metsulfuron methyl was studied in aqueous solutions by using decatungstate anion, $W_{10}O_{32}^{4-}$, as a photocatalyst. An electron transfer process involving the highly oxidizing features of the decatungstate excited state, namely $W_{10}O_{32}^{4-*}$, was clearly observed. The degradation led to the oxidation of the pollutant and the formation of the decatungstate reduced species, i.e. $W_{10}O_{32}^{5-}$. In aerated as well as in oxygen-saturated solutions, the system was found to operate in a photocatalytic way with the formation of superoxide anion and the regeneration of the starting decatungstate species. The phototransformation of the pesticide metsulfuron methyl appeared to occur through three different reaction pathways involving the three main parts of the chemical structure: the aromatic ring, the sulfonylurea bridge and to a less extent the methoxy group of the triazine moiety. Under continuous excitation a partial mineralization of metsulfuron methyl was observed owing to the presence of the triazine structure. A mechanistic scheme for complete degradation of metsulfuron methyl is proposed.

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1. Introduction

Pesticides are widely used in agriculture to enhance the efficiency of food production. Annually 5 million tons of pesticides are applied to crops worldwide [1]. The drawback of the massive pesticide use is their impact on the environment which is mainly caused by possible toxic effects. Many of these chemicals present in aqueous media can undergo photochemical transformation with sunlight via direct or/and indirect photoreactions. Nowadays, Advanced Oxidation Processes (AOPs) are considered to have considerable potential in this area. They can be used as water remediation techniques that lead to the mineralization of organic pollutants through the reaction with highly oxidizing reagents such as hydroxyl radicals. The development of new photocatalysts is attracting great interest. Among them polyoxometalates (POMs) [2–5] appear to be excellent candidates. These compounds are mostly formed by metals such as tungstate, molybdenum and vanadium in their high-valent states. Several authors have clearly demonstrated that several decatungstate ions, such as $W_{10}O_{32}^{4-}$, are efficient photocatalysts for the transformation of organic compounds [6–9].

The application of tungstate-based photocatalysts was proposed by Sattari and Hill [10]. These authors clearly showed that the light excitation of $W_{10}O_{32}^{4-}$ permits the oxidation of organic compounds with an effective cleavage of the carbon–halogen bonds. Other studies demonstrated the photocatalytic efficiency of adamantane by solar irradiation [11]. This interesting application in the field of water decontamination was seriously explored by Papaconstantinou and co-workers for the photochemical degradation and also for efficient mineralization of chlorophenols as well as various chloroacetic acids [12–14]. Within this previous work, a comparative study was carried out on the photocatalytic efficiency of TiO_2 and $Na_4W_{10}O_{32}$ at $\lambda > 300$ nm. The organic pollutants used were phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid and oxamyl in aqueous solution. TiO_2 was found to be the most effective photocatalyst in terms of the degradation rate and of the mineralization of the compounds. However, decatungstate anion appeared to be relatively more efficient in the case of formulated pesticides, such as in the presence of surfactants [15]. However, since with decatungstate anions, the mineralization occurs within a longer time range, its use should be restricted only to pollutants that produce non-toxic intermediates [15].

The present work deals with the photochemical transformation pathway of the pesticide metsulfuron methyl (MTSM) by excitation of decatungstate in aqueous solution. Such compound belongs to the sulfonylurea group which presents an important role in modern

* Corresponding author.

E-mail address: mohamed.sarakha@univ-bpclermont.fr (M. Sarakha).

agriculture because of its significant action in plant protection. It presents a high selectivity against a wide range of plants. Our aim was to study the influence of various parameters, such as oxygen concentration and pH on the photocatalytic degradation and also to elucidate the structures of the intermediate photoproducts in order to have a better insight into the pesticide degradation scheme.

2. Experimental procedures

2.1. Materials

Sodium decatungstate $\text{Na}_4\text{W}_{10}\text{O}_{32}\cdot 7\text{H}_2\text{O}$ was synthesized from $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ according to the published procedure [16] and characterized by the UV–visible spectra by dissolving the powder in water. It is important to note that several recrystallisation steps were necessary to insure the purity of the compound. The obtained value of the molar absorption coefficient was found to be in perfect agreement with that reported in the literature [16]. Metsulfuron methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]benzoate was obtained from Riedel-de Haën and was used as received. 2-Amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT) and 2-(carbomethoxy)benzenesulfonamide (2-CB) were obtained from Aldrich as the purest grade available.

2.2. Irradiations and analysis

Irradiation experiments (365 nm) were carried out in an elliptical stainless steel cylinder. A high-pressure mercury lamp (Philips HPW, 125 W) was located at a focal axis of the elliptical cylinder. An inner filter selected the emission at 365 nm permitting the selective excitation of the photocatalyst. The reactor (water-jacketed pyrex tube—diameter 2.8 cm) was centred at the other focal axis. The solution (60 mL) was continuously stirred with a magnetic bar during irradiation. For the determination of the quantum yields, solutions were irradiated at 365 nm in the parallel beam obtained from a Schoeffel monochromator equipped with a xenon lamp (1600 W). The beam was parallel and the reactor was a quartz cell of 2 cm path length. The photon flow was evaluated by means of classical ferrioxalate actinometry [17]. The quantum yield was evaluated by the following ratio:

$$\Phi = \frac{\text{number of degraded molecules of pesticide}}{\text{number of photons absorbed by the catalyst}}$$

The disappearance of metsulfuron methyl and the formation of the byproducts were followed by high performance liquid chromatography using a Waters 540 HPLC chromatograph system equipped with a Waters 996 photodiode array detector. The experiments were performed by UV detection at either 250 or 280 nm and by using a reverse phase Nucleodur column (C_{18} -5 μm ; 250–4.6 mm). The flow rate was 1.0 mL min^{-1} and the injected volume was $50\ \mu\text{L}$. The elution was accomplished with water, acetic acid (0.1%) and acetonitrile (60/40, v/v).

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 μm) and a 60/40 (v/v) mixture of acetonitrile and water with 0.2% acetic acid as mobile phase at 1 mL min^{-1} . Samples (5–10 μL) were injected either directly or after solid-phase extraction on Oasis HLB cartridges (Waters). 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 , desolvation gas temperature 400°C . Argon was used for collision activated dissociation (CAD) at a pressure of 1.5×10^{-3} torr and 10–50 eV collision energy.

The evolution of ions concentration as a function of irradiation time was obtained by ionic chromatography using a Gilson 305 pump equipped with a Waters 431 conductivity detector. The flow was adjusted to 1.0 mL min^{-1} . The system was equipped with either:

- a Hamilton cationic column (PRP-X200) for the detection of cations using HNO_3 ($2.0 \times 10^{-3}\text{ mol L}^{-1}$)/methanol (7/3, v/v) as eluent or
- an IC-PAK anion HC column from waters (4.6 mm \times 150 mm) for the detection of the anions. The elution was accomplished according to Waters 431 conductivity manual specifications. First solution A is prepared as follows: 851.5 mL deionised ultrapure water + 23.5 mL gluconic acid solution (50%, w/w) + 8.6 g lithium hydroxide + 34.0 g boric acid + 250 mL glycerin. The final elution mixture is prepared by adding 20 mL of solution A to 500 mL of deionised ultrapure water under stirring. Then addition of 20 mL *n*-butanol and 120 mL acetonitrile, and finally addition of remaining water (340 mL).

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

3. Results and discussion

3.1. Kinetics of metsulfuron methyl degradation

The absorption spectrum of the mixture metsulfuron methyl ($1.0 \times 10^{-4}\text{ M}$) with decatungstate anions, $\text{W}_{10}\text{O}_{32}^{4-}$ ($1.0 \times 10^{-4}\text{ M}$) at pH 5.5, was shown to be equal to the sum of the component spectra. This clearly indicates that under the conditions of our experiments no significant ground state interaction between $\text{W}_{10}\text{O}_{32}^{4-}$ and the pesticide was present. The mixture was found to be stable when stored in the dark and at room temperature, namely 22°C .

The evolution of MTSM ($1.0 \times 10^{-4}\text{ mol L}^{-1}$) degradation in aerated aqueous solution in presence and absence of $\text{W}_{10}\text{O}_{32}^{4-}$ ($2.5 \times 10^{-4}\text{ mol L}^{-1}$) and upon excitation at 365 nm was carried out by HPLC measurements (Fig. 1). In the absence of the photocatalyst, no significant degradation of the pesticide was observed under irradiation in complete agreement with the fact that MTSM does not

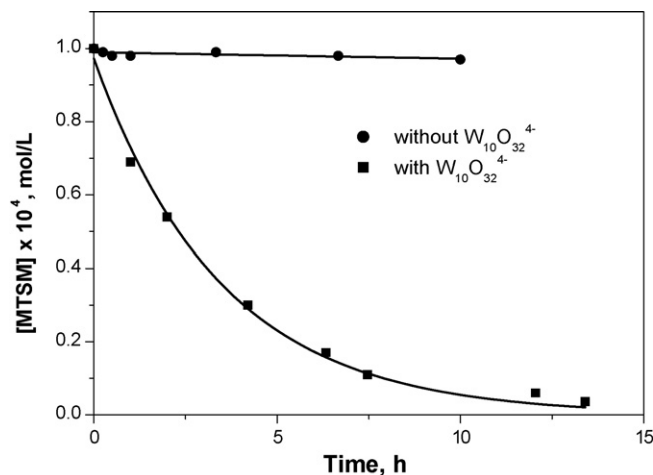


Fig. 1. Kinetic of the photodegradation of MTSM ($1.010^{-4}\text{ mol L}^{-1}$) with and without photocatalyst $\text{W}_{10}\text{O}_{32}^{4-}$ ($2.5 \times 10^{-4}\text{ mol L}^{-1}$).

significantly absorb at $\lambda > 315$ nm. However and under our experimental conditions, a total disappearance of MTSM was achieved after roughly 13 h of irradiation in the presence of $W_{10}O_{32}^{4-}$. The decay appeared to follow a first order kinetics with an estimated rate constant of $4.8 \times 10^{-3} \text{ min}^{-1}$.

It has to be pointed out that in order to have a better insight in the nature of reactive species implicated in the degradation process, the irradiation of the mixture $W_{10}O_{32}^{4-}$ /MTSM was performed in the presence of 2-propanol. The concentration of the alcohol was adjusted to be roughly one order of magnitude higher than that of MTSM, namely $1.0 \times 10^{-3} \text{ mol L}^{-1}$. Within these conditions, the irradiation leads to the complete inhibition of the degradation process in aerated as well as in oxygen-saturated solution. Such results clearly indicate that the reactive species was efficiently trapped by 2-propanol in perfect agreement with the implication of an electron or hydrogen abstraction process involving the decatungstate excited state and leading to the formation of reduced form of, $W_{10}O_{32}^{5-}$. Such reactive species was largely reported in the literature as an efficient oxidant species. The oxidation potential was estimated to be $\leq 2.23 \text{ V}$ vs. NHE [18].

3.2. Effect of oxygen concentration

In several studies, the oxygen was shown to play an important role in photocatalytic processes employing several types of photocatalysts [19,20]. In order to understand its own role in the decatungstate system, a solution of metsulfuron methyl was irradiated with three different oxygen concentrations, namely aerated, oxygen free and oxygen-saturated solutions. Fig. 2 clearly shows that oxygen played a major role in the disappearance of the pesticide. The degradation rate increased by increasing the oxygen concentration. The rate constants in oxygenated and aerated solutions were evaluated to be 7.1×10^{-3} and $4.8 \times 10^{-3} \text{ min}^{-1}$ respectively.

It is worth to note that in oxygen free medium, the degradation of MTSM rapidly levelled after 10% conversion. Such low conversion is more likely due to some residual oxygen left in the solution after nitrogen bubbling. Moreover, we can also point out that in oxygen free solution, a rapid appearance of a high wavelength absorption band with a maximum at 780 nm was observed in agreement with the development of a blue color in the irradiated solution (Fig. 3). This corresponds to the formation and accumulation of the reduced species of decatungstate, i.e. $W_{10}O_{32}^{5-}$. Such

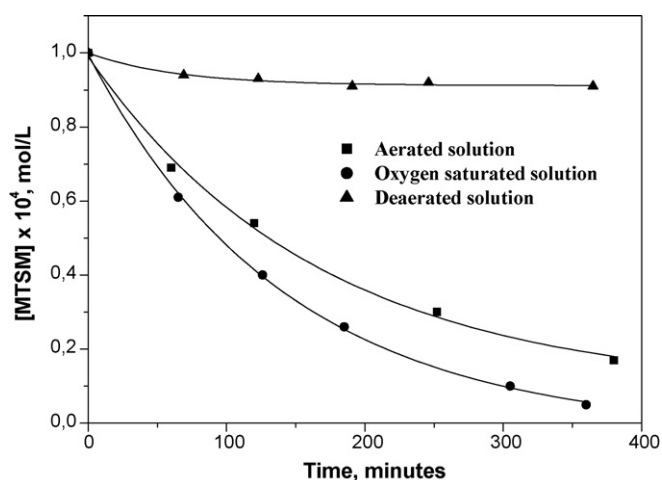


Fig. 2. Influence of the oxygen concentration on the photodegradation of MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) upon irradiation in the presence of decatungstate ion ($2.5 \times 10^{-4} \text{ mol L}^{-1}$).

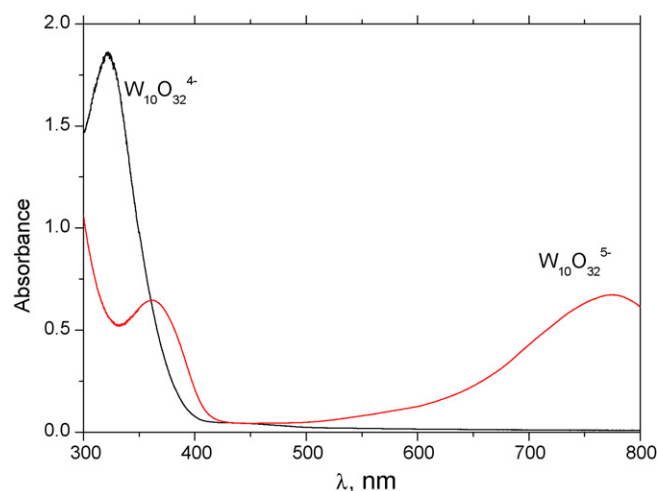


Fig. 3. Absorption spectrum of decatungstate anion and its reduced form obtained by irradiation at 365 nm of the mixture MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$)/decatungstate ion ($2.5 \times 10^{-4} \text{ mol L}^{-1}$) in oxygen free solution.

band immediately disappeared when the solution was aerated permitting the regeneration of the starting form of the photocatalyst, $W_{10}O_{32}^{4-}$.

The role played by oxygen on the pesticide degradation process was quantified by the determination of the MTSM disappearance quantum yields as a function of oxygen concentration (Table 1). The quantum yield was found to be one order of magnitude higher in aerated solution than in oxygen free solution. As usually observed in the case of several photocatalysts, the presence of oxygen represents a key condition for achieving the total degradation of the pesticide MTSM [21]. It is worth noting that, as clearly observed in Table 1 and in Fig. 2, bubbling oxygen in the solution did not improve the process. This is more likely owing to the fact that in aerated solution, the oxygen concentration was sufficient for the regeneration of the starting form of the photocatalyst.

3.3. Effect of pH

The effect of pH can represent an important parameter in the photocatalytic system. It is related to the thermal stability of the photocatalyst and also of the pollutants and may also have an important effect in the progress of the photochemical reactions. Because of these considerations, we studied the kinetics of metsulfuron methyl disappearance in presence of decatungstate anions under various pH conditions (Fig. 4). The absorption spectrum of decatungstate anion does not change significantly for $\text{pH} < 8$. However, the changes observed at higher value of pH are mainly due to the lack of stability. As shown in Fig. 4, the degradation rate was found to be constant for $\text{pH} < 6.9$ while the process is completely inhibited in basic media more likely owing to the stability of the photocatalyst. It is well known that $W_{10}O_{32}^{4-}$ requires a precise

Table 1

Quantum yield of MTSM photodegradation in aerated, de-aerated and oxygen-saturated solutions in the presence of decatungstate ion

Experimental conditions	$[O_2]$ (mol L^{-1})	Φ_{MTSM}
Oxygen-saturated solution	1.29×10^{-3}	2.29×10^{-3}
Aerated solution	2.64×10^{-4}	1.98×10^{-3}
De-aerated solution	$< 10^{-5}$	2.0×10^{-4}

The values correspond to an average of three determinations and are affected of errors equal to or less than 10%.

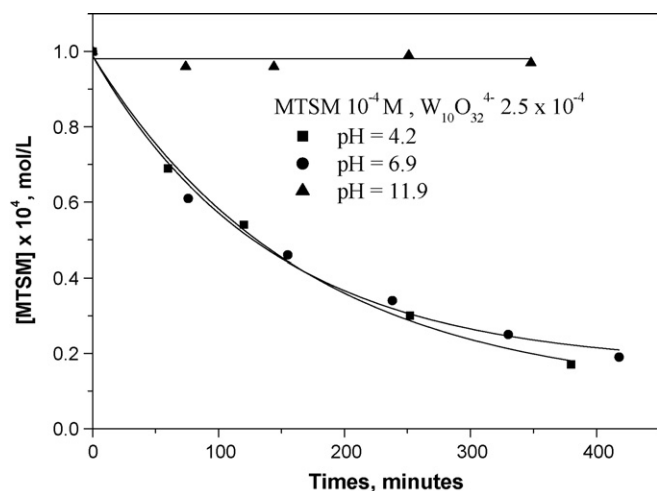


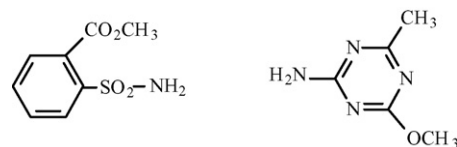
Fig. 4. Influence of pH on the photodegradation of MTSM ($1.0 \times 10^{-4} \text{ mol L}^{-1}$) in presence of decatungstate anion ($2.5 \times 10^{-4} \text{ mol L}^{-1}$) in aerated solution.

control of pH in aqueous solution, as it may lead to $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ or/and $\text{W}_7\text{O}_{24}^{6-}$ which absorb at lower wavelengths [22]. Hence, the maximum adsorption and consequently maximum efficiency in the degradation process was observed in acid and also in neutral solutions.

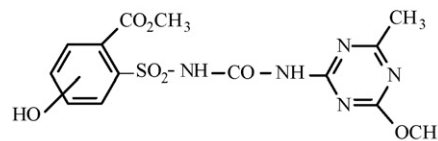
3.4. Photoproducts elucidation and mechanism

The irradiated solutions were analyzed by HPLC after 30% conversion of MTSM (Fig. 5). Different photoproducts were identified by using HPLC/MS technique with electrospray ionisation in positive mode. Several products were similar to those already identified in previous studies of metsulfuron methyl which were undertaken in presence of iron(III) aquacomplexes [22] and of titanium dioxide [23] as photocatalysts.

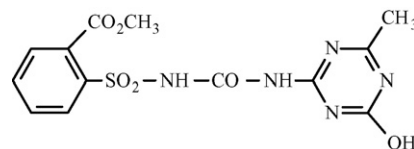
The main identified photoproducts are 2-(carbomethoxy) benzenesulfon-amide and 2-amino-4-methoxy-6-methyl-1,3,5-triazine with retention times of 3.4 and 5.8 min respectively. Since these compounds are commercial, their presence was confirmed by comparison of HPLC retention times and diode array spectra with those of authentic samples.



Four compounds with retention times between 7 and 8 min were elucidated by interpretation of the mass spectra but two of them were minor and only detected by LC/MS/MS showing that two different sites are more reactive. They exhibited the molecular ion peak at $m/z = 398$ and three fragment ions at $m/z = 167$, 141 and 151 which correspond to the hydroxylated products on the aromatic ring.



The compound eluted at $t_{\text{ret}} = 4.8 \text{ min}$, was identified as a demethylated product involving the methoxy group of the triazine moiety of MTSM. It exhibited the molecular ion at $m/z = 199$ together with the fragment ions at $m/z = 153$, 135 and 127.



The mechanistic scheme for the formation of these compounds may be presented as follows: the excitation of decatungstate anion in the presence of the pollutant leads to the formation of the reduced form of the catalyst, namely $\text{W}_{10}\text{O}_{32}^{5-}$, together with the radical cation of the pollutant (Scheme 1). The regeneration of the photocatalyst can operate in the presence of oxygen leading to the formation of the superoxide anion.

The inhibition of the MTSM degradation process in the presence of 2-propanol can be explained by an efficient reactivity of the alcohol with the decatungstate excited state through a hydrogen atom transfer leading to the formation and the accumulation of

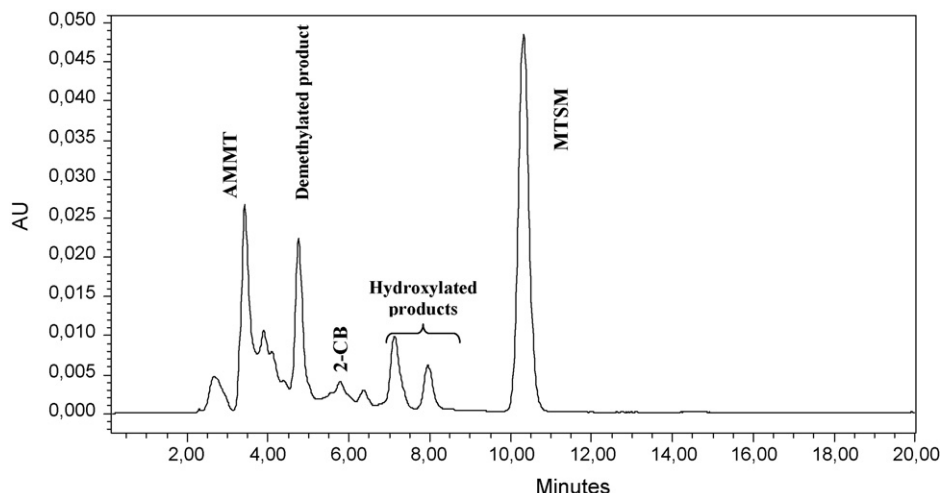
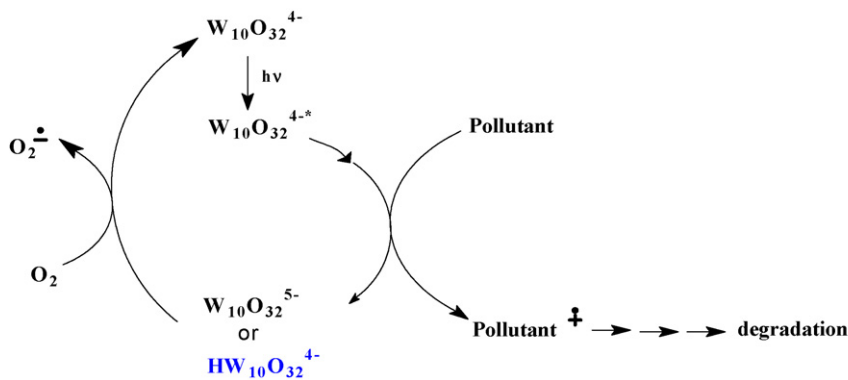


Fig. 5. HPLC chromatogram of an aqueous solution of MTSM after 30% conversion extent ($[\text{MTSM}] = 1.0 \times 10^{-4} \text{ mol L}^{-1}$; $[\text{W}_{10}\text{O}_{32}^{4-}] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$) in aerated solution.



Scheme 1.

$\text{HW}_{10}\text{O}_{32}^{4-}$ evidenced by the development of the band at 780 nm. This aspect excludes the participation of the hydroxyl radicals in the process even though these radicals are reported to be involved in some studies [14,24].

Based on the structure identification of the photoproducts, an electron transfer or/and hydrogen atom transfer process can be proposed. Such photocatalytic degradation pathway of MTSM involves several pathways (Scheme 2).

The AMMT and 2-CB are obtained from either wrenching of H^{\bullet} or electron transfer from the sulfonylurea bridge by the excited state species, i.e. $\text{W}_{10}\text{O}_{32}^{4-*}$. This attack leads to the cleavage of the bridge followed by a decarboxylation reaction (pathway 1).

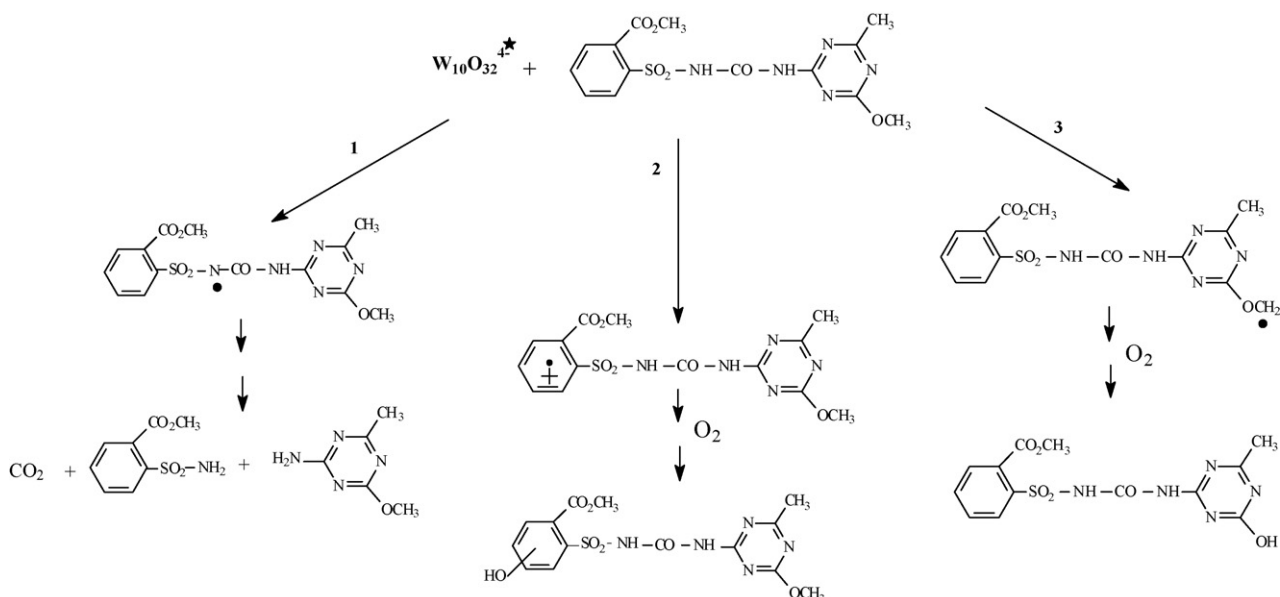
The formation of hydroxylated and demethylated products requires the presence of oxygen. An electron transfer process involving the aromatic ring and $\text{W}_{10}\text{O}_{32}^{4-*}$ results in the formation radical cation. In the presence of oxygen, the radical cation leads to four hydroxylated isomers (pathway 2).

In the case of the demethylated byproduct, its formation involves the attack of the $\text{W}_{10}\text{O}_{32}^{4-*}$ on the methoxy group. This reaction permits the formation of peroxy radicals through undergoes a β -cleavage process (pathway 3).

3.5. Mineralization process

The kinetics of the total mineralization of MTSM was followed using the total organic carbon (TOC) measurements (Fig. 6). During irradiation, a rapid decrease in TOC was observed, corresponding to the scission and oxidation of sulfonylurea bridge [22,25]. TOC rapidly disappeared and levelled off at a value of 4.5 mg L^{-1} after about 200 h irradiation time. Such level value clearly indicates the persistence of an organic photoproduct more likely arising from the triazinic part of MTSM. The formation of cyanuric acid, very stable towards oxidative attacks [26,27] may be considered as an ultimate organic product of the degradation can be proposed.

We also followed the formation of ammonia, nitrate and sulfates ions by ionic liquid chromatography. As shown in Fig. 7, an increase in the concentration of sulfates from the early stages of the irradiation was observed indicating an important photocatalytic cleavage of the sulfonylurea bridge. The concentration of sulfate ions reached a plateau value at $6.3 \times 10^{-5} \text{ mol L}^{-1}$ corresponding to more than 63% of sulfur atom present in the molecule. This result can be explained, either by the formation of small molecules containing sulfur, or by the direct transformation into SO_2 during degradation [28]. After 3 h of irradiation, the concentrations ammonia ions

Scheme 2. Proposed mechanism for the photocatalytic transformation of metsulfuron methyl in the presence of $\text{W}_{10}\text{O}_{32}^{4-}$.

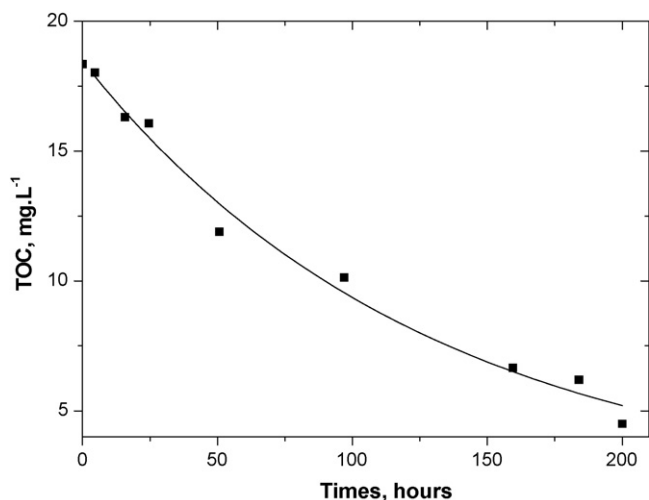


Fig. 6. The evolution of TOC as a function of irradiation time ($[MTSM] = 1.0 \times 10^{-4} \text{ mol L}^{-1}$; $[W_{10}O_{32}^{4-}] = 2.5 \times 10^{-4} \text{ mol L}^{-1}$).

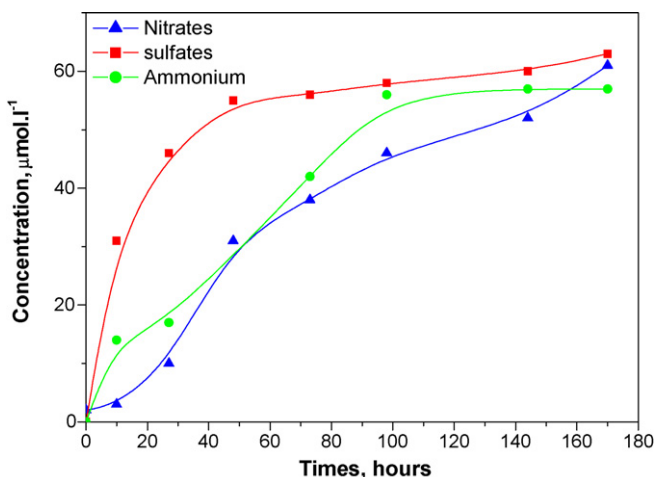


Fig. 7. Formation of inorganic ions (nitrates, sulfates and ammonium) upon irradiation of MTSM ($10^{-4} \text{ mol L}^{-1}$) in the presence of decatungstate anion ($2.5 \times 10^{-4} \text{ mol L}^{-1}$).

reached a plateau at $6.1 \times 10^{-5} \text{ mol L}^{-1}$ while that of nitrate kept increasing. The values obtained at 3 h irradiation time, 6.1×10^{-5} and $5.7 \times 10^{-5} \text{ mol L}^{-1}$ for nitrate and ammonia respectively, correspond to 60% of the nitrogen atoms in the sulfonylurea bridge (the expected value is $2.0 \times 10^{-4} \text{ mol L}^{-1}$). Such results are in complete agreement with those obtained by TOC measurements indicating the persistence of the cyanuric acid compound.

4. Conclusion

The total degradation of the pesticide metsulfuron methyl was obtained using the photocatalyst, decatungstate anion. In oxygenated solutions, an efficient electron transfer process occurred and led to the mineralization of the pesticide. Such degradation involved the intermediate formation of several primary photo-products originating from different processes, e.g. hydroxylation, demethylation and the scission of the sulfonylurea bridge.

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