



Kinetics and the mechanism of the photocatalytic degradation of mesotrione in aqueous suspension and toxicity of its degradation mixtures

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ABSTRACT

The photocatalytic degradation of the herbicide mesotrione (0.05 mM) in aqueous suspensions of TiO₂ Degussa P25 and ZnO was examined as a function of the different operational parameters. The optimum of the catalyst loading was found to be 2.00 mg mL⁻¹ under UV light at the pH 4.0 (TiO₂ Degussa P25) and pH 9.2 (ZnO). In the first stage of the reaction, the photocatalytic degradation of mesotrione followed the pseudo-first order kinetics, in which the heterogeneous catalysis proceeds mainly via •OH radicals, and partly also via holes. The results showed that the disappearance of mesotrione led to the formation of a number of organic intermediates and ionic byproducts, whereas its complete mineralization occurred after about 4 h. Tentative photodegradation pathways were proposed and discussed as a function of the type of photocatalyst. A comparison of the evolution of toxicity that was evaluated *in vitro* in the rat hepatoma (H-4-II-E) and human fetal lung (MRC-5) cell lines with the degradation kinetics indicates that the cell growth of both cell lines was only mildly affected by the mixture of mesotrione and its photocatalytic degradation intermediates obtained using TiO₂ Degussa P25, and moderately affected by the mixtures obtained using ZnO, whereby at 120 min toxicity decreased.

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1. Introduction

Not so long ago, atrazine (6-chloro-*N*²-ethyl-*N*⁴-isopropyl-1,3,5-triazine-2,4-diamine), one of the most popular herbicides among the triazine group, was introduced as an herbicide to control weeds in corn fields. Numerous studies showed that atrazine is toxic to aquatic organisms [1]. Since atrazine has been banned in the European Union countries since 2007, mesotrione {2-[(4-methylsulfonyl)-2-nitrobenzoyl]cyclohexane-1,3-dione} appeared as a new selective herbicide for use in corn, which has been substituted for atrazine [2]. Mesotrione is an herbicide from the family of benzoyl-cyclohexanedione, to control wide spectrum of broad leaf weeds, especially in corn farming. It was

developed by the company Syngenta Crop Protection and it was registered in Europe in 2000, and in the United States in 2001 [3]. The herbicide is marketed under the name Callisto®.

Mesotrione is a hot research topic since it is a relatively new substance on the market, still insufficiently investigated. Also, little is known about its intermediates and metabolites. Further, there is still insufficient data about the pathway of its degradation in nature and about toxicity of its intermediates. As far as the persistence of mesotrione in soil is concerned, Rouchaud et al. [4] reported results of their investigation based on a three-month study, carried out at four different places in Belgium with different soil composition. This study showed that in the soil surface layer of 0–10 cm there was 90% of the applied dose of mesotrione, whereas in the layers at the depths of 15–20 cm it could not be detected. According to the report of the European Commission from 2003, mesotrione is stable in water in the presence of light (DT₅₀) for about 90 days [5]. A survey of the literature shows that there are only few studies concerning the decomposition of this herbicide and the herbicides from the same family, whereas the photocatalytic degradation of mesotrione has not been reported yet. Recently, removal

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of mesotrione in aqueous medium by photolysis with simulated natural sunlight irradiation [6,7] and UV-B light [6], Fenton process [8], and electro-Fenton [9] has been reported. However, photocatalysis with UV and TiO₂/ZnO, one of the most promising advanced oxidation processes for the destruction of aquatic pollutants, as well as the toxicity of mesotrione and its photocatalytic degradation byproducts in mammalian cell lines has not been reported. One of the most important aspects of environmental photocatalysis is the selection of semiconductor materials such as TiO₂ and ZnO, two ideal photocatalysts in several respects. For example, they are relatively inexpensive and, due to their wide band gap energy, provide photogenerated holes with high oxidizing power. Since ZnO has nearly the same band gap energy (3.2 eV) as TiO₂, its photocatalytic capacity is anticipated to be similar to that of TiO₂.

The objective of this work was to monitor the kinetics of photocatalytic degradation of mesotrione in the presence of TiO₂ Degussa P25 and ZnO as photocatalysts, by irradiation of aqueous suspensions using mercury and halogen lamps, as well as natural sunlight, under different conditions of the catalyst load and pH of the solution. An attempt was also made to identify the reaction intermediates formed during the photo-oxidation process, using the LC-ESI-MS/MS technique. Also, the effect of mesotrione and its photocatalytic degradation intermediates on cell growth activity was evaluated *in vitro* in two mammalian cell lines.

2. Experimental

2.1. Chemicals, catalysts and solutions

All chemicals were of reagent grade and were used without further purification. Mesotrione (C₁₄H₁₃NO₇S, 99.9%, *M_r* = 339.3, CAS No 104206-82-8), 98.9%, pestanal quality, was manufactured by Fluka; 85% H₃PO₄ was obtained from Lachema (Neratovice, Czech Republic), Na₂SO₃ and NaOH from ZorkaPharm (Šabac, Serbia). Of the other chemicals, 96% ethanol was obtained from Centrom (Stara Pazova, Serbia), and 98–100% formic acid (HCOOH) and 60% HClO₄ from Merck, while 99.8% acetonitrile (ACN) and HPLC gradient grade methanol (MeOH) were products of J.T. Baker. All solutions were made using doubly distilled water (DDW). The pH of the reaction mixture was adjusted using a dilute aqueous solution of HClO₄ or NaOH. Dulbecco's modified Eagle's medium (DMEM), and fetal calf serum were purchased from PAA Laboratories GmbH (Pasing, Austria), penicillin and streptomycin from Galenika (Belgrade, Serbia), trypsin from Serva (Heidelberg, Germany), EDTA, trichloroacetic acid (TCA) from Laphoma (Skopje, FYR Macedonia), and tris(hydroxymethyl)amino methane from Sigma Aldrich.

TiO₂ Degussa P25 (75% anatase and 25% rutile form, 50 m² g⁻¹, about 20 nm, non-porous), TiO₂ Hombikat, anatase (Sigma-Aldrich), TiO₂, rutile [10] and ZnO (Kemika, 99.96%) were used as photocatalysts.

2.2. Photodegradation procedure

Photocatalytic degradation was carried out in a cell made of Pyrex glass (total volume of ca. 40 mL, liquid layer thickness 35 mm), with a plain window on which the light beam was focused. The cell was equipped with a magnetic stirring bar and a water circulating jacket. A 125 W high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm), together with an appropriate concave mirror, was used as the radiation source. Irradiation in the visible spectral range was performed using a 50 W halogen lamp (Philips). The outputs for the mercury and halogen lamps were calculated to be ca. 8.8 × 10⁻⁹ Einstein mL⁻¹ min⁻¹ and 1.7 × 10⁻⁹ E mL⁻¹ min⁻¹ (potassium ferrioxalate actinometry),

respectively. With the aim of examining the use of natural sunlight, the experiments were also carried out at daylight during the whole day (23 ± 1 °C) in the presence/absence of the catalyst, from February 1st to September 15th 2011.

The experiments were carried out using 20 mL of 0.05 mM solution of mesotrione containing 40 mg of TiO₂ Degussa P25 (except for the study of the effect of catalyst load and direct photolysis). After that, the aqueous suspension of TiO₂ Degussa P25 was sonicated (50 Hz) in the dark for 15 min before illumination, to make distribution of the photocatalyst particles uniform and attain adsorption equilibrium. The suspension thus obtained was thermostated at 25 ± 0.5 °C, and then irradiated at a constant stream of O₂ (3.0 mL min⁻¹). During the irradiation, the mixture was stirred at a constant speed. The control experiments, carried out under O₂ flow but by stopping the irradiation, showed that there were no losses of volatile compounds during the degradation. All experiments were performed at the natural pH (~4.0), except when studying the influence of the pH. Where applicable, ethanol (so that its concentration after the addition was 0.34 M) was added as a hydroxyl radical scavenger and Na₂SO₃ as hole scavenger (so that the concentration of sulfite after the addition was 3 mM).

Photonic efficiencies ζ have been calculated using the following equations:

$$\zeta = \frac{\text{degradation rate}[\text{mol s}^{-1}]}{\text{photon flux}[\text{mol h}^{-1} \text{v s}^{-1}]} \times 100\% = \frac{V \times \Delta c}{I_0 \times A \times \Delta t} \times 100\% \quad (1)$$

$$I_0 = \frac{I \times \lambda}{N_A \times h \times c} \quad (2)$$

where *V* is the volume of the suspension in reactor (20.0 cm³), $\Delta c/\Delta t$ the degradation rate, *A* the illuminated area (9.60 cm²), *I*₀ the photon flux, *I* is the light intensity (53.04 W m⁻²), λ is 366 nm, *N_A* is Avogadro's constant, *h* is Planck's constant and *c* is the velocity of light.

2.3. Analytical procedures

For the kinetic studies of the mesotrione photodegradation, samples of the reaction mixture were taken at the beginning of the experiment and at regular time intervals (volume variation ca. 10%). The obtained suspensions were filtered through Millipore (Millex-GV, 0.22 μm) membrane filters. The preliminary check confirmed the absence of mesotrione adsorption on the filters. After that, a 20-μl sample was injected and analyzed on an Agilent Technologies 1100 Series liquid chromatograph, with a UV/VIS DAD set at 225 nm (maximum of absorption for mesotrione), as well as at 210, 260, 270 and 280 nm (for intermediates) and an Eclipse XDB-C18 (150 mm × 4.6 mm i.d., particle size 5 μm, 25 °C) column. The mobile phase (flow rate 1 mL min⁻¹, pH 2.6) was a mixture of ACN and DDW (4:6, v/v), the water being acidified with 0.1% H₃PO₄.

For the spectrophotometric monitoring, samples were prepared in the same way as for LC measurements, and the corresponding aliquots were acidified with cc HClO₄ to the pH 2.6, and UV spectra were recorded on a T80 +UV-vis Spectrophotometer, PG Instruments Ltd (UK), at a fixed slit width (2 nm), using 1 cm quartz cell and computer-loaded UV Win 5 data software. Kinetics of the aromatic ring degradation was monitored at 225 nm.

Ion chromatographic (IC) determinations were performed on a Dionex ICS 3000 Reagent-Free IC system with conductometric detector. For the anion determinations use was made of an Ion-Pac AS18 analytical column (250 mm × 4 mm i.d., bead diameter 8 μm). The mobile phase was a solution of KOH (20–40 mM) at a flow rate of 1 mL min⁻¹. Cations were determined using an Ion-Pac CS12A analytical column (250 mm × 4 mm i.d., bead diameter 7.5 μm), and the mobile phase was a solution of 40 mM of methane sulfonic acid at a flow rate of 1 mL min⁻¹.

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