



# Photocatalytic mitigation of triazinone herbicide residues using titanium dioxide in slurry photoreactor



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## ABSTRACT

Heterogeneous photocatalysis offers an alternative for the treatment of wastewater containing refractory pollutants. The photocatalytic degradation of metamitron and metribuzin, asymmetrical triazine compounds used worldwide as herbicides, was investigated in aqueous suspension of different commercial TiO<sub>2</sub> nanopowders with different composition of anatase/rutile phases, using artificial UV-A light. In addition, we have studied the role of the most important operating parameters (catalyst loading, effect of electron acceptor, pH, light intensity, initial concentration of pollutants, and interfering substances) on the photooxidation of both herbicides. TiO<sub>2</sub> P25 (70% anatase/30% rutile) was found to be highly active for herbicide decomposition. The progress of photocatalytic degradation of both herbicides has been observed by monitoring the change in substrate concentration using HPLC/MS<sup>2</sup>. Results showed that the addition of TiO<sub>2</sub> in tandem with an electron acceptor like Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> strongly enhances the degradation rate of metamitron and metribuzin in comparison with photolytic test. The degradation of these herbicides followed a pseudo-first order kinetics. The time required for 50% degradation was lower than 8 min for both. Thus, complete disappearance was achieved after 30 min of illumination in the TiO<sub>2</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. Both herbicides were rapidly deaminated.

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## 1. Introduction

Modern agriculture depends to a large degree on the use of pesticides. All pesticides are subject to an approval procedure under EU legislation, and often under national legislation. Plant Protection Products Regulation 1107/2009 and the Sustainable Use Directive 2009/128/EC are essential elements in this context. However, some risks are inevitable because the use of pesticides has an impact on the natural environment through spray drift, leaching and run-off into water, or even affect non-target organisms.

The pollution of water bodies with agrochemical products can pose a significant threat to aquatic ecosystems and drinking water resources. More specially, triazine compounds have been among the most widely used pesticides in recent decades [1]. As a consequence, their residues are the most commonly recovered in water. The decrease in triazine usage in Europe is chiefly due to legal provisions limiting the use of these products. The banning of triazines in the EU was precipitated mainly by the fact that water sources can

be seriously contaminated by some of them. Triazine parent compounds and their metabolites have been detected in surface and groundwater in several European countries and USA [2–4]. However, other authorized compounds of this class, such as metribuzin and metamitron (asymmetrical triazine class), which are used worldwide as herbicides, are chemically stable and can penetrate through the soil and cause long-term pollution of ground water [5].

The triazinones forms a small group of herbicides developed in the 1970s for the pre- and postemergence control of grasses and broad-leaved weeds. Both metribuzin and metamitron inhibit photosystem II and are similar to s-triazines in this respect. The as-triazines are not acutely toxic but metribuzin causes liver toxicity at high doses in mice. Both compounds are deaminated photochemically, chemically, and biochemically [6]. The S-methyl group of metribuzin compared with the methyl group of metamitron is the most important distinguishing feature between the two herbicides. Both are highly water soluble and adsorption in low-organic sandy soils is rather weak.

Numerous studies have demonstrated that pollutants can be removed from wastewater by advanced oxidation processes (AOPs) such as O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV, homogeneous photo-Fenton, and heterogeneous photocatalysis [7,8]. AOPs have been

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broadly defined as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical ( $\cdot\text{OH}$ ), as the primary oxidant while the other radical and active oxygen species are superoxide radical anions ( $\text{O}_2^{\cdot-}$ ), hydroperoxyl radicals ( $\text{HO}_2^{\cdot-}$ ), triplet oxygen ( $^3\text{O}_2$ ), and organic peroxy radicals ( $\text{ROO}^{\cdot-}$ ). Clearly, the  $\cdot\text{OH}$  radical ( $E^0 = 2.8\text{V}$ ) is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation. Among AOPs, heterogeneous photocatalysis is a process of great potential for pollutant abatement in water. The basic principles of this process have been extensively reviewed in the recent literature [9–13]. This treatment allows the degradation and in most cases, the complete mineralization of some triazine herbicides [14,15]. The photocatalytic degradation of these compounds is largely dependent on the mass, composition and type of photocatalyst, pollutant type and initial concentration, interfering substances, solution pH, wavelength and light intensity and oxidizing agents/electron acceptors. An ideal photocatalyst is characterized by photo-stability, biologically and chemically inert nature, low cost and availability, and capability to adsorb reactants under efficient photonic activation ( $h\nu \geq E_g$ ).  $\text{TiO}_2$  (mainly anatase/rutile mixture) is the most widely photocatalyst studied [16].

In this view, the aim of this paper was to assess the photoactivity of  $\text{TiO}_2$  on the degradation of two triazinone (*as*-triazine) herbicides, metamitron and metribuzin, under artificial light. For this purpose, we have studied the role of the most important operating parameters (proportion of anatase/rutile, catalyst loading, effect of electron acceptor, pH, light intensity, initial concentration of pollutants, and interfering substances) on the photooxidation of both herbicides.

## 2. Materials and methods

### 2.1. Herbicides and reagents

Metamitron (MM) and metribuzin (MB) with purity >98% were purchased from Dr Ehrenstorfer (Augsburg, Germany). Titanium dioxide anatase (99.9%), titanium dioxide mixture of rutile and anatase (99.5%) and titanium dioxide P25 Degussa (99.5%) were purchased from Alfa Aesar (Karlsruhe, Germany), Sigma–Aldrich Química S.A. (Madrid, Spain) and Nippon Aerosil Co. Ltd. (Osaka, Japan), respectively. Sodium peroxydisulfate (98%) was purchased from Panreac Química (Barcelona, Spain). Acetonitrile was supplied by Scharlau (Barcelona, Spain).

### 2.2. Photocatalyst characterization

The photocatalysts were characterized by a PerkinElmer Lambda 750S UV/VIS spectrophotometer equipped with a PerkinElmer 60mm integrating sphere accessory for diffuse reflectance spectra. Software: UV WinLab DPV 1.0 (Shelton, USA). A  $\text{BaSO}_4$  standard was used as the reference spectrum. The crystalline structure of the photocatalysts was characterized by means of powder X-ray diffractometry (XRD), on a Philips PW 1700. The samples were measured at 40 kV and 24 mA using  $\text{Cu-K}\alpha$  radiation at a scanning speed of  $1^\circ (2\theta)$ . The morphology of the solids was examined by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss MERLIN VP Compact microscope (Oberkochem, Germany) with high resolution imaging up to 0.8 nm @15 kV, acceleration voltage of 0.02–30 kV and energy dispersive X-ray (EDX) attached to SEM. The surface area ( $S_{\text{BET}}$ ) of the semiconductors was measured according to the BET method by nitrogen adsorption–desorption isotherms at 77 K on a Micromeritics Tristar 3000 instrument (Micromeritics Instruments Co., USA).

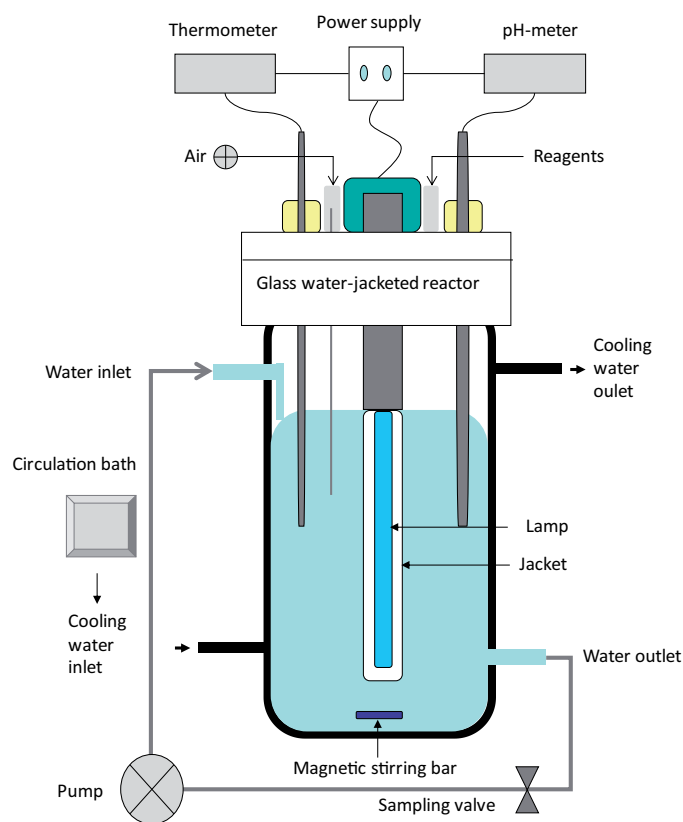


Fig. 1. Schematic drawing of the photochemical reactor.

### 2.3. Photocatalysis experiment using artificial light

The photocatalytic and photolytic experiments were performed in a 2000 mL cylindrical glass (250 mm long, 100 mm diameter) photochemical reactor (SBS, Barcelona, Spain) equipped with a magnetic stirring bar, and a 8W low pressure mercury lamp. The diagram of the experimental system used is shown in Fig. 1. The irradiated volume of suspension ( $V_{\text{reactor}}$ ) was 1660 mL. The intensity of the light was approximately  $10\text{ mW cm}^{-2}$  with major emission output at 366 nm (based on manufacturer's data). The photon flux from the lamp was controlled on the wall of the reactor using a portable photoradiometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy) fitted with a UVA sensor (range 315–400 nm).

The study was carried out in a batch recirculation mode ( $600\text{ mL min}^{-1}$ ). The reaction system was bubbled with air every 10 min, because dissolved oxygen acts as electron sink in the photodegradation process, forming the superoxide radical ( $\text{O}_2 + e^- \rightarrow \text{O}_2^{\cdot-}$ ) and avoiding the recombination of  $h^+/e^-$ . The system was continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at  $23 \pm 1^\circ\text{C}$  during the time of irradiation.

Initially, 2000 mL of type II analytical-grade water (pH 7.1, ORP 225 mV, resistivity  $>5\text{ M}\Omega\text{ cm}$  ( $25^\circ\text{C}$ ); conductivity  $<1.09\text{ }\mu\text{S cm}^{-1}$ , TOC  $<30\text{ }\mu\text{g L}^{-1}$ ; microorganisms  $<10\text{ cfu mL}^{-1}$ ) were mixed with both active ingredients (at  $0.2\text{ mg L}^{-1}$  of each herbicide), homogenizing the mixture for 20 min in the dark. After this time the appropriate amount of catalyst was added to the reaction solution. The mixture was maintained for 30 min in the dark prior to illumination in order to achieve the maximum adsorption of the herbicides onto the semiconductor surface. After this time  $\text{Na}_2\text{S}_2\text{O}_8$ , used as electron acceptor, was added. Several samples were taken during the illumination period (60 min). Two parallel blank assays, without semiconductor and oxidant (photolytic test) and only

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