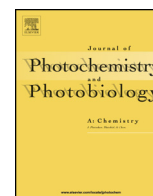




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Degradation of amicarbazone herbicide by photochemical processes


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ABSTRACT

Amicarbazone is a triazolinone herbicide developed to replace atrazine in the world market. Several technologies have been studied aiming at removing pesticides from wastewater, seeking to study the degradation mechanisms involved and the degree of toxicity of the transformation products formed. In this context, our main goal was to study the degradation of amicarbazone in aqueous solution by direct photolysis, suggesting possible chemical structures for the transformation products according to a theoretical and fundamental approach. The effects of herbicide initial concentration, pH, dissolved oxygen and nitrate concentrations, the role of singlet oxygen, and the presence of propan-2-ol as a free radical scavenger in amicarbazone photodegradation are discussed for the first time. Among these variables, pH showed influence on the photochemical degradation pathway. For instance, the transformation product amicarbazole was obtained under mildly acidic conditions, while 4-amino-5-oxo-3-(propan-2-yl)-4,5-dihydro-1H-1,2,4-triazole-1-carboxamide intermediate was found in both acidic and basic conditions. A primary degradation product formed as a result of deamination in acidic medium was found out. Concerning the effect of the variables involved in the process, the lowest AMZ half-life of 120 min was achieved under the following conditions: pH = 3; [AMZ]₀ = 50 mg L⁻¹; 75 W LP-Hg lamp.

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1. Introduction

Amicarbazone (AMZ, C₁₀H₁₉N₅O₂) is an herbicide belonging to the chemical group of triazolinones, extensively used to control a broad spectrum of weeds that compete with sugar cane and corn crops [1]. Owing to its extensive use, AMZ may represent a risk to animals and humans as well as to the environment. Many examples regarding the use of photochemical and photo-oxidative processes in the treatment of pesticide-containing wastewater are reported. Concerning AMZ, however, the literature is virtually inexistent.

The elimination of emerging pollutants can be achieved by appropriate physical methods – e.g. adsorption [2], coagulation [3], ultrafiltration [4] and reverse osmosis [5] – or chemical oxidation – e.g. ozonation [6], potassium permanganate [7]. Photodegradation processes based on the use of UV radiation are very effective in advanced water treatment technologies for groundwater and drinking water remediation [8]. Mercury vapor lamps emitting at 254 nm are the most common sources used for photolytic

processes [9,10], alone or combined with an auxiliary oxidant such as hydrogen peroxide [11–13].

Raschke et al. [14] studied the photolysis of metribuzin herbicide at 254 nm and initial concentration of 25 mg L⁻¹ in aqueous solution with the identification of oxygenated degradation products along with the determination of first order kinetic constants of degradation for all pH values (2.0, 5.6, and 11.0). According to the authors, deamination depends on the concentration of hydronium ions, and is favored in more acidic medium. The formation of the major transformation product deaminometribuzin (DA) occurs in the early stages of photolysis at higher concentrations in comparison to other transformation products.

Palm et al. [15] studied the photo transformation of metamitron herbicide with a xenon lamp ($\lambda > 290$ nm) in solvents with different polarities (water, methanol, acetonitrile, and hexane). According to the authors, photodegradation is dependent on the dissolved oxygen concentration in the aqueous medium; thus postulating that the deamination reaction occurs by the attack of hydroperoxyl radicals on the metamitron molecules.

Martinez et al. [16] studied the biological degradation of sulfentazone, a triazolinone herbicide, in a Brazilian soil. *Rhizobium radiobacter*, *Ralstonia pickettii*, *Methylobacterium radiotolerans*, *Cladosporium* sp., *Eupenicillium* sp., and *Paecilomyces* sp. were selected as potential degradation agents. Gas chromatography with an electron capture detector (ECD) and liquid chromatography equipped with photodiode array detection (DAD)

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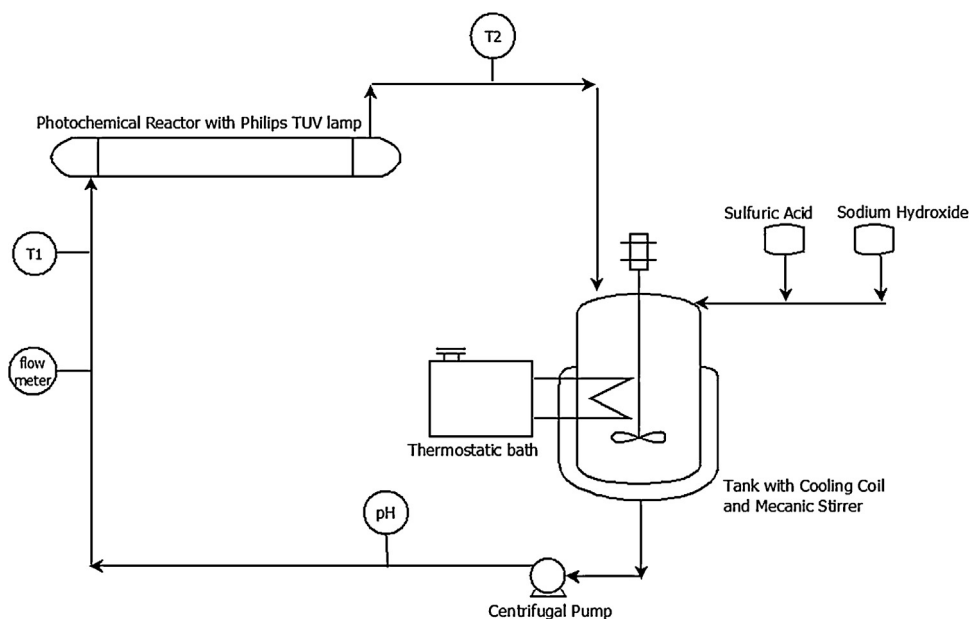


Fig. 1. Simplified diagram of the apparatus used in the amicarbazone photodegradation experiments. T1: inlet temperature of AMZ solution. T2: outlet temperature of AMZ solution.

were used to identify the transformation products sulfentrazonecarboxylic acid (SCA), 3-desmethylsulfentrazone (DMS), and 3-hydroxymethylsulfentrazone (HMS).

However, no previous work reported the degradation of the triazolinone herbicide amicarbazone by photochemical processes. In the present work, results of the photodegradation of amicarbazone in aqueous solution are reported and discussed for the first time. The time evolution of the target pollutant concentration and the formation of degradation products are discussed. Parameters such as pH, amicarbazone initial concentration, dissolved oxygen and nitrate concentrations were also examined. The study of amicarbazone photodegradation and the proposal of stable degradation products by ESI(+)-IT-TOF technique configure an original contribution.

2. Experimental

2.1. Chemical reagents

Amicarbazone ($C_{10}H_{19}N_5O_2$, CAS 129909-90-6) of technical (>95.4%, m/m) and analytical (>99.9%, m/m) grades were provided by Arysta LifeScience Corp., and used with no further purification. AMZ presents the following characteristics [1]: white crystals; density, 1.12 g mL^{-1} ; solubility, 4.6 g L^{-1} in water (20°C); melting point, 137.5°C ; vapor pressure of $1.3 \times 10^{-6} \text{ Pa}$ (20°C) and $3.0 \times 10^{-6} \text{ Pa}$ (25°C).

Propan-2-ol, acetonitrile and acetic acid were purchased from Merck. High purity (>99.999%) N_2 from Air Products was used as inert gas when needed. All the other chemicals used were analytical grade.

2.2. Photolysis study

Photolytic degradation experiments were performed in batch in a tubular photochemical reactor which consists of a borosilicate glass tube ($113.6 \text{ mm diameter} \times 1120 \text{ mm irradiated length}$) with a concentric low-pressure mercury vapor lamp (LP-Hg, TUV Philips emission mainly at 254 nm). Lamps of 36 and 75 W were used, with photon rates of 1.85×10^{19} and $2.75 \times 10^{19} \text{ photons s}^{-1}$, respectively, obtained by ferrioxalate actinometry [17]. The

solution temperature was controlled by means of a thermostatic bath (Julabo, model F 34). The photochemical reactor was fed from a non-irradiated recirculation borosilicate glass tank of 3.5 L, equipped with a mechanical stirrer. Fig. 1 shows a simplified scheme of the apparatus.

The experiments using this photochemical reactor were carried out with a compact field point programmable automation controller from National Instruments, model cFP-2020. The cFP-user interface was performed by LabView software version 8; flow rate, pH (Tecnal pHmeter, model TEC-3MP) and temperature were data logged at $\sim 1.0 \text{ s}$ intervals. The reaction temperature was kept constant at 25°C over the entire reaction time.

An additional qualitative experiment was carried out using a 1 L photochemical reactor vessel equipped with a medium-pressure mercury lamp (125 W, Philips HPLN) placed inside a quartz immersion well. The aim of this experiment was to show the behavior of AMZ photolysis in the absence of dissolved oxygen. An herbicide aqueous solution containing 50 mg L^{-1} of AMZ was previously boiled for 20 min for the complete removal of dissolved oxygen (monitored with YSI 556 MPS instrument). The boiled solution was then transferred to the reactor vessel, and purged with bubbling ultrapure nitrogen over the whole experiment. Samples collected from the vessel were analyzed by LC-ESI(+)-MS/MS without further pre-treatment.

A second qualitative experiment aimed to investigate the degradation of amicarbazone (50 mg L^{-1}) by singlet oxygen (1O_2), in order to provide information about possible mechanism routes involved in pollutant oxidation. This experiment was carried out with the 1 L photochemical reactor vessel equipped with a medium-pressure mercury lamp (125 W, Philips HPLN) placed inside a Pyrex® glass immersion well. Singlet oxygen was generated *in situ* by the photosensitization of rose bengal dye [18,19]. Homogenization was provided by magnetic stirring.

2.3. Analytical determinations

UV-vis absorption spectra were measured with a Varian Cary 50 UV-vis spectrophotometer using 1 cm path-length Suprasil® quartz cuvette, in the range 190–820 nm and 1 nm intervals.

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