

AMETRYNE DEGRADATION BY IONIZING RADIATION

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ABSTRACT

Ametryne may be released to the environment during its manufacture, transport, storage, formulation and use as selective herbicide for the control of annual broadleaf and grass weeds. It is applied as an aqueous suspension for pre-emergence or post-directed applications on crops. Depending on the pesticide formulation and type of application, ametryne residues may be detectable in water, soil and on the surfaces for months or years. The herbicide used to this study was Ametryne (commercial name, Gesapax 500), commonly used on field crops and on corn and commercialized since 1975. Ametryne was analyzed by gas chromatography (GC Shimadzu 17A), after extraction with hexane/dichloromethane (1:1 v/v) solution. The calibration curve was obtained with a regression coefficient of 0.9871. In addition, the relative standard deviation was lower than 10%. The radiation-processing yield was evaluated by the destruction G-value (Gd) (Eq. 1), that is defined by the number of destroyed molecules by absorption of 100 eV of energy from ionizing radiation. Different concentrations of the herbicide (11.4 mol L⁻¹; 22.7 mol L⁻¹; 34.1 mol L⁻¹ and 45.5 mol L⁻¹) were irradiated at the AECL "Gammacell 220" ⁶⁰Co source, with 1 kGy, 3 kGy, 6 kGy, 9 kGy, 12kGy, 15 kGy and 30 kGy absorbed doses. After irradiation processing, the ametryne highest reduction rate occurs at low doses of radiation: at 6 kGy more than 85-90% of all ametryne compounds were removed. Two products of incomplete degradation of ametryne were identified as s-triazine isomers. However, further work is needed in order to fully understand the ametryne degradation mechanisms the degradation yield of ametryne depends on its initial concentration and the process seems to be more efficient at higher concentrations.

1. INTRODUCTION

As a consequence of pesticide use in agriculture, the human population is constantly exposed to numerous chemical species present in the environment. The Brazilian agriculture activities have consumed about 288,000 tons of pesticides per year conditioned in about 107,000,000 packing with weight of approximately 23,000 tons. The discharge of empty plastic packing of pesticides can be an environmental concern, causing problems to the human health, to animals and plants if done without inspection and monitoring. [2,4]. Since is no longer allowed the uncontrolled burying and burning of the waste, only two options remain, to dispose, or to recycle the packing, in ways that protect the environment and human health.

This paper is part of the project which objective is the evaluation of pesticides degradation for decontamination of commercial plastic packing of high-density polyethylene type COEX,

used in agriculture. The studies of chlorpyrifos gamma radiolysis were evaluated elsewhere by the same group [3,5].

The herbicide used to this study was Ametryne (commercial name, Gesapax 500), commonly used on field crops and on corn and commercialized since 1975. Ametryne may be released to the environment during its manufacture, transport, storage, formulation and use as selective herbicide for the control of annual broadleaf and grass weeds. It is applied as an aqueous suspension for pre-emergence or postdirected applications on crops. Ametryne is a weak base that means that it is almost entirely dissociated at environmental pHs, and it is slightly adsorbed in soil. Depending on the pesticide formulation and type of application, ametryne residues may be detectable in water, soil and on the surfaces for months or years [1].

2. EXPERIMENTAL

To quantify the ametryne and its degradation products, a range of concentrations were used in order to obtain a GC response. Previously to analysis, the powder was dissolved in methanol, since it is insoluble in pure water. The standard solutions of the herbicide were prepared by dilution of the solution (powder and methanol) in different volumes of ultra pure water.

The analysis of the by-products and the degradation yields were performed to access the treatment efficiency. Ametryne and the by-products were analyzed by gas chromatography with a DB5 column (30 m $\times$ 0.25 mm I.D.). Col. Temp.: 50°C for 0 min., then to 150° C at 10°C/min. and hold 0 min., then to 300° C at 15°C/min. and hold 5 min. Inj. Temp.: 200°C. Det. Temp.: 300°C. Flow rate: 10 ml/min., N₂. Electronic pressure control (EPC): 37 kPa. Prior to analysis, the samples were extracted with 2 ml of an organic solution of hexane/dichloromethane (1:1 v/v). In order to maximize the extraction efficiency, the organic solution and the sample (1:2 v/v) were mixed and centrifuged. The ametryne used in this study was collected from the containers given by the Brazilian farmers.

Three samples of each standard solution were analyzed the conditions described above in order to determine the relative standard deviation (% RSD) of the analytical protocol. The spiked samples were irradiated with following absorbed doses: 1 kGy, 3 kGy, 6 kGy, 9 kGy, 12 kGy, 15 kGy e 30 kGy. Irradiation was carried out at room temperature, using a Cobalt-60 gamma irradiator in a batch system, Gammacell-type. The dosimetry research group calibrates this system routinely with Fricke dosimeter to determine the absorbed dose rate. The 20 mL vials were completely filled without headspace in triplicate.

3. RESULTS AND DISCUSSION

The calibration curve was obtained with a regression coefficient of 0.987. The detection limit, LMD, using GC-FID was 1.7 $\mu\text{mol L}^{-1}$, and the obtained experimental variability (N=10), expressed as standard deviation, was 4% (Figure 1).

As shown in Figure 2, after irradiation processing, the ametryne highest reduction rate occurs at low doses of radiation, e. g, at 15 kGy more than 99% of all ametryne concentrations were removed. The high solubility of ametryne in water can be the main responsible by this efficiency.

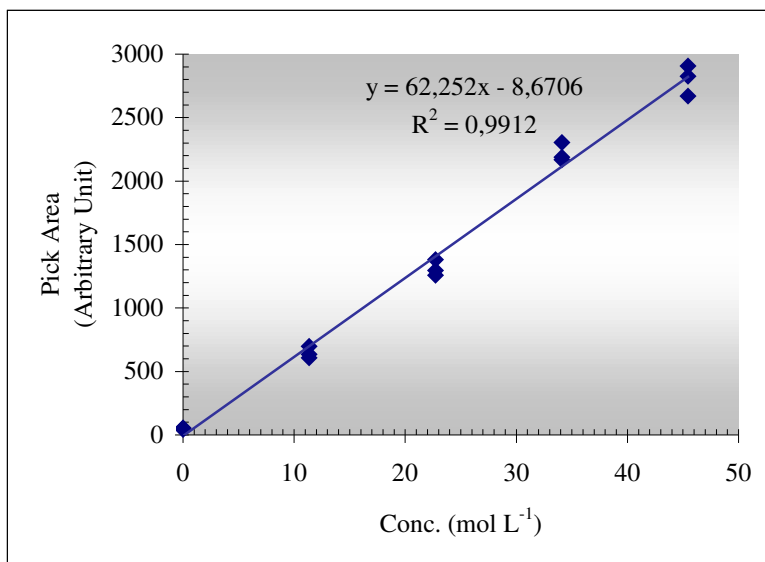


Figure 1. GC calibration curve for Ametryne.

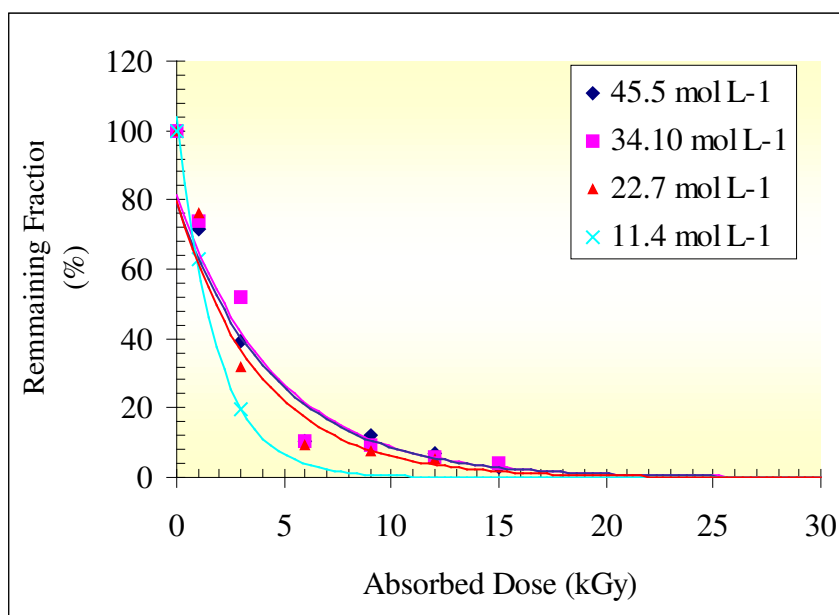


Figure 2. Degradation curves of Ametryne at different absorbed doses (0-30 kGy) using several solutions.

The degradation yield of the substrate depends on its starting concentration, hence the process is more effective when a large number of organic molecules is present, because the reaction among reactive transients produces more radicals and the process is continuous, but not directly proportional.

Two by-products were identified after the irradiation of ametryne. Using the GCMS library, they were identified as s-triazine isomers. However, further work is needed in order to fully understanding the ametryne degradation mechanisms.

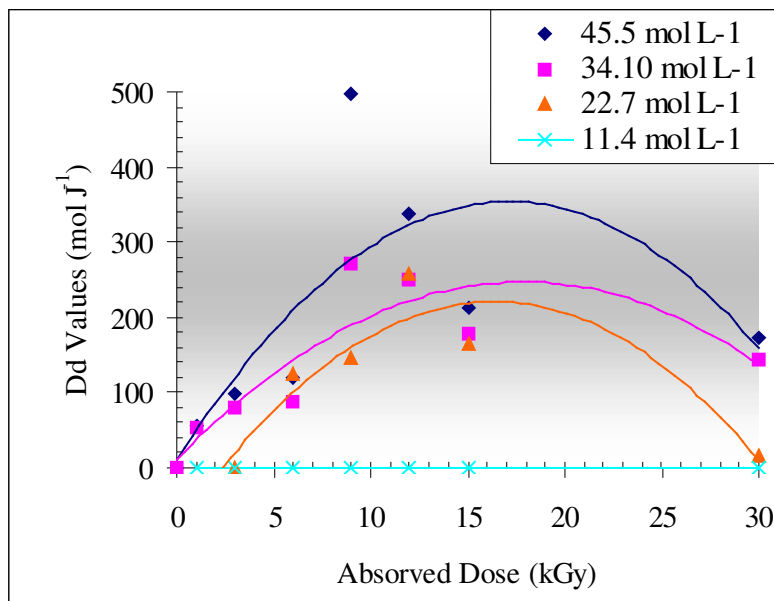


Figure 4. Ametryne Gd values obtained using different initial concentrations and absorbed doses

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, (project 03/05631-7).

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