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Decontamination of Ametryne HDPE packaging using electron beam accelerator

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ABSTRACT

This paper is part of a project to evaluate pesticide degradation on commercial polymeric (high-density polyethylene, HDPE) packaging material. The herbicide studied was Ametryne whose residues may be detectable in water, soil and on the surfaces for months or years, depending on the pesticide formulation and type of application. In order to evaluate the efficiency of radiation processing on removal of the pesticides contamination; the packaging material were irradiated using Radiation Dynamics Electron Beam Accelerator with 1,5 MeV energy and 37 kW, in batch system. The samples were irradiated with water, in various absorbed doses. Ametryne was analyzed by gas chromatography after extraction with hexane/dichloromethane (1:1 v/v) solution. The radiation processing yield was evaluated by the destruction *G*-value (Gd), and the electron beam irradiation processing, showed higher efficiency in destroying Ametryne in the HDPE packaging when the samples were irradiated in the presence of small quantities of water.

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 t of pesticides per year conditioned in about 107,000,000 packing with weight of approximately 23,000 t. 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. Since it is no longer allowed to 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.

Ametryne formulations are used as selective herbicide for the control of annual broadleaf and grass weeds, and may be released to the environment during its manufacture, transport and storage. It is applied as an aqueous suspension for pre-emergence or post-directed 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 (Acero et al., 2000; Vel Leitner et al., 1999).

This paper is part of a project to evaluate pesticide degradation on commercial polymeric (high-density polyethylene, HDPE) packaging material. Chlorpyrifos gamma radiolysis was evaluated elsewhere by the same group (Duarte et al., 2007; Mori et al., 2006). Ametryne (commercial name, Gesapax 500), commonly used on field crops, and on corn is commercialized since 1975.

2. Experimental

2.1. Sampling of Ametryne in water

To quantify the Ametryne and its degradation products, a range of concentrations were used in order to obtain a GC response. Previous to analysis, the powder was dissolved in methanol. The standard solutions of the herbicide were prepared by dilution of this solution in different volumes of ultra-pure water. The Ametryne used in this study was collected from the containers given by the Brazilian farmers. These samples were irradiated at gamma source.

2.2. Sampling of contaminated packaging

Contaminated pesticides packing, without triple rinsing, were cut in small pieces, weighted in portions of 37 g and placed in plastic bags with 200 mL of water; the amount of water was

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calculated to maintain the 4 mm width. These samples were irradiated at electron beam accelerator.

2.3. Radiation processing

The spiked samples were irradiated with the following absorbed doses: 1, 3, 6, 9, 12, 15 and 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.

The electron beam irradiation was carried out with 1.5 MeV of electrons energy, provided by the IPEN's Electron Beam Facility (Dynamitron type from Radiation Dynamics Inc., USA). The irradiation parameters were 4.0 mm sample width, 112 cm (94.1%) scan and 6.72 m/min conveyor stream velocity. All the irradiation was performed in a batch system and the delivered irradiation absorbed doses were 15, 25, 60, 100 and 200 kGy. The samples were irradiated in triplicate.

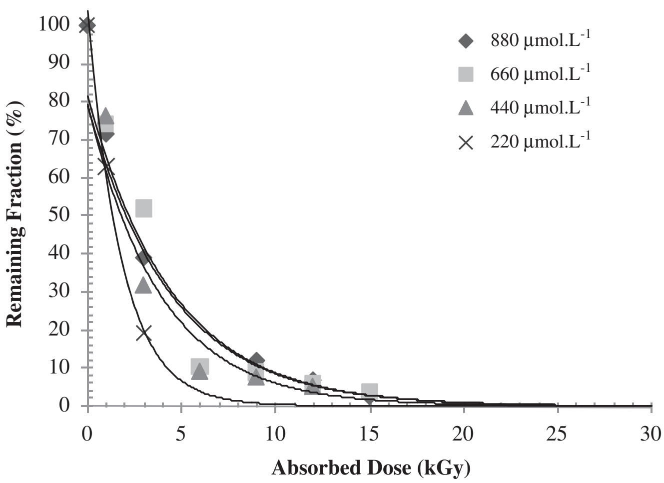

Fig. 1. Degradation curves of Ametryne at different absorbed doses.

2.4. Chemical analysis

Ametryne and the by-products were analysed by gas chromatography with a DB5 column (30 m × 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, N_2. 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). After irradiation the polymeric material was separated from water and was transferred to glass vessel, and the pesticides were extracted with 50 mL of hexane/dichloromethane 1:1 solvent, using an ultrasonic system per 30 min.

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 µmol L^{-1}, and the obtained experimental variability ($N = 10$), expressed as standard deviation, was 4%.

3.1. Ametryne in water

As shown in Fig. 1, 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.

Two by-products were identified after the irradiation of Ametryne. Using the GCMS library, they were identified as s-triazyne isomers (Fig. 2). However, further work is needed in

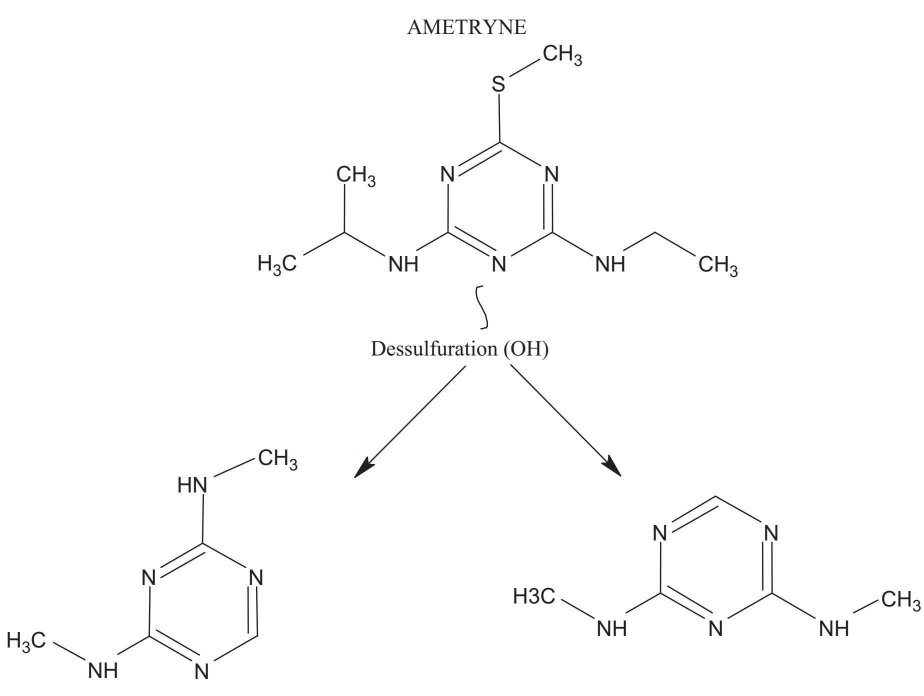

Fig. 2. Intermediate products of preliminary oxidation of Ametryne.

order to fully understand the Ametryne degradation mechanisms. The formation and degradation of s-atrazyne is presented in Fig. 3. Although 15 kGy removes almost 99% of Ametryne, in this

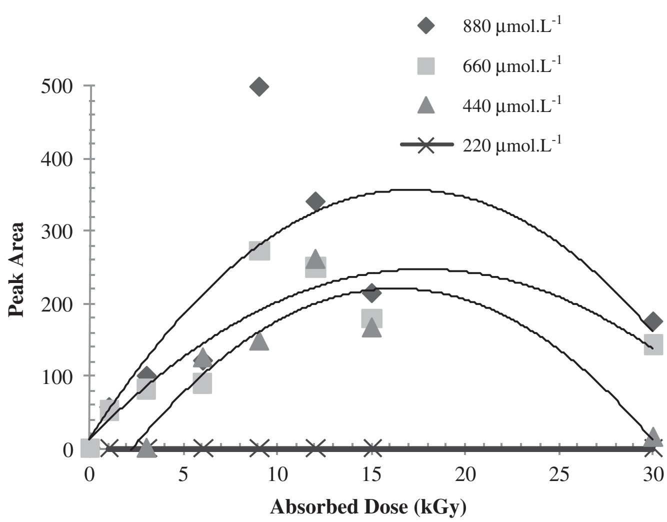

Fig. 3. Formation and degradation of S-atrazine by ionizing radiation in various absorbed doses and concentrations of Ametryne.

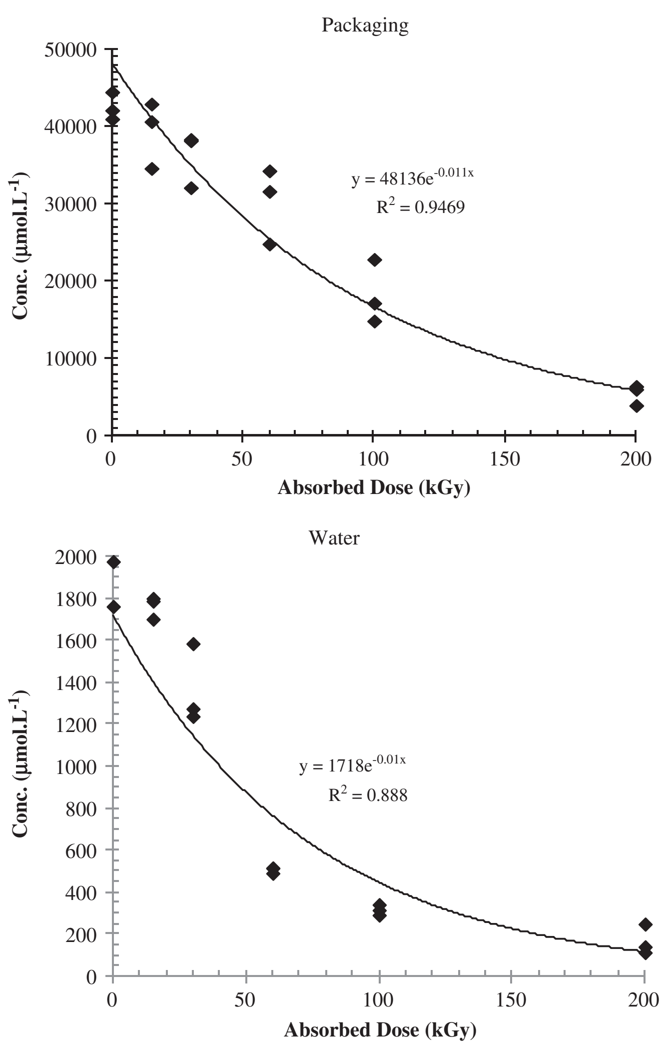

Fig. 4. Ametryne removal from high-density polyethylene, HDPE packaging, and from water using various and absorbed doses.

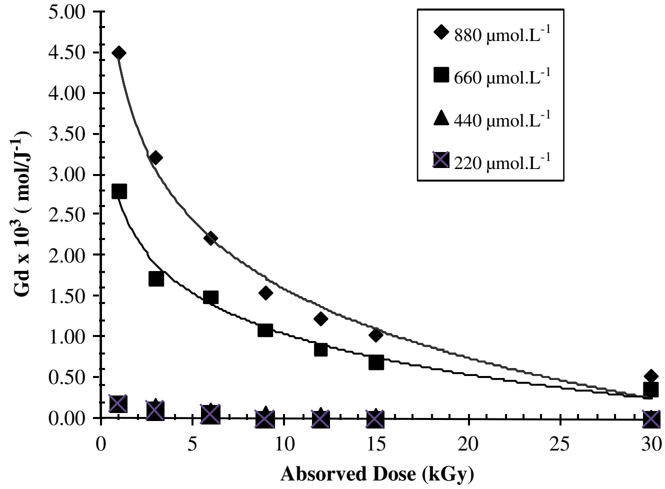

Fig. 5. Ametryne destruction grade, Gd, values obtained using different initial concentrations and absorbed doses.

absorbed dose s-atrazyne presented the higher concentration and 30 kGy is necessary to remove 99% of it.

3.2. *Ametryne in contaminated packaging*

The removal of Ametryne from packaging was not as efficient as in the water samples, considering removal rate. To removal of 50% of contamination was necessary more than 50 kGy of absorbed dose. The water samples used in this process were separated from the packing mixture after irradiation and analyzed by gas chromatography.

The organic compound removal, after irradiation, is described as the destruction Gd value and is defined by solute disappearance in aqueous solution. Usually, it is determined, experimentally, using the following equation (Duarte et al., 2007):

$$\mathrm{Gd}(\mathrm{mol\,J}^{-1}) = \Delta RDN_{\mathrm{A}}/D(6.24\times10^{15})$$

where ΔRD is the change in organic solute concentration (mol L^{-1}) at a given dose; D is the dose (kGy); 6.24×10^{15} is kGy in 100 eVL^{-1} converting constant and N_{A} is Avogadro's number.

In this study the *G*-value (Gd) were calculated for standard samples, for packaging and for the water separated from packaging samples. The results are presented in Figs. 4 and 5. The degradation yield of organic compound in general depends on its initial concentration and the process seems to be more efficient at higher concentrations. In the case of Ametryne the results are in agreements with this concept (Fig. 5). Although the removal of Ametryne from HDPE packaging was high, about 60% with 100 kGy (Fig. 5), when the Gd values of contaminated HDPE packaging, are compared to standard samples (Fig. 5), the results demonstrate lower process efficiencies, even considering that the Ametryne concentration in the second case is lower.

4. Conclusions

Advanced alternative technologies are being developed for effective treatment of herbicide-polluted waters, namely through the degradation studies of important target molecules such as Ametryne. In this work, the obtained result points out that the Ametryne degradation efficiency depends on its initial concentration and the process seems to be more efficient at higher concentrations, when contaminated water samples are irradiated.

Nevertheless, in the case of contaminated HDPE packaging processed by ionizing radiation, the efficiency decrease about five times, although the decontamination is reached with high absorbed doses.

Acknowledgment

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References

Acero, J.L., Stemmler, K., Von Gunten, U., 2000. Degradation kinetics of atrazine and its degradation products with ozone and.OH radicals: a predictive tool for drinking water treatment. Environ. Sci. Technol. 34, 591–597.

Duarte, C.L., Oikawa, H., Mori, M.N., Sampa, M.H.O., 2007. Decontamination of pesticide packing using ionising radiation. Radiat. Phys. Chem. 76 (11–12), 1885–1889.

Mori, M.N., Sampa, M.H.O., Duarte, C.L., 2006. Study of the degradation of chlorpyrifos by ionizing radiation. J. Radioanal. Nucl. Chem. 270 (1), 99–102.

Vel Leitner, N.K., Berger, P., Gehringer, P., 1999. Gamma-irradiation for the removal of atrazine in aqueus solution containing humic substances. Radiat. Phys. Chem. 55 (3), 317–322.