

# SIMULTANEOUS REMOVAL OF VARIOUS PESTICIDES FROM CONTAMINATED HDPE PACKING USING ELECTRON BEAM ACCELERATOR

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*The discharge of empty pesticide packing if done without inspection and monitoring, can be an environmental concern causing problems to human health, animals and plants. Since the uncontrolled burying and burning of waste it is no longer allowed, the only two options that remain, are to dispose, or to recycle, in ways that protect the environment and human health. Brazilian Federal law states that the disposal responsibility of the pesticide packing is by attributed to the industry that has search for new technologies to recover and recycle the material. In order to evaluate the efficiency of radiation processing on removal of the pesticides contamination; high-density polyethylene (HDPE) packing were irradiated using Radiation Dynamics Electron Beam Accelerator with 1,5MeV energy and 37kW power and gamma rays. The chemical analysis of the pesticides and their solvent were accomplished using a Gas Chromatography associated with the Mass Spectrometry - GCMS from Shimadzu, Model QP 5000. With 25 kGy absorbed dose a total removal of methomyl, dimethoate, carbofuran, and methidathion, and more than 80% removal of triazine, thiophos and atrazyne; was reached. Lower removal rates were obtained for endosulfan (54%), chlorpyrifos (69%), thiazophos (79%), and trifluralin (74%).*

## I. INTRODUCTION

As a consequence of pesticides used 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 a 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. (INPEV, 2005). Since the uncontrolled burying and burning of the waste is no longer allowed, the only two options remaining is to dispose or to recycle the packing, in ways that protect the environment and human health. Cleaning the pesticide containers is a crucial on-farm activity. Triple rinsing has proved to be effective, but not without its problems.

Brazilian Federal law attributes the disposal responsibility of the pesticide plastic packing to the industry. This fact led the segments to mobilize and create the National Institute of Processing of Empty Packing – inpEV, with the objective of coordinating this operation (6). The pesticides packing are received in a central place and are separated in two blocks, contaminated and non-contaminated. The contaminated packing material is incinerated and non-contaminated is recycled.

Radiation processing is widely used for medical product sterilization and polymeric materials irradiation. Moreover the use of irradiation is becoming a common treatment for many others applications, including wastewater, flue gases, and solid waste materials. For radiation processing, accelerators are available, supplying electron beams in the energy range up to 10MeV, as well as, radionuclide sources Co-60, which emit 1.17/1.33MeV gamma rays. Electron beams are characterized by limited penetration and the entire energy of high-energy electrons is deposited in relatively thin layers of material. In the case of gamma rays, the radiation is able to penetrate deeper into the materials but

the dose rates are a few orders of magnitude lower in comparison to electron beam. (5)

The reactive species generated by the interaction of ionizing radiation with water (OH radicals, e-aq, and H) have been successfully applied for organic pollutants removal in environmental samples and industrial effluents (2,3,4). Various research groups in the world have studied the degradation of pesticides in different matrices. (1,7,8,9).

This paper is part of the project with the objective to evaluate pesticides degradation for decontamination of commercial polymeric packing of high-density polyethylene COEX type, used in agriculture. The study of the pesticide chlorpyrifos using gamma radiation was evaluated by the same group and published elsewhere (10). The main objective of this paper is to study the efficiency of ionizing radiation on the pesticides removal from commercial polymeric packing of high-density polyethylene COEX type, used in agriculture; in order to substitute the very expensive incineration process, by the recycle.

## II EXPERIMENTAL

### II.A. Sampling

A mixture of contaminated pesticides packing prepared for incineration process was obtained in bags of approximately 30 Kg, from the National Institute of Processing of Empty Packing – inPEV. The samples, without triple rinsing, were cut in small pieces, weighted in portions of 50 g and placed in plastic bags, in two situations dried and with 200 mL of water.

### II.B. Radiation Processing

The gamma irradiation was carried out at room temperature using a Cobalt-60 gamma irradiator, semi industrial type, with 92,000 Ci at dose rate 4.5 kGy/h, in a batch system and “Perspex” dosimeter was employed to determine the absorbed dose of the system. 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, 112cm (94.1%) scan and 6.72 m/min conveyor stream velocity. All the irradiation were performed in a batch system and the delivered irradiation absorbed doses were 15 kGy, 25 kGy, 50 kGy and 100 kGy. The samples were irradiated in triplicate, and 60 results were obtained in this way.

### II.C. Chemical Analysis

After irradiation the polymeric material was separated from water and were 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. The pesticides concentration, before and after radiation processing, was determined by gas chromatography with FID detector Shimadzu, model GC-FID 17-A, and their characterization were made by gas chromatography in association with mass spectrometry, Shimadzu, model GC-MS QP-5000 using the following conditions:

- Helium gas carrier,
- DB5 fused capillary columns with low polar bonded phase,
- Mass detector operation in electron impact mode (EI), using 1.50 kV of ionizing voltage and temperature 250°C,
- Interface temperature 240°C and continuous operation mode (SCAN).

## III RESULTS AND DISCUSSION

### III.A. Chemical Analysis

Through the gas chromatography in association with mass spectrometry, the identification of the main pesticides present in the samples, was completed (Fig. 1). The pesticides with higher concentration were atrazyme, followed by methylparathion and trifluralin. The other pesticides presented similar concentrations. Naphthalene, nitrophenol and benzenedicarboxylic acid are not pesticides, but solvents normally used in commercial formulations. The main characteristics of these pesticides are showed in Table 1.

### III.B. Gamma irradiation

The presence of water was fundamental in the efficiency of this process as using gamma or electron beam irradiation. The pesticides removal in different absorbed doses are presented in Figure 4 (gamma radiation without and with water). The removal, using 25 kGy of absorbed dose, was more than 80% for the pesticides triazyme, methylparathion and atrazyme. The lower removal rates for the same absorbed dose (25 kGy) were obtained for endosulfan (54%), chlorpyrifos (69%), triazophos (79%) and trifluraline (74%). Although these removals were lower than the

others were it can be considered efficient, because these lower removal rates were due to the higher concentration of these pesticides in relation to the others (Fig. 2).

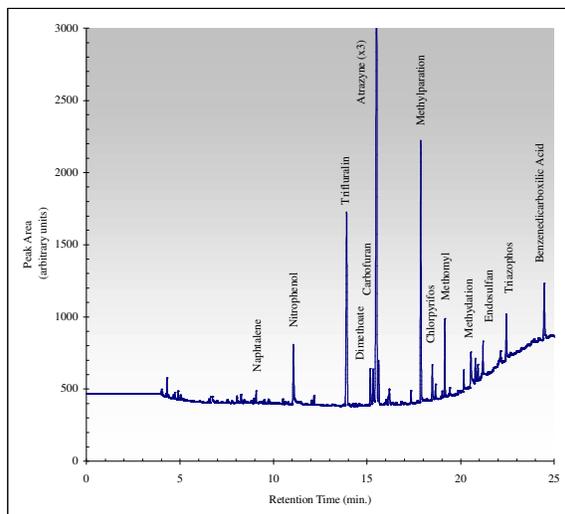


Fig. 1. Gas chromatogram showing the main pesticides present in the studied polymeric packing mixture

### III.C. Electron Beam irradiation

As expected, the presence of water was also fundamental in the electron beam processing (Fig. 4). The removal rates were lower than gamma irradiation, but the difference was not so significant. Using 25 kGy of absorbed dose, the removal was more than 80% for Dimetoate, chlorpyrifos, Carbofuran and more than 60% of Endosulfan, Triasophos, Methomyl, and Methylparathion. The lower removal rates for the same absorbed dose (25 kGy) was for Endosulfan, Atrazyn and Triazyn.

The water samples used in this process were separated from the packing mixture after irradiation and analyzed by gas chromatography. Pesticide contamination of water was expected, but no residue of pesticides in the water was detected, even after repeated extraction with organic solvents.

In terms of efficiency, both radiation sources showed equivalency, and the main differences are of a practical point of view. In the case of gamma radiation it is necessary to use containers for the with irradiation of large volumes at the same time. However the irradiation time of a gamma facility is at least several hours, while in the case of electron beam accelerator, due to a high throughput efficiency, a mobile system can be used.

TABLE I. Characterization of the main pesticides identified in the polymeric packing mixture (8).

Commercial Name	Chemical Name	Action Type
Atrazyn	2-chloro-4-(2-propylamino)-6-ethylamino-s-triazine	Herbicide-Triazyn
Carbofuran	7-Benzofuranol, 2,3-dihydro-2,2-dimethyl-methylcarbamate	Insecticide, acaricide Benzofuran Methylcarbamate
Chlorpyrifos	O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate	Insecticide, acaricide Organophosphate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate	Insecticide, acaricide Organophosphate
Endosulfan	hexachlorohexahydromethano-2-3-4-benzodioxathienpin-3-oxide	Insecticide, acaricide Chlorociclo diene
Methomyl	S-methyl-N-(methylcarbamoyloxy)-thioacetimidate	Insecticide, acaricide Oxyme Methylcarbamate
Methydatation	S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethylphosphorodithioate	Insecticide, acaricide Organophosphate
Methylparatio	O,O-dimethyl-O-0-nitrophenyl phosphorodithioate	Insecticide, acaricide Organophosphate
Triazophos	O,O-Diethyl O-(1-phenyl-1H-1,2,4-triazol-3-yl) phosphorothioate	Insecticide, acaricide Organophosphate
Trifluralin	Benzenamina, 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl) -	Herbicide Dinitroaniline

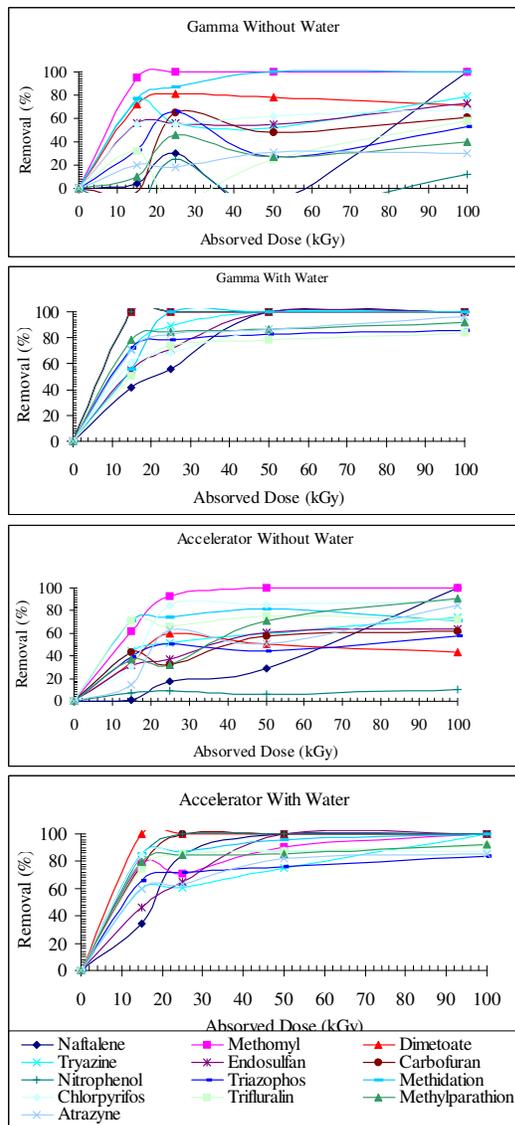


Fig. 2. Removal of pesticides in packing with and without water, with different absorbed doses, using electron beam accelerator and gamma rays.

#### IV. CONCLUSION

Ionizing radiation was efficient in the removal of pesticides and other solvents from the polymeric packing, but the presence of water during the irradiation showed to be fundamental in this process. The pesticide removal yields using electron beam accelerator were similar to gamma rays. Some minimal variations were not important for practical purposes and in the global efficiency. With 50 kGy of absorbed dose more than 60% of

pesticides were removed by using gamma rays and also by using electron beam accelerator.

When a new technology is proposed for commercial use, some factors such as applicability and practicality have to be considered. The initial idea was to irradiate the polymeric packaging material without destruction. However, grinding them before irradiation easily optimizes the process, because in this case a conveyor in the electron beam facility can be used which presents high throughput efficiency. Treatment using radiation processing in polymeric packaging materials can be advantageous in comparison with the incineration method that is a very expensive process and doesn't allow for recycling of the high density polyethylene (HDPE).

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