

Simultaneous Removal of Various Pesticides from Contaminated HDPE Packaging by Radiation Processing: Electron Beam and Gamma Radiation Comparison

ABSTRACT

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. In order to evaluate the efficiency of radiation processing on removal of pesticides contamination, high-density polyethylene (HDPE) packaging were irradiated using Radiation Dynamics Electron Beam Accelerator with 1.5MeV energy and 37 kW power, and a Cobalt-60 gamma irradiator, Gammacell type, at the rate 3.5 kGy/h. The chemical analyses of the pesticides 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 methyathion, and more than 80% removal of triazine, thiophos, and atrazine were reached. Lower removal rates were obtained for endosulfan (54%), chlorpyrifos (69%), thiazophos (79%), and trifluralin (74%).

KEYWORDS: Packaging wastes, pesticides, radiation processing.

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INTRODUCTION

As a consequence of pesticides 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 packaging with a weight of approximately 23,000 tons. The discharge of empty plastic packaging of pesticides can be an environmental concern, causing problems to the human health, to animals and plants if done without inspection and monitoring [6]. 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 packaging, in ways that protect the environment and human health.

Brazilian Federal law attributes the disposal responsibility of the pesticide plastic packaging to the industry. This fact led the segments to mobilize and create the National Institute of Processing of Empty Packaging - inpEV, with the objective of coordinating this operation [6]. The pesticides packaging are received in a central place and are separated in two blocks, contaminated and non-contaminated. The contaminated packaging 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]. The study of pesticide chlorpyrifos and ametryne removal using ionizing radiation were evaluated and published elsewhere [3,10].

The main objective of this paper is to study the efficiency of ionizing radiation on the pesticides removal from commercial polymeric packaging of high-density polyethylene COEX type, used in agriculture; in order to substitute the very expensive incineration process, by the recycle.

EXPERIMENTAL

Sampling

A mixture of contaminated pesticides packaging prepared for incineration process was obtained in bags of approximately 30 Kg, from the National Institute of Processing of Empty Packaging - 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.

Radiation Processing

The gamma irradiation was carried out at room temperature using a Cobalt-60 gamma irradiator, gammacell type, at dose rate 3.5 kGy/h, 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 irradiations 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.

Chemical Analysis

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. 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 250oC,
- Interface temperature 240oC and continuous operation mode (SCAN).

RESULTS AND DISCUSSION

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 thirfluralin. 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.

Gamma irradiation

The presence of water was fundamental in the efficiency of this process as using gamma or electron beam irradiation. The pesticides removals 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

atrazine. 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 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).

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 Dimethoate, chlorpyrifos, Carbofuran and more than 60% of Endosulfan, Triasophos, Methomyl, and Methylparathion. The lower removal rate for the same absorbed dose (25 kGy) was for Endosulfan, Atrazine, and Triazine.

The water samples used in this process were separated from the packaging 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 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 high throughput efficiency, a mobile system can be used.

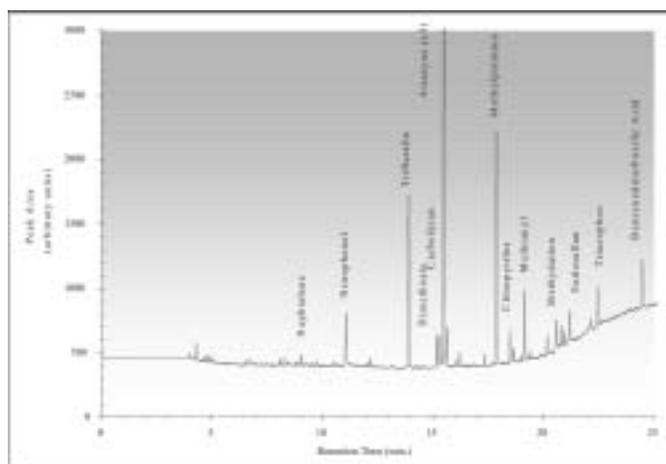


Figure 1 - Gas chromatogram showing the main pesticides present in the studied polymeric packaging mixture

Table 1 - Characterization of the main pesticides identified in the polymeric packaging mixture (8)

Commercial Name	Chemical Name	Action Type
Atrazine	2-chloro-4-(2-propylamino)-6-ethylamino-s-triazine	Herbicide- Triazine
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 Organophos phorate
Dimethoate	O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate	Insecticide, acaricide Organophos phorate
Endosulfan	hexachlorohexahydromethano-2-3-4-benzodioxathienpin-3-oxide	Insecticide, acaricide Chlorociclo diene
Methomyl	S-methyl-N-(methylcarbamoyloxy)-thioacetimidate	Insecticide, acaricide Oxyme Methylcarba mate
Methydatihion	S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethylphosphorodithioate	Insecticide, acaricide Organophos phorate
Methylparatio	O,O-dimethyl-O-0-nitrophenyl phosphorodioate O,O-Diethyl O-(1-phenyl-1H-1,2,4-triazol-3-yl)	Insecticide, acaricide Organophos phorate
Triazophos	phosphorothioate Benzenamina, 2,6-dinitro-N,N-dipropyl-4-	Insecticide, acaricide Organophos phorate
Trifluralin	(trifluoromethyl)-	Herbicide Dinitroaniline

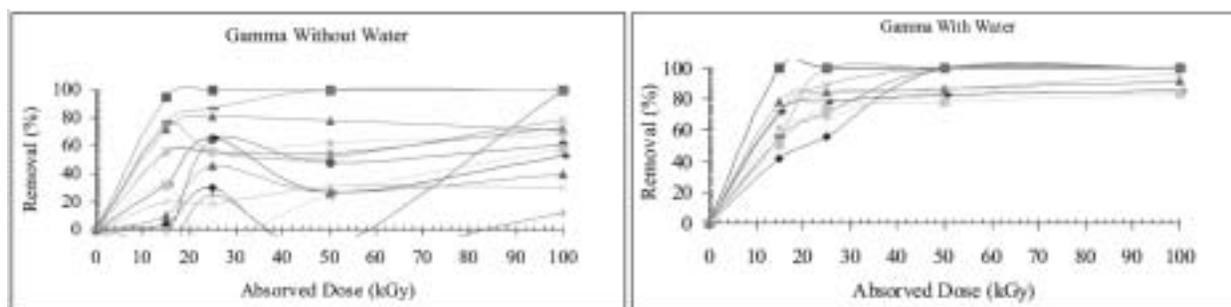


Figure 2 - Pesticides removal in packaging with and without water, in different absorbed doses, using electron beam accelerator and gamma rays.

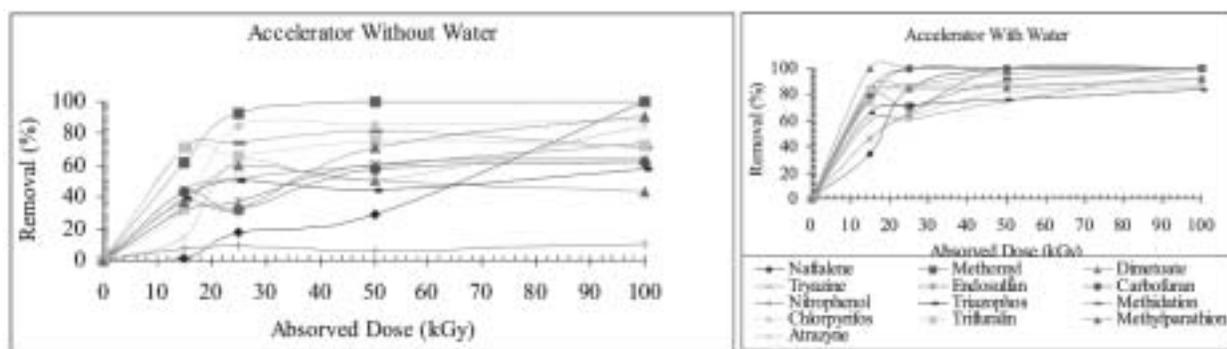


Figure 3 - Pesticides removal in packaging with and without water, in different absorbed doses, using electron beam accelerator and gamma rays.

CONCLUSION

Ionizing radiation was efficient on removal of pesticides and other solvents from the polymeric packaging, but the presence of water during the irradiation processing showed to be fundamental. 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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