2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

DECONTAMINATION OF CHLORPYRIFOS PACKING USING IONIZING RADIATION: PROCESSING OPTIMIZATION

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ABSTRACT

The discharge of empty plastic packing of pesticide can be an environmental concern causing problems to human health, animals and plants if done without inspection and monitoring. Among the commercial pesticides, chlorpyrifos, o, o- Diethyl - o- (3,5,6 – trichloro – 2 - pyridyl) phosphorothioate, has significant importance because of its wide distribution, extensive use and persistence. The most commonly used formulations include the emulsified concentrate, granule, wet powder and dispersible granule has significant importance because of its wide distribution and extensive use and persistence. The hydroxyl $^{\cdot}OH$ attack is the most efficient process of chemical oxidation. The degradation-induced of chlorpyrifos by gamma radiolysis was studied in packaging of high-density polyethylene tree layer coextruded, named COEX, irradiated intact and fragments. The intact packing was irradiated with water and the fragmented packing was irradiated with water and with a solution of 50% of water and 50% of acetonitrile. An AECL "Gammacell 220" ^{60}Co source and a multipurpose gamma irradiator were used in the processing. The chemical analysis of the chlorpyrifos and by-products were made using a gas chromatography associated to the mass spectrometry (MSGC-Shimadzu QP5000. Radiation processing of packing in pieces showed higher efficiency in removing chlorpyrifos than whole packing. The presence of water showed fundamental to promote the formation of frees radicals and acetonitrile facilitate the dissolution of chlorpyrifos and consequently its removal.

1. INTRODUCTION

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 [5]. The disposal responsibility of the pesticide plastic packing is by Brazilian Federal law attributed to the industry. This fact led the segment to mobilize and create the National Institute of Processing of Empty Packing, INPEV, with the objective of coordinating this operation [5].

Silage wrap, bags and sheets, heavily contaminated with organic material, are notoriously difficult to reprocess into any form of commercial commodity. Since is no longer allowed the uncontrolled burying and burning of the waste, only two options remain, to dispose, or to recycle, in ways that protect the environment and human health. Cleaning the pesticide containers is the crucial on-farm activity. Triple rinsing has proved to be effective, but not without its problems. Chlorpyrifos, o, o- Diethyl - o- (3,5,6 – trichloro – 2 - pyridyl)

phosphorothioate, has significant importance because of its wide distribution, extensive use and persistence. The most commonly used formulations include the emulsified concentrate, granule, wet powder and dispersible granule [6,9].

The generated OH radicals "in situ" by the interaction of ionizing radiation with water was successfully applied for organic pollutants removal in environmental samples and industrial effluents [2,3,4]. The other main radicals formed by ionizing radiation are the reducing radical solvated electron (e-aq), and H. atoms. These reactive species react with organic compounds inducing their decomposition. Various research groups in the world have studied the degradation of pesticides in different matrices. [1,7].

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 [8]. It was detected that the major products of initial degradation of chlorpyrifos are the desulphuration product, Chlorpyrifos-oxon and the hydrolysis product, 3,5,6-trichloro-2-pyridinol (TCP). It is interesting to note that gamma radiolysis follows the same pathway as chlorpyrifos environmental degradation, involving chemical and microbiological processes. Others studies have found both Chlorpyrifos-oxon and the hydrolysis product 3,5,6-trichloro-2-pyridinol (TCP), in urine of contaminated animals and in environmental samples.

For this research it was evaluated the most efficient system for irradiation, if it is necessary to mill the packing or if it is better irradiate the whole packing, as well as the chemical formulation influence in that efficiency.

2. EXPERIMENTAL

Packing with one liter volume contaminated with two types of chlorpyrifos commercial formulation called as "A" and "B", were used (Table 1). For the first experiment, 11 packing contaminated with pesticide "A" type, were used; from these, five packing were triple rinsed using 250 mL of distilled water and six packing were used without triple rinse.

For the second experiment, packing contaminated with pesticide "A" and "B", without triple rinsing, were cut in small pieces and placed in bag with 20 g each one. The purpose was simulating the grinding in the recycle process. These samples were irradiated in triplicate in two ways: with 50 mL of distilled water (packing with water) and with 50 mL of distilled water plus 25 mL of acetonitrile (packing with acetonitrile).

TABLE 1. Characteristics of commercial pesticides used in the present study

Commercial Formulation	**Class**	**Chemical Characteristic**	**Concentration (g/L)**	**Viscosity (cP a 20^0C)**
Emulsionable Concentrate **(B)**	insecticide	Organofosphorate	480	10,1
Concentrate emulsion **(A)**	insecticide	Organofosphorate	450	364

2.1 Radiation processing

The packing samples of pesticide "A", as described in the Table 2, were irradiated with 17.0 kGy and 26.0 kGy absorbed doses. The 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 packing in pieces of pesticide "A" and "B" was irradiated with 25 kGy, 50 kGy, 100 kGy, 150 kGy and 200 kGy absorbed doses at Cobalt-60 gamma irradiator, Gammacell-type, at dose rate 3.4 kGy/h, and Fricke dosimeter was employed to determine the absorbed dose rate of the system.

TABLE 2. Concentration and removal of chlorpyrifos from packing "A", in the packing after radiation processing and extraction with acetonitrile for 30 minutes and 24 hours, in different conditions.

PACKING	ABSORVED DOSE (kGy)	TRIPLE RINSING	FILLING	CHLORPYRIFOS ($\mu MolL^{-1}$)	
				∑ extraction in acetonitrile	Removal rate (%)
E0A*	00	no	Empty	146,943.0	
E1	26	no	Empty	110,282.0	**25.0**
E0B*	00	no	Distilled water	38,919.9	
E2	17	no	Distilled water	24,291.9	**37.6**
E3	26	no	Distilled water	22,725.7	**41.6**
E0C*	00	yes	Empty	570.5	
E4	17	yes	Empty	254.2	**55.5**
E5	26	yes	Empty	158.3	**72.3**
E0D*	00	yes	Distilled water	115.6	
E6	17	yes	Distilled water	7.8	**93.2**
E7	25	yes	Distilled water	<5.0	**99.0**

2.2 Chemical Analysis

Chlorpyrifos was extracted with acetonitrile. After irradiation, samples in pieces were separated from water and sonicated with 25 mL of acetonitrile for 15 minutes. The water was analyzed after dilution 1:1 in acetonitrile.
The chemical analysis of the Chlorpyrifos and other organic compounds were performed using gas chromatography with FID detector Shimadzu, model GC-FID 17-A, and gas chromatography associated to mass spectrometry using Shimadzu, model GC-MS QP-5000 in the following conditions:

- 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).

3. RESULTS AND DISCUSSION

The chemical analyze parameters, as the solvent study and calibration curve were discussed elsewhere [8]. Commercial chlorpyrifos showed to contain other toxic organic compounds used as solvent and stabilizer. These organic compounds were identified by mass

spectrometry; in the pesticide "A" the main compounds were hexylenoglicol, trimethylbenzene, 1,2- dimethyllindane, naphthalene, 1-methylnaphtalene, 1,4-dimethylnaphtalene and in the pesticide "B" were methylethylbenzene, trimethylbenzene, propenylbenzene and very small quantities of naphthalene. The main differences between the two commercial formulations of the pesticides is the high concentration of naphthalene and its methyl derivatives in the pesticide "A" and the very high concentration of trimethylbenzene in the pesticide "B".

3.1 Whole packing decontamination

The obtained results after packing processing by radiation in different conditions and absorbed doses (E1 to E7) plus respective control (E0A to E0D) is showed in Table 2. In all conditions the packing presented a contamination reduction, but the triple rinsing before irradiation showed to be fundamental to the contamination reduction. Only triple rinsing reduced the Chlorpyrifos concentration from 140352.0 µM/L (E0A) to 484.9 µM/L (E0C).

Comparing the removal rate in the packing E4 (55.5%) and E5 (72.3%) against E6 (93.2 %) and E7 (99%) all triple rinsed, it was observed higher chlorpyrifos removal rate in the packing E6 and E7, where water was present. The presence of water showed to be more efficient than the applied absorbed dose. In this preliminary experiment, the total removal (99%) of chlorpyrifos was reached in the packing E7, triple rinsed, in presence of water and with 26 kGy of absorbed dose.

3.2 Packing Pieces Decontamination

The obtained results of the packing in pieces experiments are condensed in the Figure 1, where the variation of the chlorpyrifos concentration with the absorbed doses in pesticide packing are present. In the samples irradiated without acetonitrile, the concentration of chlorpyrifos was too low, because it was not dissolved, but in presence of acetonitrile, the dissolution was complete and it was possible to measure the concentration of the pesticide. This effect was observed as in the formulation A well as in the formulation B.

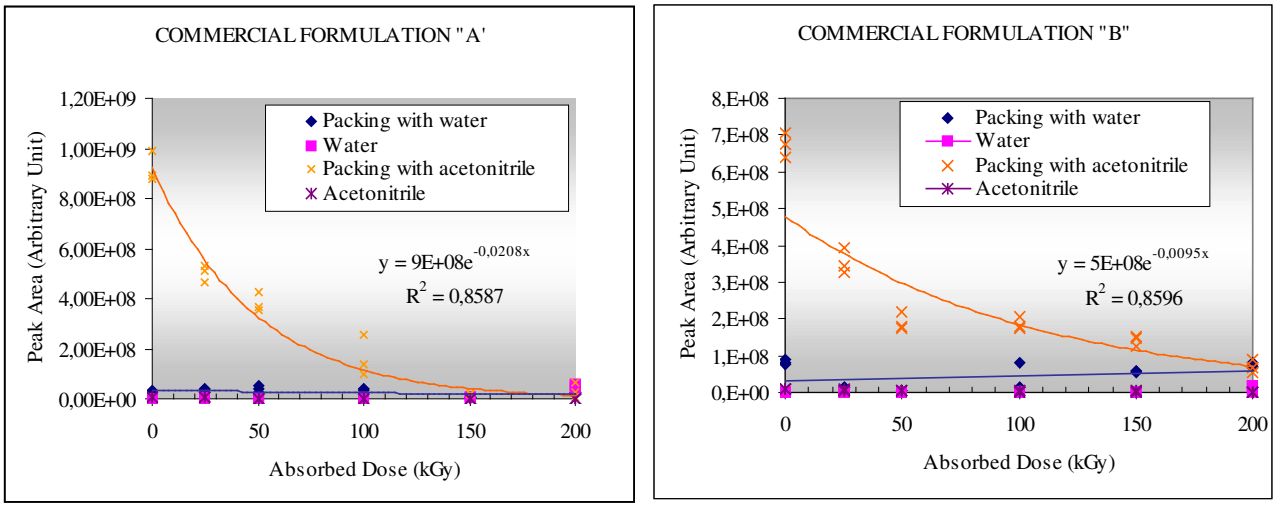

Figure 1. Degradation of chlorpyrifos of pesticide "A" and "B" from packing in pieces, and residues in water and in acetonitrile

A chlorpyrifos removal of about 70% was reached with 50 kGy absorbed dose, in the formulation A while with the same dose; the chlorpyrifos removal was about 40% in the pesticide B.

The formulation showed affect the degradation yield of chlorpyrifos (Fig.2). The viscosity and solubility in the solvents could be the responsible for the different behavior, interfering in the hydroxyl radicals reaction. The pesticide formulation "B" presented lower proportion of solvent/chlorpyrifos than pesticide formulation A, and the detected solvents are from 20 to 60 times more soluble in water than chlorpyrifos; this fact may be the responsible for its lower removal rate.

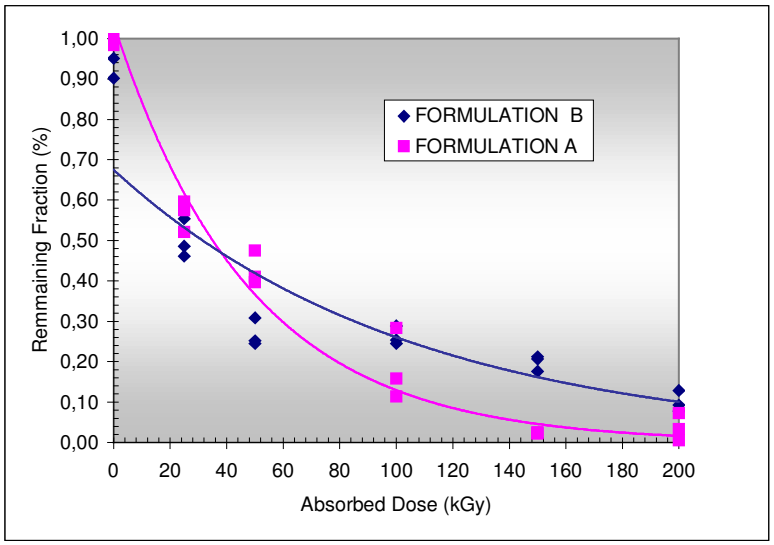

Figure 2. Degradation of chlorpyrifos from pesticide "A" and "B"

The whole packing without triple rinsing (E0A) presented a lower removal rate (25%) than the packing in pieces (>90%) for the same absorbed dose. The irradiation of packing in pieces showed better yield than the whole packing, due to in that case the interaction of the radiation with the pesticide is facilitate, because the sample volume decrease and the water contact and consequent production of free radicals increase. While in wet samples only the direct interaction of the radiation with the pesticide molecule is responsible by the degradation.

4. CONCLUSION

Radiation processing of packing in pieces showed higher efficiency in removing chlorpyrifos than whole packing. The presence of water showed be fundamental to promote the formation of free radicals and acetonitrile facilitate the dissolution of chlorpyrifos and consequently its removal.

The irradiation of the packing can be advantageous considering that the contaminated pesticide packing are destroyed by incineration that is a very expensive process that obstruct the recycle of the high density polyethylene (HDPE).

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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