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Degradation of chlorpyrifos by ionizing radiation

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Chlorpyrifos is an organophosphate pesticide commercialized since 1965 and it is now one of the top five commercial insecticides. It is registered for use in over 900 different pesticide formulations in the world. Chlorpyrifos poisoning usually affects many organs of the body, such as the central and peripheral nervous system, eyes, respiratory system, and the digestive tract. Depending on the pesticide formulation and type of application, chlorpyrifos residues may be detectable in water, soil, and on the surfaces from months to years. This paper presents preliminary studies of the removal of chlorpyrifos by exposition to ionizing radiation, to be applied in pesticide container decontamination. Samples containing various concentrations of chlorpyrifos in acetonitrile were irradiated with absorbed doses varying from 5 to 50 kGy, using a ^{60}Co gamma-source with 5,000 Ci activity (Gamma cell type). The chemical analysis of the chlorpyrifos and the by-products resulted from the radiolitic degradation were made using a gas chromatography associated to mass spectrometry (GC-MS) and gas chromatography with flame ionization detector (GC-FID).

Introduction

Human population is constantly exposed to numerous chemical species present in the environment. Chlorpyrifos, o,o-Diethyl-o-(3,5,6-trichloro-2-pyridyl)-phosphorothioate, has significant importance because of its wide distribution, extensive use and persistence.[1]

The Brazilian agriculture activities have consumed about 288,000 tons of pesticides per year conditioned in about 107,000,000 containers with weight of approximately 23,000 tons. When the empty containers of pesticides are discharged without inspection and control, they may cause problems to the human health, animals and environment. A Federal Law attributes to the pesticides industries the responsibility over the final destination of the containers. This fact has led the segment to mobilize itself and create the National Institute for Processing Empty Containers (inpEV) with the objective of the coordination of this operation.[2]

Chlorpyrifos is an organophosphate pesticide commercialized since 1965 and now is one of the top five commercial insecticides. It is registered for use in over 900 different pesticide formulations in the world. Because of its versatility, chlorpyrifos products are used in a wide range of pest control applications in the world. Chlorpyrifos-ethyl and methyl insecticides are both available to be formulated into many different commercial products. The most commonly used formulations include the emulsified concentrate, granule, wet powder and dispersible granule.[1]

Chlorpyrifos poisoning usually affects many organs of the body, such as the central and peripheral nervous system, eyes, respiratory system and the digestive tract. Depending on the pesticide formulation and type of application, chlorpyrifos residues may be detectable in water, soil, and on the surfaces from months to years, and the residues may remain active for up to 18 years.[1,3,4]

Advanced Oxidation Process (AOP), using ozone, hydrogen peroxide, ultra-violet and gamma-irradiation, is a promising technology for generation of OH radicals and removal of organic pollutant from the environment. The most simple and efficient method for generating OH radicals "in situ" is the interaction of ionizing radiation with water. This method was successfully applied for liquid samples containing chlorinated aliphatic, aromatics hydrocarbons and pesticides.[5–11]

The reactive species formed by the water irradiation are the reducing radical's solvated electron (e-aq), H atoms and the oxidizing radical hydroxyl OH. The reactive species react with organic compounds in the water inducing their decomposition. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical-chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds.[9,10,12–14]

This paper presents a preliminary study of chlorpyrifos removal in liquid samples by exposition to ionizing radiation. This study is part of the project of pesticides plastic container decontamination using the Advanced Oxidation Process by ionizing radiation.

Experimental

Sampling

Two types as chlorpyrifos standards, such as pure chlorpyrifos and commercial formulation with 450 g/l of active ingredient, were used in this study. Standard stock samples were prepared in methanol containing 360 mg/l of chlorpyrifos. Work solutions with 13.7, 27.4, 68.5, 136.9 and 273.8 μMol/l of chlorpyrifos in acetonitrile, were prepared.

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Radiation processing

Samples were irradiated at 5, 10, 20 and 50 kGy absorbed doses. The irradiations were carried out at room temperature using a ^{60}Co gamma-irradiator, Gammacell-type, at a dose rate of 4.5 kGy/h, in a batch system. A Fricke dosimeter was used to determine the absorbed dose rate of the system. The vials were completely filled without headspace.

Chemical analysis

The chemical analysis of the chlorpyrifos and the radiolytic by-products after irradiation processing was done using gas chromatography with flame ionization detector (FID) Shimadzu, Model GC-FID 17-A, and gas chromatography-mass spectrometry using the 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, and interface temperature of 240 °C and continuous operation mode (SCAN).

Results and discussion

Chemical analysis

Finding an appropriate extraction method was the first problem for chlorpyrifos, due to its low solubility in water (2 mg/l) and in organic solvents. It was necessary to evaluate the most adequate solvent that was simultaneously good for chromatographic analysis and for chlorpyrifos dissolution.

Liquid-liquid extraction is the classical approach for pesticide extraction from water samples. Dichloromethane is the most used solvent, because it is capable of extracting compounds with a wide range of polarities and it is easy to evaporate.

The n-hexane extracts selectively the non-polar pesticides, but the drawback is its volatility, whereas the dichloromethane extraction will cover a wider polarity range but obviously also include more matrix interference's.

Acetronitrile showed to be more adequate because of the total dissolution of chlorpyrifos and its low volatility. To reduce the volume of organic waste, batch extraction of 1 ml of solvent and 1 ml of water sample was applied.

GC-MS has proved being an advantageous and powerful technique for pesticide analysis mainly because of its high sensitivity, versatility and selectivity. Selective detectors have progressively been replaced by GC-MS, mainly using Electron Impact and CI, but in the case of chlorpyrifos the FID detector showed more sensitivity and reproducibility (Fig. 1). The detection limit (LMD), using GC-FID was 1.7 μMol/l, while using the MS-GC was 5.7 μMol/l, and the obtained experimental variability ($N = 10$), expressed as standard deviation, was 4% and 10%, respectively.

After gamma-irradiation, the concentration of chlorpyrifos decreased as can be seen at the Fig. 2, which shows the percentage removal as a function of absorbed dose and concentration. The decomposition radiation yield decreases when the chlorpyrifos concentration increases. Even 50 kGy was not enough for total removal in the case of higher concentration of chlorpyrifos in acetonitrile.

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.

These results suggest that at higher absorbed doses the recombination of radicals decreases the removal efficiency and that there is not enough water molecule to deliver OH radical to the system. Exposure of water or dilute aqueous solutions to ionizing radiation leads to the primary species reducing radical's solvated electron (e-aq), H atoms and the oxidizing radical hydroxyl, OH.

Using the GC-MS it was possible to evaluate the pathway and the intermediate by-products of chlorpyrifos radiodegradation in acetonitrile. The major products have been identified as the desulphuration product, chlorpyrifos-oxon and the hydrolysis product, 3,5,6-trichloro-2-pyridinol (TCP).

The formation of both by-products increased with the initial concetration of the chlorpyrifos and the absorbed dose. No by-products were detected for concentrations of 13.7 μMol/l and 27.4 μMol/l because they were also removed with 5 kGy and 10 kGy (Fig. 3).

It is interesting to note that gamma-radiolysis follows the same pathway as chlorpyrifos environmental degradation, involving chemical and microbiological processes. Other 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.[14]

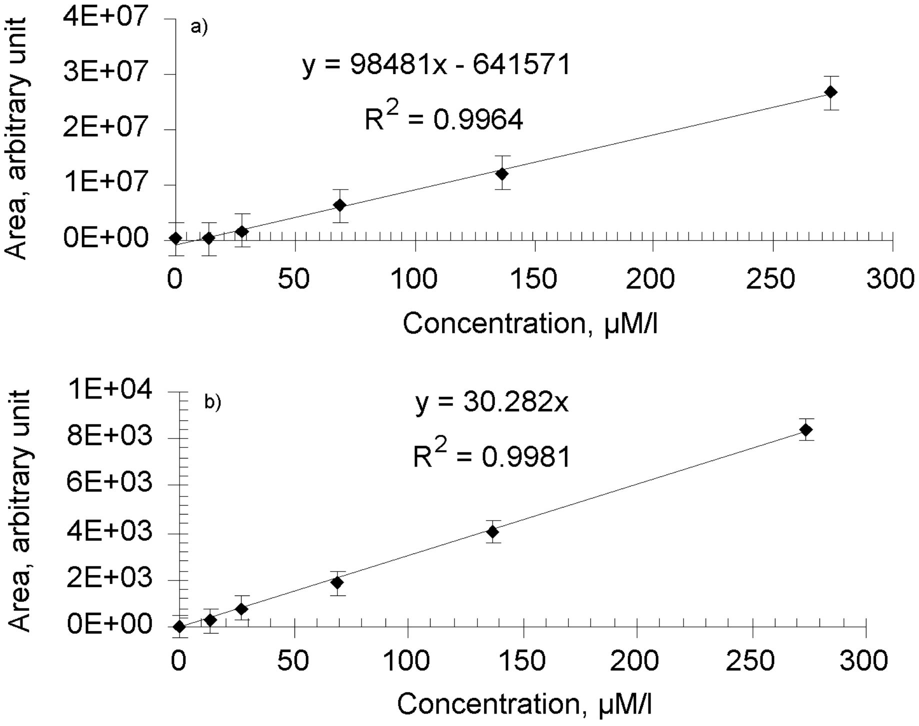

Fig. 1. Calibration curve of chlorpyrifos using gas chromatography with mass detector (GC-MS) (a) and with flame ionization detector (GC-FID) (b)

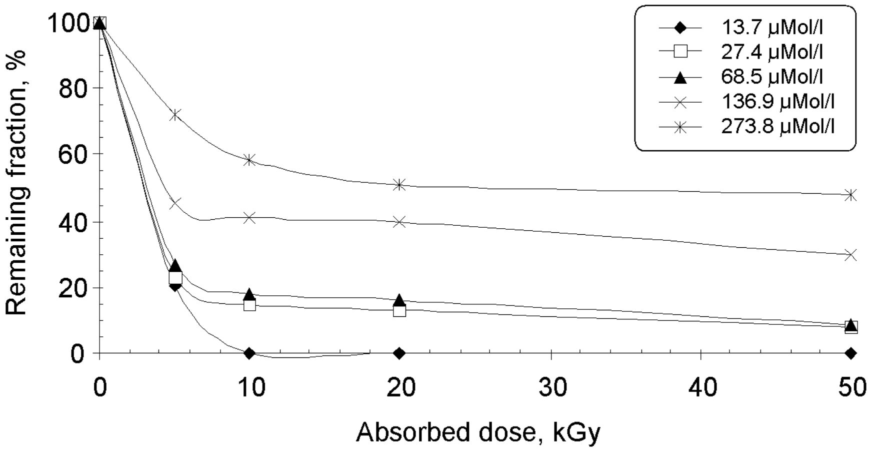

Fig. 2. Decomposition of chlorpyrifos after gamma-irradiation, analyzed by gas chromatography with FID detector (GC-FID), in various absorbed doses and concentrations

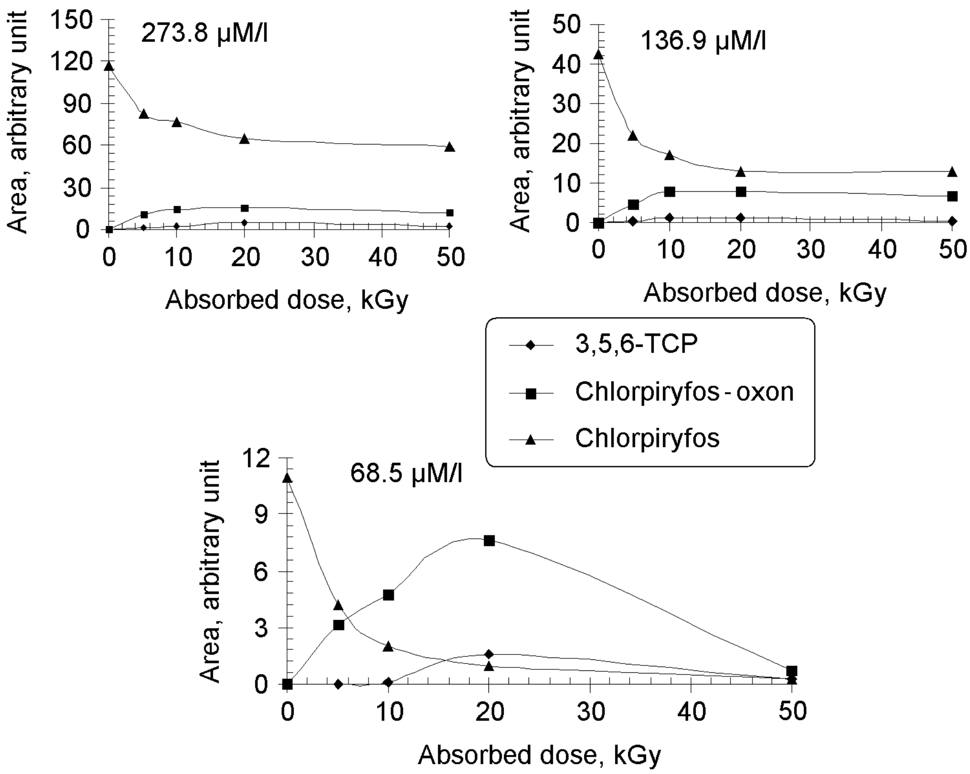

Fig. 3. Decomposition of chlorpyrifos and formation of chlorpyrifos-oxon and 3,5,6-trichloro-2-pyridinol (TCP) in the gamma-radiolysis of different concentrations as a function of the absorbed dose

Conclusions

Chlorpyrifos in 13.7 µMol/l concentration in acetonitrile was promptly degraded by ionizing radiation at 10 kGy absorbed dose. The minimal removal was 50% for 273.8 µMol/l. The main intermediate by-products of incomplete chlorpyrifos degradation are chlorpyrifos-oxon and 3,5,6-trichloro-2-pyridinol (TCP).

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