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Degradation kinetics of pirimiphos-methyl residues in maize grains exposed to ozone gas

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ABSTRACT

This work investigates the kinetics of degradation of pirimiphos-methyl residues in maize grains exposed to ozone gas and evaluates the effect of ozonation on grain quality. The assays employed maize grains treated with the insecticide, namely Actellic 500 CE® (pirimiphos-methyl), which were exposed for different periods to ozone gas at a concentration of 0.86 mg L^{-1}, provided at a continuous flow rate of 1.0 L min^{-1}. The insecticide residues were extracted from the grains using solid-liquid extraction with low temperature partitioning. The extracts were analyzed by gas chromatography with electron capture detection. Ozone effectively degraded more than 91% of the pirimiphos-methyl residues, with the degradation efficiency increasing in direct proportion to the duration of exposure to the gas. A first order kinetic model provided the best fit to the degradation data. The use of ozone gas did not alter the qualitative characteristics of the maize.

1. Introduction

Insecticides are widely used to protect stored grains and other products against attack by insect pests (Arthur, 1996; Wakil et al., 2013). In Brazil, the insecticides authorized for the treatment of stored maize belong to the organophosphorus and pyrethroid chemical groups, among which is pirimiphos-methyl, an organophosphorus compound (MAPA, 2017).

Higher dosages of insecticides are increasingly required for the effective control of pests, due to the development of pesticide resistance by insects (McDonough et al., 2011). This can lead to serious risks to humans, since insecticide residues can remain in foods at levels capable of harming health (Wakil et al., 2013).

In order to evaluate the safety of food for hazardous products like pesticides, several governments and international organizations have established protocols or programmes to supervise the residues of pesticides in food. In Brazil, the National Health Surveillance Agency (ANVISA) created, since 2001, a programme called PARA (Programa de Análise de Resíduos de Agrotóxicos em Alimentos) that evaluates whether the food for final consumers have residues of pesticides above the maximum residue limits (MRL) established for a given product (ANVISA, 2016). Similarly, the European Union annually publishes the European Union report on pesticide residues in food (EFSA, 2017). A total of 729 samples of maize were evaluated between 2013 and 2015 and 323 of them were found to contain residues of pirimiphos-methyl (ANVISA, 2016).

Greater awareness of consumers, together with new trends in food consumption, has increased the demand for products free from pesticide residues (Tiwari et al., 2010; Wakil et al., 2013). This has motivated the development of techniques capable of degrading pesticide residues in foods prior to their consumption. These methods include the use of ultraviolet (UV) radiation, ultrasound (US), and ozone gas (O_3). The use of ozone is especially attractive, due to its high oxidation potential (2.07 V) and ready availability.

Previous studies have reported the effectiveness of ozone in degrading several pesticide residues in different products, like the removal of residual fenitrothion in strawberries by ozonated water

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and removal of difenoconazole by ozone gas (Ikeura et al., 2011; Heleno et al., 2014), the removal of fenitrothion in lettuce by ozonated water (Ikeura et al., 2011), the removal of the fungicides boscalid, iprodione, fenhexamid, cyprodinil and pyrimethanil in grapes by ozone gas and removal of chlorothalonil by ozonated water (Karaca et al., 2012; Heleno et al., 2015), the removal of azinphos-methyl, captan, formetanate hydrochloride and mancozeb in apples by ozonated water (Ong et al., 1996; Hwang et al., 2001), the removal of fenitrothion in cherry tomatoes by ozonated water (Ikeura et al., 2011) and the removal of chlorothalonil in potatoes by ozonated water (Heleno et al., 2016). Thus, the aim of the present work was to study the degradation kinetics of pirimiphos-methyl residues in grains of maize (*Zea mays* L.) exposed to ozone gas. In addition, the effect of the ozonation process on the quality of the maize grains was evaluated.

2. Material and methods

The assays were performed in the Pre-Processing and Storage of Agricultural Products Section of the Department of Agricultural Engineering and in the Analytical Chemistry Laboratory of the Department of Chemistry, both at the Federal University of Viçosa (UFV), in Viçosa (Minas Gerais, Brazil). The insecticide-free maize grains variety LG 6036 (Limagrain, Goianésia, Brazil) were produced in the summer harvest in the municipality of Senador Firmino (Minas Gerais, Brazil). The characteristics of the grains were as follows: water content = 12.0% (wet basis); pest insect infestation = 1.0%; apparent specific mass = 714.6 kg m^{-3}; electrical conductivity = 8.5 μS cm^{-1} g^{-1}; germination capacity = 91.8%. The grains were treated with the insecticide Actellic 500 CE (50% w/v pirimiphos-methyl, Syngenta, São Paulo, Brazil) and were subsequently exposed to ozone for degradation of the insecticide.

2.1. Application of pirimiphos-methyl to the maize grains

The maize grains were spread in a thin layer on a plastic tarpaulin and were treated with the insecticide at a dosage of 24.0 mL (insecticide dilution) t^{-1}, equivalent to a theoretical pirimiphos-methyl concentration of 12.0 mg kg^{-1}. The insecticide was applied following the manufacturer's recommendation, with dilution in 1.0 L of water and spraying onto the grains with a compression hand sprayer (Guarany, Itu, Brazil). The grains were mixed using a rake and were then left for around 6 h to allow evaporation of the excess water. After this period, the grains were divided into 1.0 kg samples, which were stored in plastic bags under refrigeration (4 ± 2 °C) until the ozonation was performed.

2.2. Ozonation of the maize grains

The insecticide treated grain samples were individually exposed to ozone gas produced using an ozone generator (model O&L3. ORM, Ozone & Life, São José dos Campos, Brazil), in cylindrical PVC containers (0.20 × 0.25 m, diameter x height). For the generation of ozone gas, the oxygen from air was concentrated with an oxygen concentrator (model Mark 5 Plus, OxxiSul, Curitiba, Brazil) and fed into the ozone generator that operates by dielectric-barrier discharge (DBD). Ozone inlet and outlet connections were installed in the lower and upper caps of the cylinders, respectively. In each container, a metal screen was installed 10.0 cm from the base to support the grains and form a plenum that improved the spatial distribution of the ozone gas. Ozone was supplied at a concentration of 0.86 mg L^{-1}, using a continuous flow of 1.0 L min^{-1}, for different exposure periods from 0.0 to 1.0 h (0, 10, 20, 30, 40, 50 and 60 min). The ozone concentration was determined by indirect titration using the iodometric method, as recommended by the International Ozone Association (APHA, 2005). As a control, grains treated with the insecticide were exposed to pure oxygen gas, using the same conditions and exposure periods employed for ozonation (Fig. 1).

2.3. Determination of pirimiphos-methyl residues in the maize grains

The maize samples exposed to ozone or oxygen were removed from the fumigation chambers and homogenized individually using a Boerner type homogenizer. Each sample was then ground in a knife mill (Pulverisette 14, Fritsch, Oberstein, Germany) until a material with the consistency of flour was obtained. The pirimiphos-methyl residues remaining in the grains were quantified by submitting this material to the solid-liquid extraction with low temperature partitioning (SLE/LTP) procedure, followed by analysis using gas chromatography with electron capture detection (GC/ECD), according to the method developed by Freitas et al. (2014).

Preparation of the samples for extraction of pirimiphos-methyl consisted of weighing out 2.0000 g of ground maize grains, packing this material into 22.0 mL transparent glass flasks, and adding 4.0 mL of distilled water and 8.0 mL of acetonitrile. This mixture was agitated for 1.0 min using a vortex (Certomat®, MV, São Paulo, Brazil) and was then left in a freezer (model 280, Consul, São Paulo, Brazil) at −20 °C for around 3 h. The organic phase was collected and passed through a filter paper containing 2.0 g of anhydrous sodium sulfate, in order to eliminate the water present in the extract. After filtration, a 1.5 mL aliquot of the resulting extract was collected and transferred to a 1.8 mL vial, followed by addition of 15 μL of the internal standard (methyl parathion, 10.0 mg L^{-1}).

Chromatographic analysis of the extracts was performed by using a gas chromatograph (model GC-17-A, Shimadzu, Kyoto, Japan) equipped with an electron capture detector. A DB-5 capillary column was used (Agilent Technologies, Palo Alto, USA) (30 m × 0.25 mm i.d., 0.10 μm film thickness, and stationary phase composed of 5% phenyl and 95% dimethylsiloxane). The injector and detector temperatures were 280 and 300 °C, respectively. The column oven temperature started at 150 °C, maintained for 1.0 min, followed by a ramp at 30 °C min^{-1} to 210 °C, a ramp at 2 °C min^{-1} to 220 °C, and a ramp at 40 °C min^{-1} to 290 °C, maintained for 3.0 min.

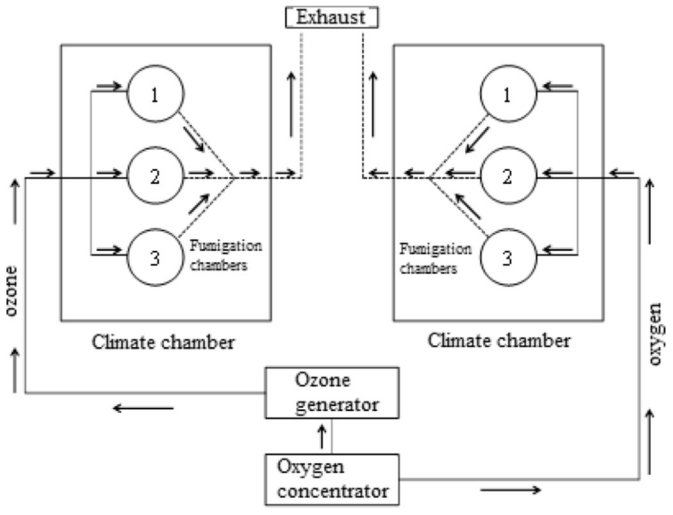

Fig. 1. Schematic diagram of the system used for ozone and oxygen fumigation of the maize grains.