Ozone as degradation agent of pesticide residues in stored rice grains

Mariane B. R. de Ávila¹ · Lêda Rita A. Faroni¹ · Fernanda F. Heleno² ·
Maria Eliana L. R. de Queiroz³ · Luiz P. Costa³

Revised: 6 September 2017 / Accepted: 19 September 2017 / Published online: 26 September 2017
© Association of Food Scientists & Technologists (India) 2017

Abstract This work aimed to study the kinetics of bifenthrin and deltamethrin residues degradation in rice grains under exposure to ozone and evaluate the effect of ozonization on rice grains marketing standards. The grains sprayed with pesticides were exposed to ozone at a concentration of 3 mg L^{-1} and continuous flow of 1.0 L min^{-1} for defined periods of up to 10 h. Residues of pesticides were extracted from grains using solid liquid extraction method with low-temperature partition analyzed by gas chromatography with electron capture detection (SLE/LTP-GC/ECD). Data from residual concentrations of bifenthrin and deltamethrin, due to the ozone exposure period, were adjusted to kinetic models of zero order, first order and second order. It was observed that ozone was effective in the degradation bifenthrin and deltamethrin residues, removing 91.9% of bifenthrin and 92.7% of deltamethrin. The kinetic model that best fitted deltamethrin and bifenthrin residues degradation data by ozone, was the one of first order. The marketing standards evaluated were the water content and yield. It was observed the ozone did not alter the rice grains water content and yield.

Keywords Pesticide residues · Stored grain · Fumigation

Introduction

Rice production must increase in the coming years since consumption is expected to grow above the estimate. This consumption growth is supported by a steady increase in the use of rice in human and animal food, besides other purposes (FAO 2014). Therefore, production and storage techniques should be used to meet such demand. High productivity and high end product quality require the use of pesticides both in the field and in grain storage units to control pests (Wang et al. 2012; Hou et al. 2013; Ikeura et al. 2013).

Two groups of insecticides are typically used in grain storage, namely, organophosphates and pyrethroids, due to their effectiveness against insects and low toxicity to mammals (Hirata 1995; Santos et al. 2007; Yu et al. 2014). In Brazil, the pyrethroid insecticide bifenthrin and deltamethrin have been used for the treatment of stored rice grains, among other products.

Bifenthrin and deltamethrin are widely used to control stored grain pests, in various field crops and for health control in homes because of its low toxicity to mammals (Sharma et al. 2005; Gu et al. 2008; Kaushik et al. 2009). However, these compounds can be harmful to non-target organisms, such as bees and fish, and consequently to the environment (Pimpão et al. 2007; Prestes et al. 2009; Pandher et al. 2012).

In Brazil, inappropriate insulation in grain warehouse structures favor infestation by insect pests. To minimize the problem, protective insecticides are misused, which arises concern about the quality of the products that reach consumers' table (Prestes et al. 2009). Consumers have increasingly demanded foods without pesticides residue (Dórea and Sobrinho 2004; Uddin et al. 2011). Oxidation techniques in an aqueous medium, such as chemical

✉ Lêda Rita A. Faroni
lfaroni@ufv.br

¹ Departamento de Entomologia, Universidade Federal de Viçosa, Viçosa, MG 36570-900, Brazil

² Departamento de Engenharia Agrícola, Universidade Federal de Viçosa, Viçosa, MG 36570-900, Brazil

³ Departamento de Química, Universidade Federal de Viçosa, Viçosa, MG 36570-900, Brazil

oxidation, photochemical degradation and chemical oxidation have been studied to optimize pesticide residue degradation (Chiron et al. 2000; Selma et al. 2008).

Recent studies have shown ozone gas efficiency in the removal of pesticide residues (Wu et al. 2007) and mycotoxins in plant products (Inan et al. 2007; Alencar et al. 2012). The availability of this gas and its oxidation capacity have been reported in some studies (Tiware et al. 2010; Silva et al. 2011). We emphasize the use of this gas for the removal of pesticides in corn (Freitas et al. 2014), strawberry (Heleno et al. 2014), lettuce (Ikeura et al. 2011), apples (Ong et al. 1996; Hwang et al. 2001), cherry tomato (Ikeura et al. 2011) and grape (Heleno et al. 2015). However, there are no reports of ozone use in the removal of pesticide residues in stored rice. This work aimed to study the kinetics of bifenthrin and deltamethrin residues degradation in rice grains exposed to ozone. In addition to that, we evaluated the effect of ozonation process on the trading patterns of the rice grains.

Materials and methods

This study used unhulled rice grains, free from pesticides, provided by the Agricultural Research Company of Minas Gerais (EPAMIG) and stored at 10 °C until the analysis was conducted. The grains presented the following characteristics: water content = 14.0%; infestation by insect pests = 1.0% and a yield of 69% of unbroken grains and 6% of broken grains. The grains were treated with the insecticide bifenthrin and deltamethrin and then exposed to ozone for pesticide residue degradation.

Insecticides spraying in rice grains

Rice grains were spread on plastic canvas, in a thin layer, and treated with the insecticide ProStore 25 CE[®], at the dose of 160 mL t⁻¹ and K-Obiol 25 CE[®], at the dose of 200 mL t⁻¹. These doses provide the theoretical bifenthrin and deltamethrin concentrations of 4.0 and 5.0 mg kg⁻¹, respectively. The insecticides were applied singly to the grains with the aid of a hand sprayer. The process was conducted as recommended by the manufacturer, each dose was diluted in 2.0 L of water and the solutions were sprayed on the grains. Then, the grains were homogenized with the aid of a squeegee, and remained at rest for about 2 h, to allow the evaporation of the excess water left by the insecticide spray. Next, the mass of grains was divided into samples of 0.6 kg, which were packed in plastic bags and stored under refrigeration until the time of ozonation.

Rice grains ozonation

Ozone gas was obtained from an ozone generator developed by the company Ozone & Life (São José dos Campos, Brazil). The oxygen gas was used as an input for ozone generation (Linde Gases, Canoas, Brazil, 99.5% purity).

The samples of rice grains treated with the insecticides were exposed to ozone gas in PVC cylindrical containers (0.20 × 0.35 m). Connections for gas input and output, respectively, were installed in the upper and lower lids of these cylinders. A metal plate was installed in each container, at 10.0 cm from the bottom, for the support of the grains and formation of a plenum, seeking to improve gas distribution. The fumigation container was divided into three equal parts supported by the plenum, for the performance of replications. Ozone was applied at a concentration of 3.0 mg L⁻¹ (1.600 ppm) and continuous flow of 1.0 L min⁻¹ in different periods of exposure. Grains treated with bifenthrin were exposed to ozone in periods ranging from 1.0 to 10.0 h and regular intervals of 1.0 h. Grains treated with deltamethrin were exposed to ozone in periods of 0.25, 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00 and 5.00 h. The periods of exposure were determined by preliminary tests. The ozone concentration was quantified by indirect titration, using the iodometric method (Silva et al. 2011). As a control, the grains were exposed to room air under the same conditions and periods used for ozonation.

Saturation of the chamber

The fumigation chamber was saturated with ozone gas introduced in concentration of 3.0 mg L⁻¹ (1.600 ppm), in continuous flow of 1.0 L min⁻¹. The concentration of ozone in the chamber was monitored every hour for 18 h, to establish the time required for the saturation of the chamber with 1.8 kg of rice.

The data of the chamber saturation with ozone was subjected to regression analysis Linear Response Plateau in function of time, using software SAEG (UFV, Viçosa, Brazil).

Method to quantify the insecticide residues in rice grains

Samples of rice grains (ozonated or exposed to room air) were removed from the fumigation chambers and homogenized separately. Then, each sample was ground in a Wiley mill (Fritsch Pulverisette 14, Oberstein, Germany) until the achievement of a product with flour consistency.

For the quantification of the bifenthrin and deltamethrin residues remaining in the grains, the milled samples were subjected to the solid–liquid extraction method with low

temperature partition, according to the method optimized and validated by Ávila et al. (2017).

The samples were prepared for the extraction of the active principles bifenthrin and deltamethrin by weighing a mass of two grams of milled rice, conditioning this material in a 22.0 mL clear glass and adding 2.0 mL of distilled water and 4.0 mL of acetonitrile. These mixtures were vortexed (Marconi, MA 162, Piracicaba, Brazil) for 1.0 min and kept in a freezer (Consul Slim 160, Joinville, Brazil) ($-20\text{ }^{\circ}\text{C}$) for about 6 h. Then, a 1.0 mL aliquot of the supernatant extract obtained was collected, transferred into a 1.8 mL vial for gas chromatography analysis.

The chromatographic analyses of the extracts were performed in a Shimadzu (Kyoto, Japan) gas chromatograph, model GC-2014, equipped with an electron capture detector (ECD) and AOC-20i auto injector. The chromatographic separation of the analyte was achieved using a HP-5 capillary column (Agilent Technologies, Palo Alto, CA, USA) with a stationary phase consisting of 5% diphenyl and 95% dimethylpolysiloxane (30 m $\times$ 0.25 mm, film thickness of 0.1 μm). Nitrogen was used as carrier gas (1.2 $\text{cm}^3\text{ min}^{-1}$). It was injected 1 μL extract/standard solution into the chromatograph, at 1:5 ratio, under the following chromatographic conditions: injector temperature of $280\text{ }^{\circ}\text{C}$; the column starts at $200\text{ }^{\circ}\text{C}$, and is heated at a rate of $30\text{ }^{\circ}\text{C min}^{-1}$ up to $290\text{ }^{\circ}\text{C}$. The column was maintained at this temperature for 5 min, and the temperature of the detector was $300\text{ }^{\circ}\text{C}$. The total analysis lasted 8 min. The compounds were identified by comparing the retention time of the peaks present in the extracts of the samples with the standard retention time.

The insecticides were quantified by the matrix-matched method. Working solutions were prepared using stock solutions from standard bifenthrin (98.8% w/w) and deltamethrin (99.7% w/w) solubilization, purchased from Sigma Aldrich (Steinheim, Germany), in acetonitrile (99.5% v/v), purchased from the Vetec company (Rio de Janeiro, Brazil). Thus, the nine-point calibration curves were obtained by applying the optimized extraction method in fortified matrices, at concentration interval between 0.090 and 1.400 mg kg^{-1} of bifenthrin, and between 0.060 and 2.000 mg kg^{-1} of deltamethrin, in the unhulled rice matrix.

Kinetics of pesticide degradation

Bifenthrin and deltamethrin residues levels according to exposure to ozone were fitted to the zero-order, first-order and second-order kinetic models. The model that best fitted the data was selected based on the value of the coefficient of determination and significance of the equation parameters related to the linear and angular coefficients.

Evaluation of trading standards of rice grains

The grain trading standards evaluation was performed after each grain exposure period to ozone gas or room air, in three replications. The selected analyses were moisture content and yield of the grains.

The grain moisture content was determined using the oven method, according to the rules established by the Rules for Seed Analysis (Brasil 2009), which prescribe the use of an oven with forced air at a temperature of $105 \pm 3\text{ }^{\circ}\text{C}$ for 24 h. Three replicates of 50 g of the grains were used to each treatment. Results were expressed in percentage, wet basis (w.b.).

The yield of grain was determined using the rice tester machine Suzuki, MT.34 (Santa Cruz do Rio Pardo, Brazil), which can hold samples of 100 g. In the machine, the samples passed through the stripper and then the vacuum chamber, where the shells were removed. After this process, the rice was removed from the center of the discharge record mug, and sharps, the side mugs. The husked rice was placed in a cylindrical *trieur* classifier coupled to the machine. After running the machine for 1 min, the *trieur* was removed to collect rice from the trough and from the wall. The yield of product was obtained directly in percent, by weight of the grains retained in *trieur* (unbroken) and by weight of the grains retained in the trough (broken). This evaluation aimed to determine the yield of rice to evaluate the trading standards after both treatments.

Statistical analyses

It was used a subdivided plot scheme, being the plots composed by treatment with ozone gas and the ambient air, and the subplots, the ozone exposure periods and the ambient air, in a completely randomized design with three replications. The data were submitted to analysis of variance, using the SAEG software (UFV, Viçosa, Brazil), and the averages were compared by Tukey test at 1 and 5% probability.

Results and discussion

Saturation of the chamber

The ozone gas is unstable, has a short half-life and is very reactive (von Gunten 2003). This way, the ozone concentration in the chamber is always lower than the concentration injected. In order to determine the necessary time to saturate the chamber with ozone gas and to allow a better evaluation of insecticide degradation kinetics in exposure periods, we studied the ozone gas behavior into the chamber as function of the initial concentration.

Fig. 1 Residual concentration of ozone as a function of the exposure period to the saturation process of the chamber with rice grains

In the fumigation chamber, ozone gas was introduced with constant flow of 1.00 L min^{-1} , in the concentration of 3.0 mg L^{-1} or 1.600 ppm . At the beginning of the process the concentration of ozone is zero at the outlet of the chamber thus the reactions with the chamber walls and with the grains. The gas behavior, Fig. 1, was described by the equation Linear Response Plateau, $\hat{y} = 118.4180 + 45.712 \text{ ep}$ ($0 \leq \text{ep} \leq 11.67$), in which ep = exposure period (h) and $\hat{y}$ = ozone concentration (ppm) and determination coefficient $R^2 = 0.90$. The outlet concentration stabilized at 11.67 h on the concentration of 651.81 ppm (1.22 mg L^{-1}) indicating saturation of the chamber. Part of the inlet ozone gas is degraded due to the reactions taking place inside the chamber, causing the saturation to occur at a concentration lower than the one initially injected.

Kinetics of insecticide degradation

The analysis of variance (ANOVA) for the concentrations of bifenthrin and deltamethrin in rice grains exposed to ozone gas and room air is presented in Table 1. The residual concentration of the pyrethroids bifenthrin and

deltamethrin varied significantly between grains exposed to ozone and room air, as well as between periods of exposure. There was also significant interaction between treatments and exposure periods for both insecticides.

Table 2 presents the mean concentrations of bifenthrin and deltamethrin in rice grains exposed to ambient air and to ozone, respectively. Removals of both insecticides were proportional to the increase in the ozone exposure period.

The behavior of the bifenthrin concentration as a function of the period of exposure of the grains to the ozone is explained by the model $\hat{y} = 3.6060 - 1.9717 \sqrt{\text{ep}} + 0.2868 \text{ep}$ ($R^2 = 0.99$), and the grain exposed to room air, by the model $\hat{y} = 3.5832 + 0.4380 \sqrt{\text{ep}} - 0.1955 \text{ep}$ ($R^2 = 0.69$), in which $\hat{y}$ = bifenthrin concentration and ep = exposure period.

The behavior of the concentration of deltamethrin as a function of the period of exposure of the grains to the ozone is explained by the model $\hat{y} = 3.6518 - 2.0439 \sqrt{\text{ep}} + 0.2235 \text{ep}$ ($R^2 = 0.97$), and that of the grains exposed to room air, by the model $\hat{y} = 3.23$, in which $\hat{y}$ = deltamethrin concentration and ep = exposure period.

It is also found that residues of bifenthrin (0.29 mg kg^{-1}) and deltamethrin (0.26 mg kg^{-1}) remaining in the grains at the end of the ozonation process were below the maximum residue limit (MRL) established by ANVISA (0.7 mg kg^{-1} for bifenthrin and 1.0 mg kg^{-1} for deltamethrin). These values are equivalent to a removal percentage of 91.9% for bifenthrin and 92.7% for deltamethrin.

The insecticides bifenthrin and deltamethrin have aromatic rings and double-bond radicals in their molecular structure. Ozone gas, as a strong oxidant, reacts with the insecticide molecule and interacts with the double bonds and aromatic chains (Chiron et al. 2000; von Gunten 2003). Ozone is among the main oxidizing agents, and has the second highest oxidation potential (2.07 mV) (Manley and Niegowski 1967). The oxidative power of ozone gas

Table 1 Summary of variance analysis for concentrations of bifenthrin and deltamethrin in rice grains exposed to ozone gas and room air

SV	DF	Average squares	
		Bifenthrin concentration	Deltamethrin concentration
Oz	1	102.117**	51.129**
R (a)	4	0.055	0.062
EP	10	2.139**	2.025**
Oz × EP	10	1.269**	1.742**
R (b)	40	0.0229	0.024
CV (%) plot		10.39	10.58
CV (%) subplot		6.71	6.59

** Significant by F test at 1% and 5% probability; *DF* degree of freedom, *SV* source of variation, *Oz* exposure to ozone and room air, *R (a)* residue A, *EP* exposure period, *R (b)* residue b, *CV* coefficient of variation

Table 2 Mean concentrations of bifenthrin and deltamethrin in rice grains exposed to room air and ozone

Exposure period (h)	Concentration (mg kg ⁻¹)		Removing percentage (%)
	Room air	Ozone gas	
Bifenthrin			
0.00	3.57 A	3.57 A	0.00
1.00	3.90 A	1.87 B	47.62
2.00	3.67 A	1.55 B	56.60
3.00	3.64 A	1.17 B	67.23
4.00	3.80 A	0.78 B	78.15
5.00	3.94 A	0.51 B	85.71
6.00	3.14 A	0.35 B	90.20
7.00	3.23 A	0.28 B	92.16
8.00	3.29 A	0.46 B	87.11
9.00	3.24 A	0.29 B	91.90
10.00	3.00 A	0.29 B	91.90
Deltamethrin			
0.00	3.58 A	3.58 A	0.00
0.25	3.20 A	2.73 B	23.74
0.50	3.13 A	2.56 B	28.49
1.00	2.62 A	1.56 B	56.42
1.50	3.15 A	1.72 B	51.96
2.00	3.58 A	0.92 B	74.30
2.50	3.50 A	1.13 B	68.43
3.00	3.22 A	0.64 B	82.12
3.50	3.50 A	0.69 B	80.73
4.00	3.30 A	0.41 B	88.55
5.00	2.79 A	0.26 B	92.74

Means followed by the same letter in the line do not differ from each other by the Tukey test at 5% probability

Table 3 Kinetic models adjusted to the concentration of bifenthrin and deltamethrin residues in rice grains, as a function of the exposure period to ozone

Order	Bifenthrin		Deltamethrin	
	Linearized equation	r ²	Linearized equation	r ²
Zero	$C = 2.4397 - 0.2798t$	0.71	$C = 2.7300 - 0.5970t$	0.85
First	$\ln C = 0.9682 - 0.2725t$	0.90	$\ln C = 1.1524 - 0.4945t$	0.96
Second	$1/C = -0.0284 + 0.4199t$	0.88	$1/C = 0.0559 + 0.6088t$	0.85

explains its efficiency in the degradation of bifenthrin residues. It is noteworthy that reports have been made on the efficiency of this gas in the degradation of many pesticides, including pyrethroids (Segal-Rosenheimer and Dubowski 2007; Wu et al. 2007; Freitas et al. 2014).

The rates of pesticide oxidation with ozone gas can reach more than five orders of magnitude (von Gunten 2003). In the study on the kinetics of bifenthrin degradation by ozone, it was found that the first order kinetic model showed a coefficient of determination ($r^2 = 0.90$), higher than the others (Table 3), although the second order kinetic model also presented high coefficient of determination

($r^2 = 0.88$). Since both models are linear and the r^2 values are quite close, the first order model was used to describe bifenthrin degradation in rice grains.

In relation to the degradation of deltamethrin by ozone, it was observed that the first-order model showed the highest coefficient of determination ($r^2 = 0.96$) in relation to the others (Table 3). In this case, this was the model that best represented the degradation process of deltamethrin by ozone. As the first-order model was also the one that best represented the degradation of bifenthrin by ozone, we chose to use it to represent the degradation of both insecticides in rice grains exposed to the gas (Fig. 2).

Fig. 2 Kinetic models adjusted to the residual concentration of bifenthrin (a) and deltamethrin (b), as a function of the exposure period to the ozone gas

The study of the kinetics of pesticide degradation is important in the knowledge of the behavior of the molecule in the grain under exposure to the ozone gas. By means of this study, it is known the speed at which the degradation reaction occurs. The first order model to represent the kinetics of pesticide degradation was reported by several authors. For the degradation of pirimiphos-methyl in industrial water (Chiron et al. 1998); for the permethrin degradation kinetics data (Segal-Rosenheimer and Dubowski 2007) and atrazine degradation data (Acero et al. 2000). Chelme-Ayala et al. (2010) also reported the degradation kinetics of bromoxynil and trifluralin in aqueous solution and concluded that the second-order model was the best fit. These studies reinforce the results obtained in this research, in which the first-order kinetic model describes the linearization of the data by means of the neperian logarithm (ln) of the insecticide concentration as a function of the ozone exposure period. The negative value of the degradation rate constant obtained in the

equation (Table 3) indicates that the degradation process is directly proportional to the increased time of exposure to gas.

The half-life times ($t_{1/2}$) calculated for bifenthrin and deltamethrin ($t_{1/2} = \ln(2)/k$, in which k = reaction rate constant) in rice grains exposed to ozone, according to the fitted model, were 2.54 and 1.40 h, respectively. These results demonstrate that the efficiency of ozone in the process of degradation of deltamethrin is superior to the efficiency in the degradation process of bifenthrin.

Evaluation of marketing standards for rice grains

The evaluation of the marketing standards of rice is important for the knowledge of the effect of grains exposure to ozone gas in its main physical properties, which influence the market price of the product.

In the bifenthrin removal process under ozone and room air exposure, the average percentage of unbroken and broken grains was 72.16 and 5.95%, respectively. And when exposed to room air, the average percentage of unbroken and broken grains was 69.87 and 6.54%, respectively. It is observed that the average percentage of unbroken grains is higher for grains exposed to ozone. As a function of the exposure period, the mean percentage of whole grains adjusted to the model $\hat{y} = 71.02\%$, and that of broken grains, to the model $\hat{y} = 6.25\%$. The water content was not significant by F test at 1 and 5% (Table 4).

In the deltamethrin removal process under ozone and room air exposure, it was observed a significant difference for water content and unbroken grains ($P \leq 0.05$) (Table 4). A significant difference was observed, for unbroken grains, in periods of exposure of 0.5 and 2.0 h between rice grains exposed to room air and ozone gas. And, for water content, a significant difference was observed during the exposure periods of 0.5, 1.0, 1.5, 3.5, and 5.0 h. Regarding a interaction behavior observed of the unbroken grains and the water content according to the period of exposure (Table 4), the percentage of unbroken grains adjusted to the model $\hat{y} = 68.56\%$, for the treatment with room air, and $\hat{y} = 68.28\%$, for treatment with ozone gas. The water content was adjusted to the model $\hat{y} = 14.1\%$, for the treatment with room air, and $\hat{y} = 14.0\%$, for the treatment with ozone gas. The percentage of broken grains was lower in grains exposed to room air (6.97%) than those exposed to ozone gas (7.39%). The behavior of the broken grains according to the exposure period was adjusted to the model $\hat{y} = 7.18$.

According to Brazilian law, is attributed to rice a yield of 40% of unbroken grains and 20% of broken grains. The results obtained in this work corroborate those described by the national classification legislation for commercial purposes. These results are further reinforced by reports in the

Table 4 Summary of variance analysis of the characteristics of water contents, unbroken and broken grains in the bifenthrin and deltamethrin removal process in rice grains

SV	DF	Average squares		
		Water content	Unbroken grains	Broken grains
Bifenthrin				
Oz	1	0.2840 ^{NS}	86.0579 ^{**}	5.6844 ^{**}
R (a)	4	0.1013	0.7279	0.5537
EP	10	0.3803 ^{NS}	15.8864 ^{**}	2.9876 ^{**}
Oz × EP	10	0.1503 ^{NS}	11.4174 ^{NS}	1.5507 ^{NS}
R (b)	40	0.2178	5.6422	0.9631
CV (%) plot		2.33	1.20	11.91
CV (%) subplot		3.42	3.34	15.72
Deltamethrin				
Oz	1	0.0882 ^{**}	1.2533 ^{NS}	2.9813 ^{**}
R (a)	4	0.0077	0.8445	0.1838
EP	10	0.8141 ^{**}	12.064 ^{**}	1.4691 ^{**}
Oz × EP	10	0.1164 ^{**}	4.3833 ^{**}	0.4649 ^{NS}
R (b)	40	0.0257	1.8877	0.3060
cv (%) plot		0.62	1.34	5.96
CV (%) subplot		1.14	2.00	7.69

^{NS} not significant, ^{**} Significant by F test at 1 and 5% probability, *DF* degree of freedom, *SV* source of variation, *Oz* exposure to ozone and room air; *R (a)* residue A, *EP* exposure period, *R (b)* residue b, *CV* coefficient of variation

literature that ozone does not affect the grading parameters of maize (Pereira et al. 2007) and peanut (Alencar et al. 2012), as specific mass, electrical conductivity and oil content.

Conclusion

Ozone gas was efficient in removing bifenthrin's and deltamethrin's residues in rice grains. The percentage of the insecticides' removal was proportional to the period of exposure to the gas. In addition, after ozonation the rice grains were not affected. Therefore, the ozonation technique is promising for the removing of insecticide residues in rice grains.

Acknowledgements We thank the Brazilian Agencies: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for their financial support.

References

- Acero JL, Stemmler K, von Gunten U (2000) Degradation kinetics of atrazine and its degradation products with ozone and oh radicals: a predictive tool for drinking water treatment. *Environ Sci Technol* 34:591–597
- Alencar ER, Faroni LRA, Soares NDFF, Silva WA, Carvalho MCS (2012) Efficacy of ozone as a fungicidal and detoxifying agent of aflatoxins in peanuts. *J Sci Food Agric* 92:899–905
- Ávila MBR, Faroni LRA, Heleno FF, Queiroz MELR, Almeida RI (2017) Chemometrically assisted optimization of SLE/LTP procedures for determination of dissipation and translocation of pesticide residues in rice grains. *J Food Sci Technol* (in press)
- Brasil. Ministério da Agricultura, Pecuária e Abastecimento (2009) Regras para análises de sementes. First edit. Brasília: MAPA/ACS
- Chelme-Ayala P, El-Din MG, Smith DW (2010) Kinetics and mechanism of the degradation of two pesticides in aqueous solutions by ozonation. *Chemosphere* 78:557–562
- Chiron S, Rodriguez A, Fernandez-Alba A (1998) Application of gas and liquid chromatography-mass spectrometry to the evaluation of pirimiphos methyl degradation products in industrial water under ozone treatment. *J Chromatogr A* 823:97–107
- Chiron S, Fernandez-Alba A, Rodriguez A, Garcia-Calvo E (2000) Pesticide chemical oxidation: state-of-the-art. *Water Res* 34:366–377
- Dórea HS, Sobrinho L (2004) Analysis of pesticide residues in rice using matrix solid-phase dispersion (MSPD). *J Brazil Chem Soc* 15:690–694
- FAO (2014) FAO rice market monitor April 2014–Volume XVII–Issue No. 1, XV
- Freitas RS, Queiroz MELR, Faroni LRA, Heleno FF, Moura VV (2014) Desenvolvimento do método de extração sólido-líquido com partição em baixa temperatura para determinação de inseticidas em grãos de milho ozonizados. *Quim Nova* 37:238–243
- Gu X, Zhang G, Chen L, Dai R, Yu Y (2008) Persistence and dissipation of synthetic pyrethroid pesticides in red soils from the Yangtze River Delta area. *Environ Geochem Health* 30:67–77
- Heleno FF, Queiroz MELR, Neves AA, Freitas RS, Faroni LRA, Oliveira AF (2014) Effects of ozone fumigation treatment on the removal of residual difenoconazole from strawberries and on their quality. *J Environ Sci Health B* 49:94–101

- Heleno FF, Queiroz MELR, Neves AA, Faroni LRA, Sousa FA, Oliveira AF (2015) Ozone treatment for the removal of residual chlorothalonil and effects on the quality of table grapes. *J Braz Chem Soc* 26:687–694
- Hirata R (1995) Piretróides: estrutura química-atividade biológica. *Quim Nova* 18:368–374
- Hou X, Han M, Dai X, Yang X, Yi S (2013) A multi-residue method for the determination of 124 pesticides in rice by modified QuEChERS extraction and gas chromatography-tandem mass spectrometry. *Food Chem* 138:1198–1205
- Hwang ES, Cash JN, Zabik MJ (2001) Postharvest treatments for the reduction of mancozeb in fresh apples. *J Agric Food Chem* 49:3127–3132
- Ikeura H, Kobayashi F, Tamaki M (2011) Removal of residual pesticide, fenitrothion, in vegetables by using ozone microbubbles generated by different methods. *J Food Eng* 103:345–349
- Ikeura H, Hamasaki S, Tamaki M (2013) Effects of ozone microbubble treatment on removal of residual pesticides and quality of persimmon leaves. *Food Chem* 138:366–371
- Inan F, Pala M, Doymaz I (2007) Use of ozone in detoxification of aflatoxin B1 in red pepper. *J Stored Prod Res* 43:425–429
- Kaushik G, Satya S, Naik SN (2009) Food processing a tool to pesticide residue dissipation—a review. *Food Res Int* 42:26–40
- Manley TC, Niegowski SJ (1967) Ozone. *Encyclopedia of Chemical Technology*, New York
- Ong KC, Cash JN, Zabik MJ, Siddiq M, Jones AL (1996) Chlorine and ozone washes for pesticide removal from apples and processed apple sauce. *Food Chem* 55:153–160
- Pandher S, Sahoo SK, Battu RS, Singh B et al (2012) Persistence and dissipation kinetics of deltamethrin on chili in different agro-climatic zones of India. *Bull Environ Contam Toxicol* 88:764–768
- Pereira AM, Faroni LRA, Sousa AH, Urruchi WI, Roma RCC (2007) Efeito imediato e latente da fumigação com ozônio na qualidade dos grãos de milho. *Rev Bras Arm* 32:100–110
- Pimpão CT, Zamprônio AR, Assis HCA (2007) Effects of deltamethrin on hematological parameters and enzymatic activity in *Ancistrus multispinis* (Pisces, Teleostei). *Pestic Biochem Phys* 88:122–127
- Prestes OD, Friggi CA, Adaime MB, Zanella R (2009) QuEChERS—um método moderno de preparo de amostra para determinação multirresíduo de pesticidas em alimentos por métodos cromatográficos acoplados à espectrometria de massas. *Quim Nova* 32:620–1634
- Santos MAT, Areas MA, Reyes FGR (2007) Piretróides—uma visão geral. *Alim Nutri* 18:339–349
- Segal-Rosenheimer M, Dubowski Y (2007) Heterogeneous ozonolysis of cypermethrin using real-time monitoring FTIR techniques. *J Phys Chem C* 111:11682–11691
- Selma MV, Allende A, López-Gálvez F, Conesa M, Gil MI (2008) Disinfection potential of ozone, ultraviolet-C and their combination in wash water for the fresh-cut vegetable industry. *Food Microbiol* 25:809–814
- Sharma J, Satya S, Kumar V, Tewary DK (2005) Dissipation of pesticides during bread-making. *Chem Health Saf* 12:17–22
- Silva S, Luvielmo M, Geyer M, Pra I (2011) Potencialidades do uso do ozônio no processamento de alimentos. *Semin Cien Agrar* 32:659–682
- Tiwari BK, Brennan CS, Curran T, Gallagher E, Cullen PJ, O'Donnell CP (2010) Application of ozone in grain processing. *J Cereal Sci* 51:248–255
- Uddin R, Iqbal S, Khan MF, Parveen Z, Ahmed M, Abbas M (2011) Determination of pesticide residues in rice grain by solvent extraction, column cleanup, and gas chromatography-electron capture detection. *Bull Environ Contam Toxicol* 86:83–89
- von Gunten U (2003) Ozonation of drinking water: part I. Oxidation kinetics and product formation. *Water Res* 37:1443–1467
- Wang K, Wu JX, Zhang HY (2012) Dissipation of difenoconazole in rice, paddy soil, and paddy water under field conditions. *Ecotox Environ Safe* 86:111–115
- Wu J, Luan T, Lan C, Wai T, Lo H, Yuk G, Chan S (2007) Removal of residual pesticides on vegetable using ozonated water. *Food Control* 18:466–472
- Yu C, Li Y, Zhang Q, Zou N, Gu K, Li X, Pan C (2014) Decrease of pirimiphos-methyl and deltamethrin residues in stored rice with post-harvest treatment. *Int J Environ Res Public Health* 11:5372–5381