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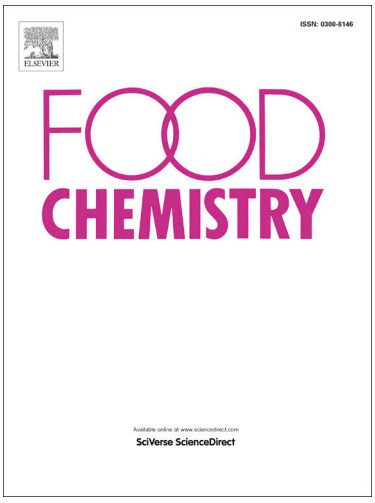

Short communication

Optimization of a rice cooking method using Response Surface Methodology with desirability function approach to minimize pesticide concentration

María Belén Medina, Silvia Liliana Resnik, Martín Sebastián Munitz

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Optimization of a rice cooking method using Response Surface Methodology with desirability function approach to minimize pesticide concentration.

María Belén Medina [a, b], Silvia Liliana Resnik [c, d, e], Martín Sebastián Munitz [a, *]

[a] *Facultad de Ciencias de la Alimentación, Universidad Nacional de Entre Ríos, Concordia, Argentina.*

[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), CABA, Argentina.*

[c] *Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), La Plata, Argentina.*

[d] *Fundación de Investigaciones Científicas Teresa Benedicta de la Cruz, Luján, Buenos Aires, Argentina.*

[e] *Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, CABA, Argentina.*

Abstract

Rice is contaminated with pesticides applied in pre and post-harvest. These contaminations could be reduced through household operations like washing and cooking. Therefore, in the present research, a pre-soaking rice cooking method was used to reduce pesticides residues. Response Surface Methodology with Central Composite Design was applied to minimize pesticides concentration by choosing the best soaking time and water:rice grain relation before cooking. A quadratic polynomial equation was obtained. Desirability function approach gave the optimal cooking conditions as 14 h soaking time and water:rice grain relation of 3. This process allowed a pesticide elimination of 100.0 %, 93.5 %, 98.4 %, 98.5 %, 99.0 %, and 95.0 %, of azoxystrobin, cyproconazole, deltamethrin, epoxiconazole, kresoxim-methyl and penconazole, respectively.

Key words: Rice cooking method – Pesticide residues – Chromatographic determination – Response surface methodology

Chemical compounds studied in this article

Deltamethrin (PubChem CID: 40585); Penconazole (PubChem CID: 91693); Kresoxim-methyl (PubChem CID: 6112114); Cyproconazole (PubChem CID: 86132); Epoxiconazole (PubChem CID: 3317081); Azoxystrobin (PubChem CID: 3034285)

1. Introduction

* Corresponding author. Email: munitzm@fcal.uner.edu.ar

The increased pesticide application in the fields has turned into a worldwide concern in the last decades, because it puts human health in a potential risk due to the accumulation of pesticide residues in the edible parts of the crops, which are an important part of the diet (Lee et al., 2008; Yang et al., 2012; Jeong, Kwak, Ahn & Jeong, 2012; Amirahmadi et al., 2017).

The concentration of pesticides in food can be reduced through home operations prior to consuming them (Cámara, Cermeño, Martínez & Oliva, 2020; Li, Hu, Qian, Wang & Zhang, 2019; Mekonen, Ambelu & Spanoghe, 2019). Keikotlhaile, Spanoghe and Steurbaut (2010) mentioned that this effect could be related to physicochemical properties of pesticide or the physical location of it in the commodity. Abdullah et al. (2016) studied the reduction of pesticides residues in spinach washing with acetic and citric acid solutions. Household food processing such as cooking, roasting, baking, and others are able to minimize the pesticide concentration (Chung, 2018).

Rice (Oryza sativa L.) is one of the most consumed cereals in the world (Sharafi, Yunesian, Mahvi, Pirsaheb, Nazmara & Nodehi, 2019), with the highest caloric intake (De Bernardi, 2017). Medina, Munitz and Resnik (2019) found six pesticides commonly used in Argentinian rice fields, in rice samples collected from supermarkets. They were azoxystrobin, cyproconazole, deltamethrin, epoxiconazole, kresoxim-methyl and penconazole. The concentration of some of these pollutants were above Maximum Residue Limits (MRL) stablished by Codex Alimentarius (Codex Alimentarius, 2013), SENASA (SENASA, 2010) and the European Commission (EC, 2005).

In general, there are different household rice cooking methods (Yu, Turner, Fitzgerald, Stokes & Witt, 2017). The most common ones in Argentina are cooking with just the right amount of water, with excess water, and pre-soaking the rice before cooking. Rice can also be cooked with steam; under elevated temperature and pressure; or using a microwave (Boluda-Aguilar, Taboada-Rodríguez, López-Gómez, Marín-Iniesta & Barbosa-Cánovas, 2013; Leelayuthsoontorn & Thipayarat, 2006; Metcalf & Lund, 1985; Son, Do, Kim, Cho, Suwonsichon & Valentin, 2013). Medina, Munitz and Resnik (2020) compared the three rice cooking methods commonly used in Argentina, finding that pre-soaking the rice previously to the cooking step generated the highest pesticide concentration reduction, and it would be important to improve this cooking method to reach the lowest pesticide concentration.

Response surface methodology (RSM) is a useful statistical tool to evaluate the effect of different factors and their interactions on response variables. There are different experimental designs that allow finding optimal

conditions when a RSM is applied, using a minimum number of determinations. Three of the most used ones are Factorial Design (Salas, Pok, Resnik, Pacin & Munitz, 2016; Pok, Salas, Resnik, Pacin & Munitz, 2018), Box-Behnken Design (BBD) (Hu, Zhang, Liu, Wang & Wang, 2018) and Central Composite Design (CCD) (Ooi et al., 2018). A desirability function approach is widely used on the optimization of the mean of multiple responses (Khoobbakht, Kheiralipour, Yuan, Seifi, & Karimi, 2020; Lee, Jeong & Kim, 2018).

The aims of this study were to optimize the pre-soaking rice cooking process to allow the greatest reduction of deltamethrin, penconazole, kresoxim-methyl, cyproxonazole, epoxiconazole and azoxystrobin, using the response surface methodology.

2. Materials and methods

2.1. Reagents and materials

All pesticides standards were purchased from Sigma-Aldrich (Seelze, Germany). The working standard solutions for pesticide residues analysis (50 mg/L) were prepared in acetonitrile (ACN) of high purity grade, provided by Merck (Darmstadt, Germany), and stored under freezing condition (-18°C ± 1°C) in dark bottles sealed with PTFE/silicone caps.

Anhydrous Na_2SO_4 and NaCl were obtained from Biopack (Buenos Aires, Argentina); sodium hydrogencitrate sesquihydrate and sodium citrate dihydrate were purchased from Sigma-Aldrich (Seelze, Germany). Primary Secondary Amine (PSA) and C18 were obtained from Agilent Technologies (Santa Clara, United States).

2.2. Samples

During 2019, 15 kg of rice, containing residues of the six studied pesticides, were obtained from industrial producers of Entre Ríos province, Argentina. The sample was divided in 3 fractions of 5 kg each, homogenized and stored under freezing condition (-18 ± 1°C) until the analyses. Water was obtained from the local supply network, because it is commonly used for rice cooking by population.

2.3. Analytical methods

Pesticides were analysed using a GC-MS validated methodology described by Medina et al. (2019). Briefly, a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology technique, with 10 g rice,

and 10 mL ACN, was used. Then, 1 g NaCl, 4 g anhydrous Na_2SO_4, 0.5 g sodium hydrogencitrate sesquihydrate and 1 g sodium citrate dehydrate were added and blended at high speed for 1 min. A centrifugation step during 5 min at 4000 rpm was performed. The upper layer was separated and mixed with 1.5 g Na_2SO_4, 0.25 g PSA and 0.25 g C18, hand-shaken for 1 min, and the centrifugation was repeated (4000 rpm for 5 min). The supernatant was vacuum evaporated to dryness. Then 2 mL hexane were added and the extract was filtered with 0.45 µm filter.

A Gas Chromatography system (GC) Agilent 6890N fitted with a micro-electron capture detector (µECD), and an Agilent 6890 N GC coupled with an Agilent 5973 Mass Spectrometer (MS) were used. An HP-5MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness) was employed for separation. The oven temperature started at 80 °C and remain at this temperature for 0.2 min, then it was increased at 40 °C/min ramp rate up to 195 °C, at 12 °C/min ramp up to 280 °C and finally, at 5 °C/min ramp up to 290 °C, holding that temperature for 8 min. Helium (99.999 % purity) was used as carrier gas at a constant flow of 1 mL/min. Injection port was adjusted at 250 ºC and detector temperature was set at 290 ºC. Electron Impact (EI) mass spectra were got at 70 eV and the system was programmed in selected ion monitoring (SIM) mode. Ion source and MS quad temperature were set at 230 °C and 150 °C, respectively.

The analytical method was validated by Medina et al., (2019) and it is summarized as follow: calibration curve for rice ranged from 5 to 2000 µg/kg (n=9), with a correlation coefficient (r^2) higher than 0.9996, for all analytes. Limits of detection (LOD) and limits of quantification (LOQ) ranged from 0.22 to 0.27 mg/kg and 0.72 to 0.90 µg/kg, respectively. The method was accurate and precise, with recoveries of 98.9 – 107.8 %, and relative standard deviations lower than 8.1 %.

2.4 Pre-soaking and cooking procedures

Rice samples (50.0 g) were pre-soaked before cooking with excess of water. This process consisted in placing the rice in a container with a certain volume of water, in stagnant conditions (24 – 26ºC), for a few hours. Different soaking times and relations between water and rice grain were tested. The water:rice grain relation was defined as the quotient between the volume of water added per one volume of rice (filled with the 50.0 g).

Then the soaking water was removed and the rice was cooked with six parts of water during 10 minutes (91 ± 1°C). Once the cooking was finished, excess water was eliminated. A single input digital thermometer Fluke 53 II was used during the cooking process (Fluke, Washington, United States).

2.5 Experimental design for response surface methodology

In this study, response surface methodology (RSM) and central composite design (CCD) were used for experimental design and to optimize the pesticide removal during the rice cooking process.

The low, middle and high levels of each variable were designated as -1, 0 and 1, respectively, and 1.681 is the axial distance from the center point. All experiments were performed in triplicate. A total of 13 experiments were designed and are shown in Tables 1 and 2.

A quadratic polynomial regression model was assumed for predicting the Y response (concentration of pesticides). The model proposed for the response of Y fitted Equation 1 as follows:

$$Y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i<j=2}^{n} a_{ij} x_i x_j \quad (1)$$

Y is the response function, a_0 is a constant term, a_i is the coefficient of the linear effect, a_{ii} is the coefficient of the squared effect and a_{ij} is the coefficients interaction effect, respectively. Accordingly, Xi and Xj are the coded independent variables (Li, Ma, Ma, Li, Zhou & Xu, 2007; Salas et al., 2016).

Single response optimization determines how input parameters affect desirability of individual response, whereas the numerical optimization finds a point that maximizes the desirability function (Khoobbakht et al., 2020).

The goal for response in desirability function approach was simultaneously obtaining a minimum for pesticide residue concentration. The desirability function analysis transforms response to a desirability function that takes values in range $0 < d < 1$. Desirability will be 1 if the response variable is at its goal, and will become zero if the response variable is outside the acceptable range.

2.6 Statistical analysis

The study of RSM and the optimization of results were carried out by using the software STATGRAPHICS Centurion version XV.

3. Results and discussion

3.1 Initial pesticide concentration

149 The calibration curve for all pesticides were higher than 0.9996. One sample of each rice fraction was
150 separated and evaluated for pesticide initial concentration, in triplicate. The mean value and the RSD %, for
151 deltamethrin, penconazole, kresoxim-methyl, cyproconazole, epoxiconazole and azoxystrobin, were 84.9 ± 2.8,
152 242.2 ± 5.2, 298.5 ± 3.5, 230.7 ± 2.4, 253.4 ± 5.3 and 293.5 ± 8.1 µg/kg, respectively. No pesticide residues
153 were found in the water used for soaking and cooking.
154
155 3.2 Response surface optimization of pesticide removal during the rice cooking process
156 Figure 1 shows the response surfaces obtained for each pesticide. The ANOVA of the quadratic regression
157 model for pesticide destruction during cooking process were significant (p-values < 0.05). The R^2 were higher
158 than 0.9426, and there was no significance in the lack of fit (p-values > 0.05) for all analytes, respectively. This
159 indicated that the model can be used to predict responses correctly. These results are described in Table 3, with
160 the second degree equation.
161 The results indicated that interaction between rice soaking time and water:rice grain relation is an important
162 parameter for pesticide elimination, and optimal conditions are summarized in Table 3.
163 The data obtained from the optimization procedure were used in a real sample to confirm the results. The
164 concentration reduction after individual optimization, and the real data (n=1) for validating the model are shown
165 in Table 4. The pesticide elimination may be consequence of washing by the water used for soaking and cooking
166 (Medina et al., 2020), and decomposition by the application of heat during cooking (Abou-Arab and Abou
167 Donia, 2001).
168 The desirability function analysis was employed in the optimization procedure to obtain the best pesticide
169 reduction simultaneously (Figure 2). The optimized desirability value was 0.9894. The concentration reduction
170 after multivariate optimization is shown in Table 4. These results were higher than those reached with individual
171 optimization, with exception of cyproconazole. However, it was accepted as a compromised solution.
172 Medina et al. (2020) performed a pre-soaking rice method with 12 h of soaking time, 50 g of rice and
173 117.29 g of water (volume water:rice grain relation 2), and the pesticides reduction are shown in Table 4. As can
174 be observed, optimized method allowed a higher pesticide reduction, increasing only 2 h the soaking time and
175 adding one more part of water.
176 Horigane, Takahashi, Maruyama, Ohtsubo & Yoshida (2016) demonstrated water penetration mechanism
177 during rice grain soaking. Amvrazi (2011) mentioned that heat pesticides degradation proceeds at higher speed in

liquid phase. For these reasons, it is likely that pre-soaking before cooking would destroy not only the pesticides deposited on the surface of the grain, but also, a greater quantity of those that penetrated inside it.

Optimized results were tested by carrying out the corresponding rice cooking in triplicate. The results obtained coincided with those predicted by RSM. The mean value and the RSD %, for deltamethrin, penconazole, kresoxim-methyl, cyproconazole, and epoxiconazole were 1.4 ± 0.2, 12.2 ± 0.5, 3.1 ± 0.3, 15.0 ± 0.4, and 3.8 ± 0.2 µg/kg, respectively. Azoxystrobin concentration was lower than LOD.

4. Conclusions

Pesticides are hazardous to human health, so it is essential to understand how to reduce their content in products household consumed. The optimization of the variables of the cooking process through the response surface methodology using the experimental data based on the central composite design, allowed obtaining the best combination of soaking time and water:rice grain ratio, to reduce the pesticide content in cooked rice. Desirability function approach predicted pesticides reduction from 93.5 to 100 % of the initial concentration, with 14 h soaking time and 3 water:rice grain relation. A 2 h higher pre-soaking time and 1 extra part of water allowed higher pesticide reduction in comparison with the 12 h and 2 parts of water commonly used in household cooking.

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300

301

Figure Captions

Fig. 1. Response surface plots describing the effect of rice soaking time and water:rice grain relation on the pesticide residues concentration (μg/kg) on cooked rice.

Fig. 2. Response surface plot estimated for desirability function approach.

CRediT author statement

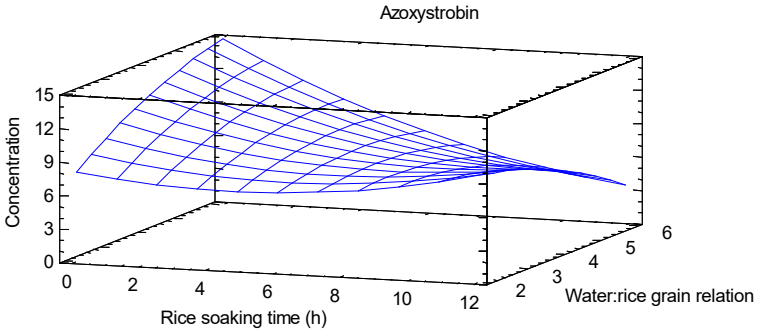
María Belén Medina: Investigation, Methodology, Validation, Resources, Writing – Review & Editing

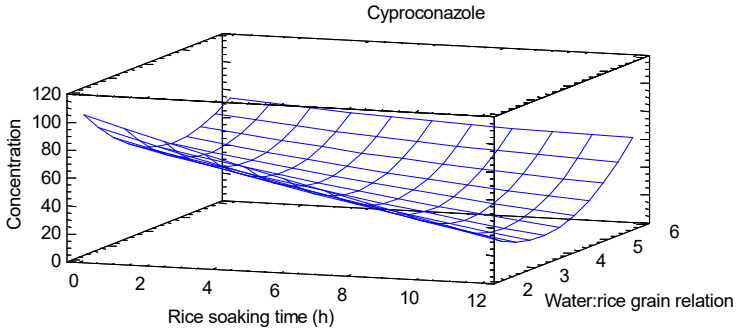
Martín Sebastián Munitz: Formal Analysis, Validation, Writing – Original Draft - Supervision

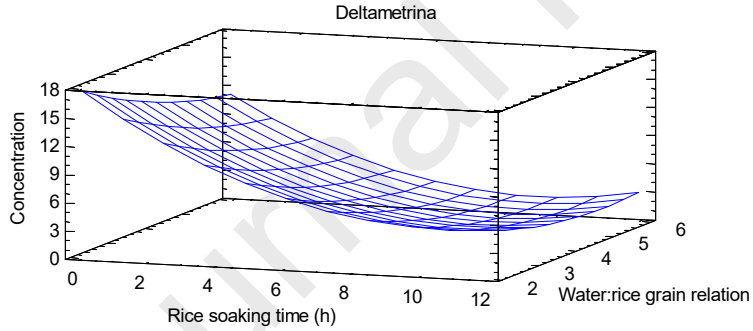
Silvia Liliana Resnik: Conceptualization, Writing – Review & Editing

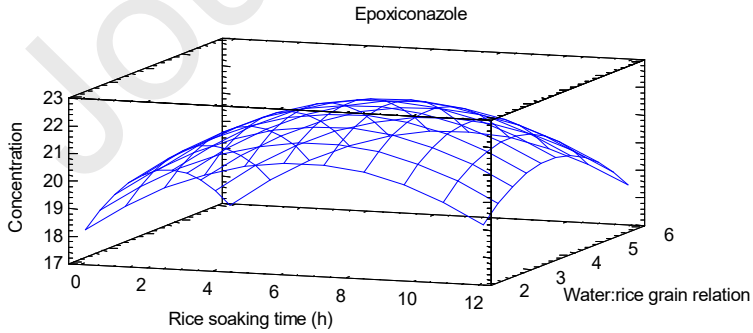
Highlights

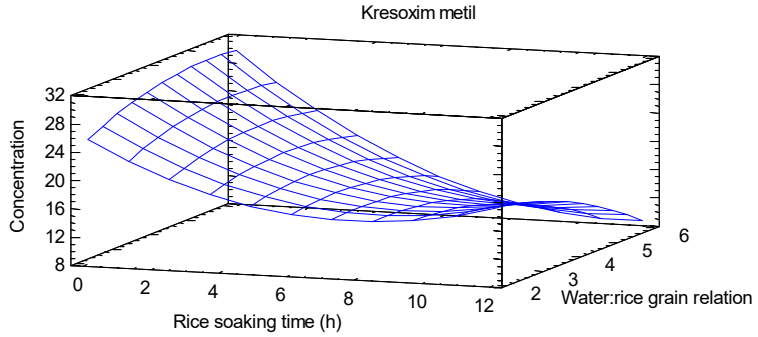
- A greater pesticides reduction was achieved by increasing the soaking time from 12 to 14 hours.
- Desirability function approach was used, and the optimized value was 0.9894.
- Pesticides concentration was reduced between 93.5 and 100.0 % simultaneously.

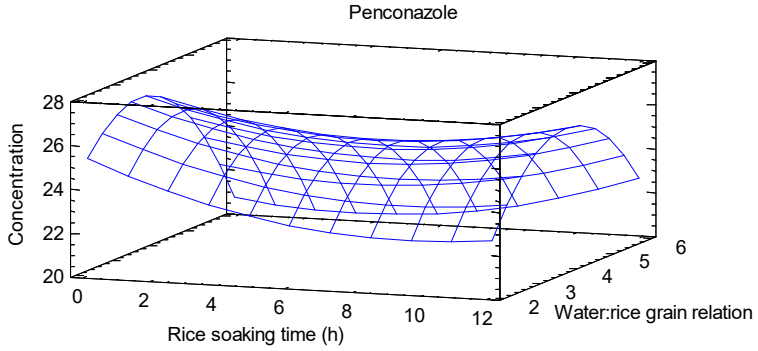












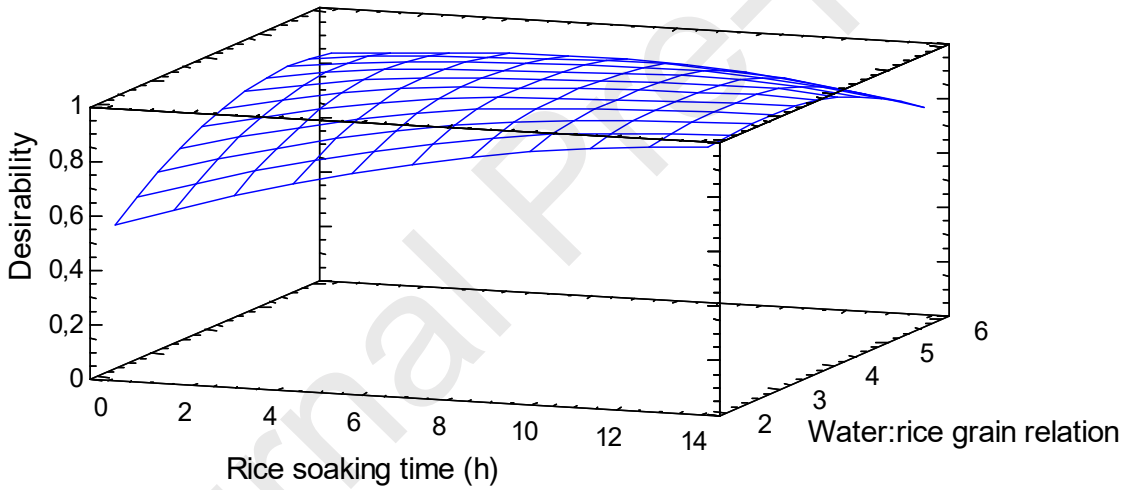


Table 1
Levels of variables in the experimental design.

Independent Variables	Coded levels[a]				
	-1.682	**-1**	**0**	**1**	**1.682**
Rice soaking time (h)	0	2	7	12	14.07
Water:rice grain relation	1.17	2	4	6	6.83

[a] Low, middle and high levels of each variable were designated as -1, 0 and 1, respectively

Table 2
Composite Design for RSM, and its experimental (Exp) and predicted (Pred) values.

Test	A: Rice soaking time (h)	B: Water:rice grain relation	Concentration (µg/kg)								
			Azoxystrobin		Cyproconazole		Deltamethrin		Epoxiconazole		Kres
			Exp [a]	Pred	Exp [a]	Pred	Exp [a]	Pred	Exp [a]	Pred	Exp

1	12	6	3.44	3.65	57.53	62.21	3.09	3.10	18.26	18.51	9.82
2	7	4	8.31	7.89	31.66	33.61	3.55	3.56	22.19	22.27	16.62
3	7	4	8.24	7.89	33.14	33.61	3.53	3.56	22.3	22.27	17.12
4	14.07	4	7.92	8.11	17.62	13.06	4.61	4.63	19.1	18.86	16.9
5	12	2	9.92	9.60	30.36	32.60	5.25	5.22	18.98	19.13	19.23
6	2	2	7.04	7.36	94.07	90.93	13.44	13.43	19.7	19.63	19.23
7	7	4	7.18	7.89	31.33	33.61	3.58	3.56	22.38	22.27	14.6
8	7	4	7.58	7.89	36.69	33.61	3.57	3.56	22.12	22.27	14.58
9	0	4	13.11	12.38	57.96	61.04	13.52	13.50	19.25	19.32	31.99
10	7	1.17	6.38	6.49	86.97	87.92	8.32	8.35	19.47	19.45	16.16
11	7	4	8.13	7.89	35.31	33.61	3.55	3.56	22.37	22.27	16.39
12	2	6	11.17	12.02	72.89	72.18	7.62	7.66	18.54	18.57	21.73
13	7	6.83	6.23	5.59	98.08	95.59	2.80	2.77	18.42	18.26	9.84

[a] Mean values of experiments carried out in triplicates.

Table 3

Results for response surface quadratic model and its equation. Optimal conditions for pesticide reduction during cooking.

	Second degree equation obtained by RSM	R^2	Lack of fit (p-value)	Op
	$C = 1.88817 + 0.0860062*A + 3.54815*B + 0.0477179*A^2 – 0.26525*A*B – 0.231442*B^2$	0.9570	0.1757	A (
e	$C = 205.746 – 9.2568*A – 65.2466*B + 0.0719004*A^2 + 1.20875*A*B + 7.26771*B^2$	0.9893	0.0870	A (
	$C = 24.0155 – 2.56877*A – 3.62024*B + 0.111729*A^2 + 0.0915*A*B + 0.250385*B^2$	0.9999	0.0911	A (
e	$C = 13.6393 + 0.827954*A + 3.1268*B – 0.0642913*A^2 + 0.011*A*B – 0.426764*B^2$	0.9936	0.0892	A (
yl	$C = 18.2202 – 1.89327*A + 4.59659*B + 0.160612*A^2 – 0.29825*A*B – 0.437573*B^2$	0.9427	0.1203	A (
	$C = 16.5089 – 0.813529*A + 6.27303*B + 0.0328406*A^2 + 0.09575*A*B – 0.924465*B^2$	0.9892	0.7867	A (

A: Rice soaking time (h); B: Water:rice grain relation; C: Pesticide concentration (µg/kg)

Table 4

Comparison of percentage of pesticide concentration reduction with the traditional pre-soaking method, the theoretical optimization through desirability function and the data for validation of the model

		Individual pesticide optimization		Multivariat
Pesticide	**Pre-soaking method (Medina et al. 2020)**	**Theoretical values obtained from RSM**	**Data for validation of the model (n=1)**	**Theoretical values o desirability functio**
Azoxystrobin	90.33 %	99.8 %	99.5 %	100 %
Cyproconazole	71.31 %	99.7 %	99.4 %	93.5 %
Deltamethrin	87.98 %	97.5 %	97.5 %	98.4 %
Epoxiconazole	78.18 %	94.0 %	94.2 %	98.5 %
Kresoxim-methyl	85.93 %	98.2 %	98.0 %	99.0 %
Penconazole	73.69 %	93.4 %	93.1 %	95.0 %

* < LOD (limit of detection)