REACTION KINETICS OF OZONE GAS IN WHEAT FLOUR

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ABSTRACT: The implementation of the ozonation process in the milling industry to control insect pests and improve wheat flour qualities requires understanding the behavior of ozone during ozonation. Therefore, this study aimed to investigate the reaction kinetics of ozone gas in wheat flour. Wheat flour ozonation at concentrations of 0.54, 1.07, 1.61 and 2.14 mg L^{-1} was used in a prototype consisting of a cylinder and a mixing system with a helical thread. The iodometric titration method was used to quantify the ozone concentration in the air stream. The reaction kinetics were characterized by determining the saturation time and the decomposition kinetics (decay rate and half-life time). With increasing ozone concentration, less time was required to saturate the wheat flour. The saturation times were 812, 434, 370 and 342 min for ozone concentrations of 0.54, 1.07, 1.61 and 2.14 mg L^{-1}, respectively. Increasing the ozone concentration did not influence the constant decay rate and half-life time. The ozone decomposition kinetics could be represented by a first-order model, with a decay rate constant of 0.23±0.008 min^{-1} and a half-life time of 3.02±0.081 min.

KEYWORDS: ozonation, saturation, decay rate, half-life time.

INTRODUCTION

The effectiveness of ozone gas used to disinfect and control insect pests in grains and subproducts has been demonstrated by the 92–100% mortality of *Tribolium castaneum* and *Sitophilus zeamais* adults and *Plodia interpunctella* larvae and by a 63% reduction in the contamination level of *Aspergillus parasiticus* following the application of 50 ppm ozone gas for 3 d in maize (KELLS et al., 2001). In addition, 100% mortality of *Sitophilus oryzae* and *T. castaneum* adults was observed after 2 and 4 d, respectively, following the application of 50 or 70 ppm ozone gas in wheat (BONJOUR et al., 2011); and 100% mortality of *S. zeamais* and *T. castaneum* adults and a 96% reduction of *Aspergillus flavus* was observed following the addition of ozone gas at 258,120 ppm/min in corn kernels (MCDONOUGH et al., 2011a). Full mortality of *T. castaneum* pupae and eggs and *P. interpunctella* eggs required a treatment of 180 min, and *S. zeamais* and *S. oryzae*, respectively, required 120 and 60 min at 1800 ppm ozone (MCDONOUGH et al., 2011b). Full mortality of the internal stages of eight species of *Coleoptera* and three species of Lepidoptera within kernels was observed when using 135 ppm ozone for 8 d (HANSEN et al., 2012). However, to implement the ozonation process in the milling industry, additional studies are needed to obtain information regarding the behavior of this gas in the flour. According to HARDIN et al. (2010), understanding the behavior of ozone gas is fundamental for its implementation as a fumigant at the industrial level.

The study of gas behavior in a porous medium includes, in part, the assessment of its reaction kinetics by determining the saturation time of the medium with the gas and the gas decomposition kinetics in the medium. The reaction kinetics can be characterized by the decay rate and half-life time. For ozone gas, the reaction kinetics have only been studied in maize (KELLS et al., 2001; HARDIN et al., 2010), wheat (HARDIN et al., 2010) and peanut (ALENCAR et al., 2011) grains.

Assessing the reaction kinetics of ozone gas through a porous medium is important to determine its appropriate concentration and time of exposure to avoid the failure of the process

since the ozone concentration is reduced due to the decomposition process. Furthermore, based on the knowledge of the gas reaction kinetics in a porous medium, it is possible to evaluate the technical feasibility of the ozonation process and to estimate the dimensions of industrial systems by using gaseous ozone (ALENCAR et al., 2011). Therefore, this research aimed to evaluate the reaction kinetics of ozone gas in wheat flour based on the saturation time, decay rate and half-life time.

MATERIAL AND METHODS

This research was conducted at the Laboratory of Pre-processing and Storage of Agricultural Products of the Agricultural Engineering Department of the Universidade Federal de Viçosa in Viçosa, Minas Gerais State, Brazil.

Wheat (*Triticum aestivum*) flour without the use of additives was used in this study. The moisture content of the flour was 13.9% (wet basis, w.b.), with particle sizes of 195 μm according to granulometry, and the experiments were performed at a temperature of 25 °C.

The flour moisture content was determined according to the methodology proposed by the AACC (1999), which recommends using a temperature of 130 °C for 1 h. Analyses were performed in duplicate.

A prototype was constructed for the ozonation of wheat flour (Figure 1). The prototype was comprised of a cylindrical roll (Figure 1A) with an internal double helical mixing system (Figure 1B). Both of these components were made of stainless steel. The cylindrical roll (20 cm diameter and 40 cm length) was placed horizontally on a supporting structure. In the lids located at each end of the cylinder, connections in opposing positions for injection with an output of 4.0 L min^{-1} and an exhaust ozone were set up.
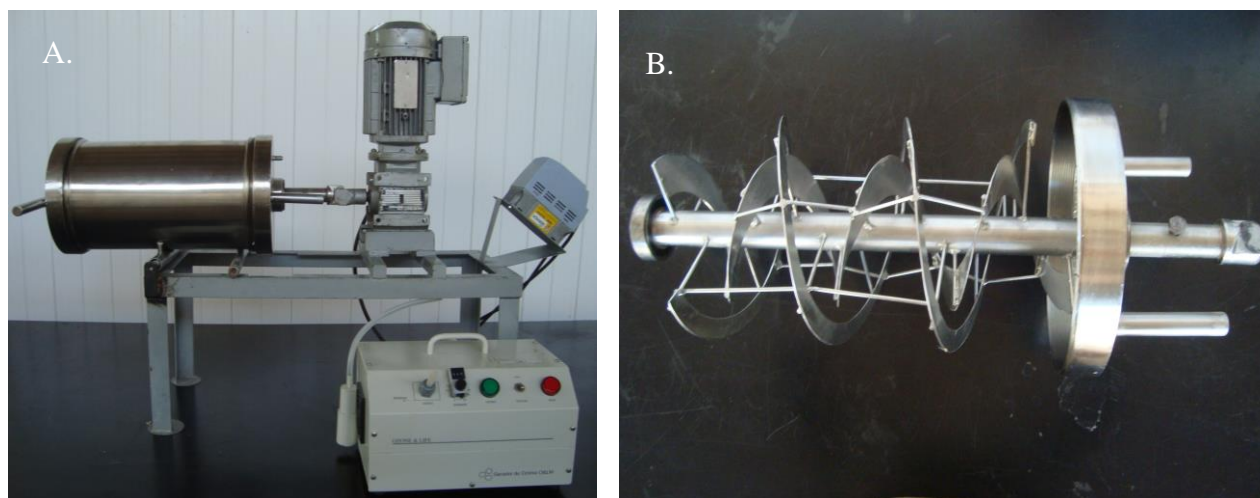

FIGURE 1. Prototype for the ozonation of wheat flour: A. cylindrical roll, induction motor and frequency inverter and B. double helical mixing system.

The helical mixing system was constructed to maintain the movement of the wheat flour during the ozonation process, thereby providing a homogenous mixture of flour and gas. The helical system was formed by a central axis and two propellers. The central axis was 60 cm long and 4.1 cm in diameter, the external helix was 2.0 cm wide and located 8.0 cm from the central axis, and the inner helix was 3.5 cm wide and located 5.0 cm from the central axis (Figure 1B).

To rotate the helical mixing system, the central axis was attached to a 1.5 hp induction motor. A frequency inverter adjusted the rotation speed of the mixing system to 28.5 rpm (Figure 1A).

Ozone gas was obtained through an O&LM ozone generator that was developed by Ozone & Life® Company, São José dos Campos, São Paulo, Brazil. In the process of ozone generation, industrial oxygen with a purity of 90±3% and free of humidity was used as the input. The ozone

concentration level was established by varying the voltage of the generator and the oxygen flow, which was continuously measured with a rotameter. The iodometric method by indirect titration was used (APHA, 1985) to quantify the ozone gas concentration, as recommended by the International Ozone Association.

A 3.5 kg sample of wheat flour was placed in the cylindrical roll of the prototype and exposed to ozone at concentrations of 0.54, 1.07, 1.61 and 2.14 mg L^{-1} and a flow rate of 4.0 L min^{-1}. These concentrations were established based on preliminary tests. The experiment was repeated in triplicate for each concentration.

The reaction kinetics were characterized by determining the saturation time, decay rate, and half-life time. The study of the reaction kinetics due to the interactions between a gas and the porous medium was conducted in two steps. In the first step, ozone gas was injected in the prototype until it saturated the wheat flour. The saturation time was determined by quantifying the residual ozone concentration by using the iodometric method every 20 min until it reached a constant value. These experimental results of flour saturation were subjected to linear response plateau regression analysis by using the statistical program SAEG (SAEG, 2007).

The second step was conducted after saturation of the wheat flour was reached to determine the decomposition kinetics (decay rate and half-life time). For this purpose, the ozone injection port was closed, and the gas was left to react with the porous medium for one minute (decomposition time). After this period, the remaining ozone gas was measured by using the iodometric method. This process was carried out until the residual concentration of ozone gas remained almost constant (decomposition period). The residual concentrations of ozone gas relative to the decomposition times were fitted to zero-, first- and second-order kinetics models, as shown in Table 1 (WRIGHT, 2004).

TABLE 1. Decomposition kinetics models.

Models	Differential equation	Integrated and linearized equations	
Zero order	$\dfrac{dC}{dt} = -k$	$C = C_0 - kt$	(1)
First order	$\dfrac{dC}{dt} = -kC$	$\ln C = \ln C_0 - kt$	(2)
Second order	$\dfrac{dC}{dt} = -kC^2$	$\dfrac{1}{C} = \dfrac{1}{C_0} + kt$	(3)

C=ozone concentration (mg L^{-1}). C$_0$=initial ozone concentration (mg L^{-1}). t=decomposition period (min). k=decay rate constant (min^{-1}).

The adjustment of the kinetic models (Table 1) was performed by regression analysis, using the determination coefficient (r^2) as a selection parameter. The determination coefficient can be used as a selection parameter because the zero-, first-, and second-order kinetic models are simple linear regression models. SigmaPlot 2001 software system version 7.0 for Windows was used to analyze the decomposition data. The constant decay rate was given by the slope of the line after adjusting the integrated, linearized models. With this value, the half-life time ($t_{1/2}$) can be calculated by using [eq. (4)] (WRIGHT, 2004).

$$t_{1/2} = \frac{\ln 2}{k} \qquad\qquad (4)$$

The experiments were conducted in a completely randomized design with three replicates.

RESULTS AND DISCUSSION

The residual ozone concentrations related to the exposure period during the saturation process of wheat flour at 0.54, 1.07, 1.61 and 2.14 mg L^{-1} are shown in Figure 2.
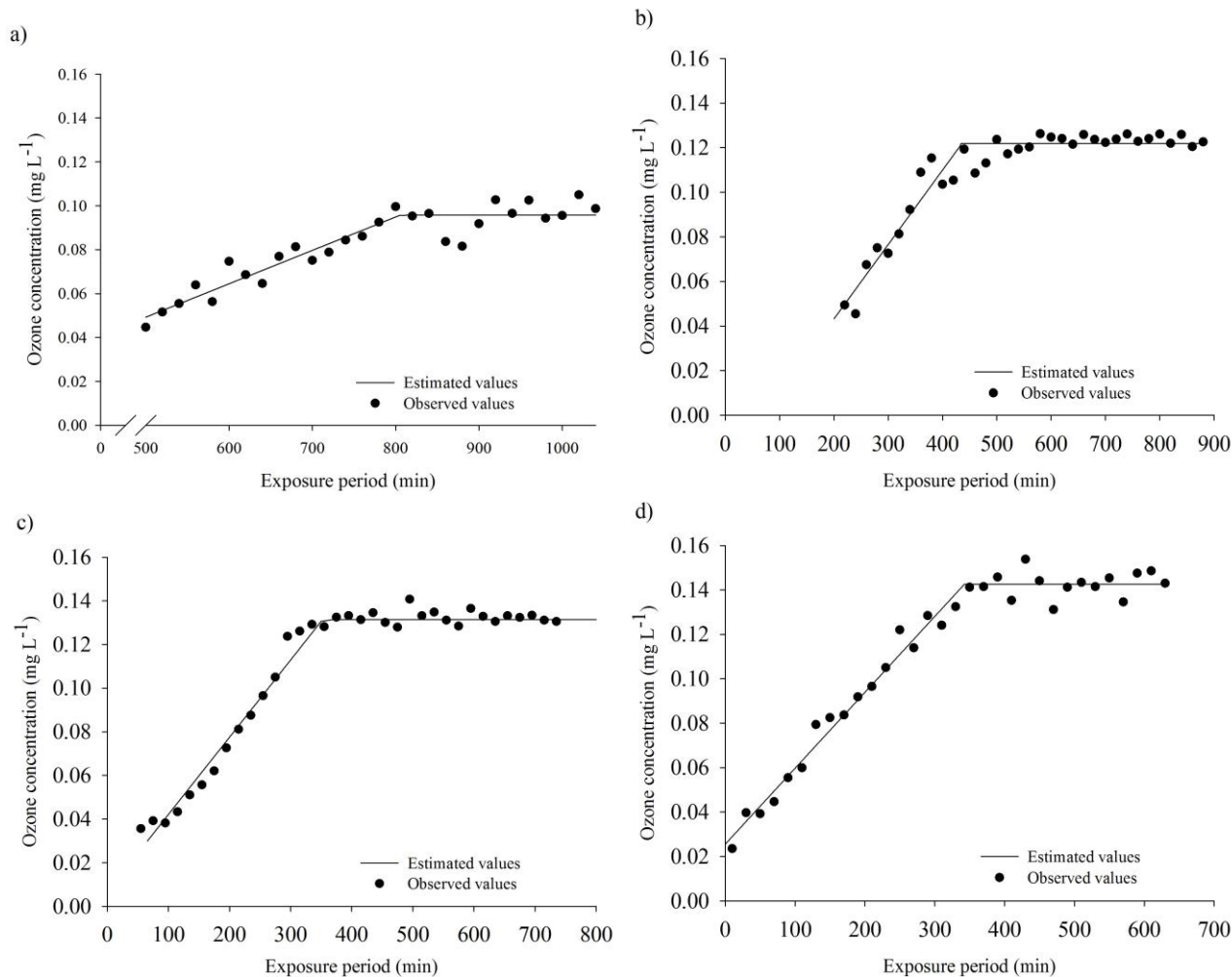
FIGURE 2. Residual ozone concentration related to the exposure period during the saturation process of wheat flour. a) Concentration of 0.54 mg L^{-1}; b) Concentration of 1.07 mg L^{-1}; c) Concentration of 1.61 mg L^{-1}; and d) Concentration of 2.14 mg L^{-1}.

The equations used to describe the behavior of the residual ozone concentration with respect to the exposure period during the wheat flour saturation process, according to the linear response plateau regression analysis, are presented in Table 2.

TABLE 2. Regression equations fitted to the data of residual ozone concentration as a function of the gas exposure period and their respective determination coefficients.

Concentration (mg L^{-1})	Intervals of exposure period (min)	Equation	Determination coefficient (r^2)
0.54	$x_i < 812$	$\hat{y} = -0.0239 + 1.47\ 10^{-4}\ x_i$	0.88
	$812 \leq x_i \leq 1040$	$\hat{y} = 0.096$	
1.07	$x_i < 434$	$\hat{y} = -0.0248 + 3.38\ 10^{-4}\ x_i$	0.88
	$434 \leq x_i \leq 880$	$\hat{y} = 0.1219$	
1.61	$x_i < 370$	$\hat{y} = 0.0096 + 3.30\ 10^{-4}\ x_i$	0.96
	$370 \leq x_i \leq 735$	$\hat{y} = 0.1315$	
2.14	$x_i < 342$	$\hat{y} = 0.0256 + 3.42\ 10^{-4}\ x_i$	0.98
	$342 \leq x_i \leq 630$	$\hat{y} = 0.1425$	

x_i = exposure period (min). $\hat{y}$ = residual ozone concentration (mg L^{-1}).

By increasing the ozone concentration, the time required to detect the gas in the wheat flour becomes shorter (Figure 2). At a concentration of 0.54 mg L^{-1}, the residual concentration of the gas was only detected at 500 min, ranging from 0.04 to 0.10 mg L^{-1} until 1040 min of gas injection in the wheat flour. At 1.07 mg L^{-1}, the residual concentration was not detected until 220 min of exposure; after that period, the residual concentration of ozone ranged from 0.05 to 0.12 mg L^{-1} until 880 min. When the process was performed at a concentration of 1.61 mg L^{-1}, the residual concentration was detected after 55 min of gas injection, ranging from 0.04 to 0.13 mg L^{-1} until 735 min. In wheat flour ozonated at a concentration of 2.14 mg L^{-1}, the residual gas concentration was detected after 10 min, ranging from 0.02 to 0.14 mg L^{-1} until 630 min of gas injection into the wheat flour.

The required time to saturate the wheat flour with gas was reduced as higher ozone concentrations were used (Figure 3), while the saturation concentration remained almost unchanged with increasing concentrations of ozone gas. At a concentration of 0.54 mg L^{-1}, the saturation time was reached after 812 min, when the residual concentration of ozone gas remained almost constant. At concentrations of 1.07, 1.61 and 2.14 mg L^{-1}, the saturation times were 434, 370 and 342 min, respectively. The saturation concentrations were 0.10, 0.12, 0.13 and 0.14 mg L^{-1} with ozone gas concentrations of 0.54, 1.07, 1.61 and 2.14 mg L^{-1}, respectively.
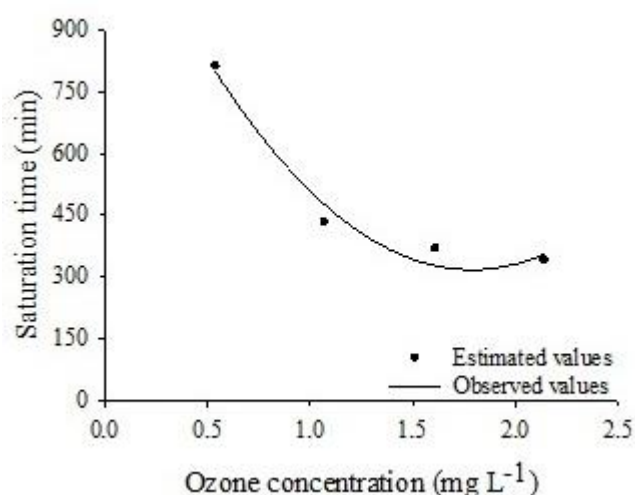

FIGURE 3. Saturation time versus the ozone concentration.

The ozone behavior in wheat flour during the saturation process can be explained by the phenomenon described as ozone demand by the medium. This phenomenon is related to the need for saturation of the active sites responsible for gas decomposition at the beginning of the ozonation process (KIM et al., 1999). According to KELLS et al. (2001), the beginning of ozonation is characterized by rapid gas decomposition and its slow movement through the porous medium due to its reaction with the active sites present on the product surface. Since these sites are saturated, the gas flows freely through the grain interstices with a lower decay rate. Thus, with increasing ozone concentration, more active sites are saturated in a shorter time and the required time to saturate the medium is consequently reduced.

The saturation process with ozone gas at a concentration of 0.45 mg L^{-1} was studied with peanut grains (ALENCAR et al., 2011). The time to saturate these grains with moisture contents of 7.1 and 10.5% w.b. at a temperature of 25 °C was up to 230 min, i.e., lower than the value observed for wheat flour in this study (812 min at a concentration of 0.54 mg L^{-1}, 434 min at 1.07 mg L^{-1}, 370 min at 1.61 mg L^{-1}, and 342 min at 2.14 mg L^{-1}).

By comparing the results reported by these authors and those obtained in this work, it is possible to conclude that, besides the initial application concentration, the type of product affects the saturation process of a porous medium with ozone gas. The smaller the particle size of the product, the greater the total exposed surface area, which increases the rate of reaction (WRIGHT,

2004) and slows the process of saturation. As the surface area of the wheat flour particles is much greater than that of peanut grains, a longer time to achieve flour saturation is anticipated when using the same ozone concentration.

In the study of the decomposition kinetics of ozone gas in saturated flour, the residual ozone concentration decreased as a function of the decomposition period (Figure 4). At the beginning of the decomposition process, the ozone concentrations, i.e., the saturation concentrations, ranged from 0.10, 0.12, 0.13 and 0.14 mg L^{-1}, which changed after 5.15, 5.76, 5.69 and 5.42 min of exposure of wheat flour to gas, respectively, to 0.02 mg L^{-1} (decomposition concentration) (Figure 4). From these periods, the residual gas concentration remained constant.

It was observed that the residual concentration of ozone in the flour after the decomposition period was independent of the saturation concentration. This phenomenon may have occurred because the saturation concentrations are very similar for all initial concentrations of applied ozone.
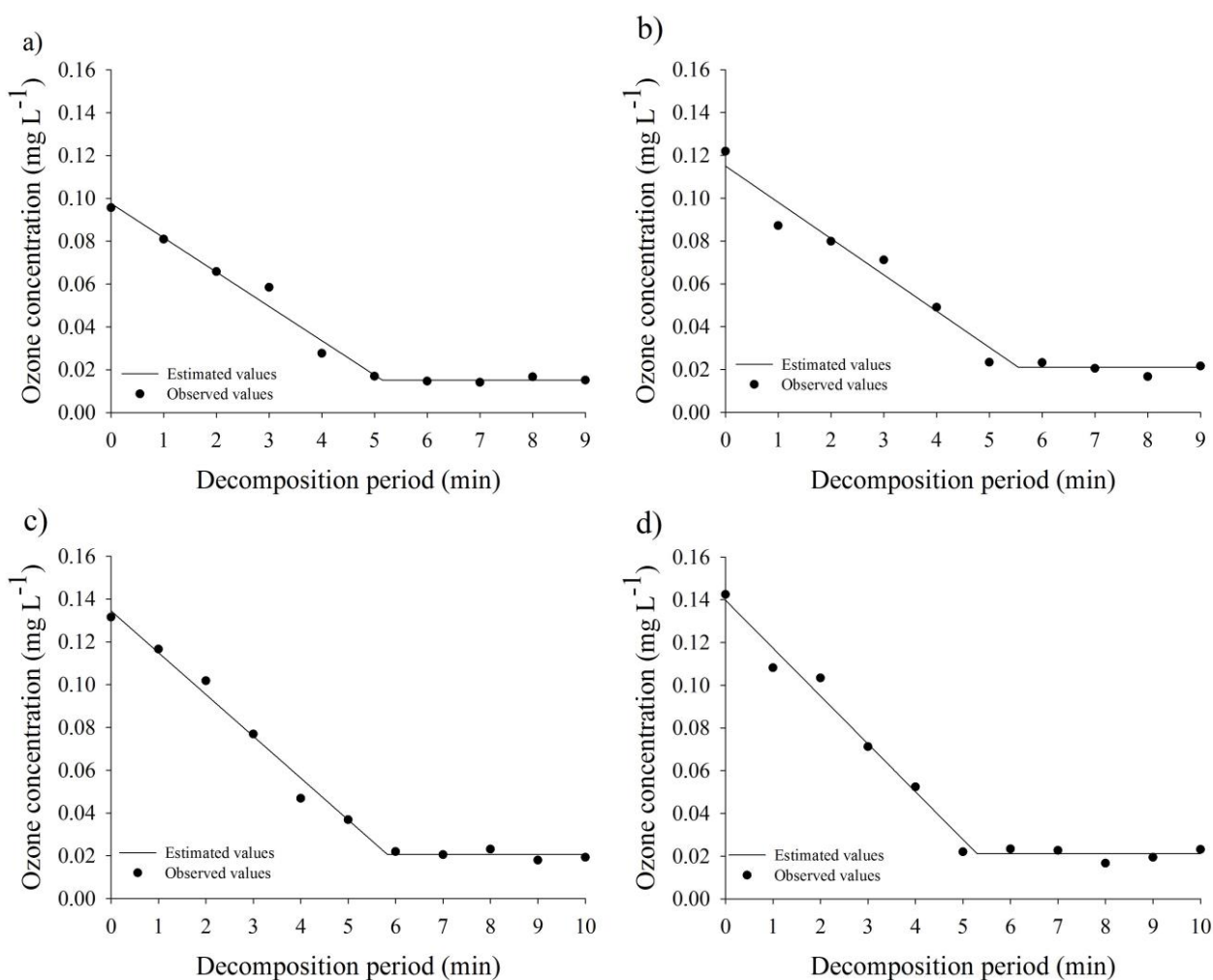

FIGURE 4. Residual ozone concentration as a function of the decomposition period in wheat flour. a) Saturation concentration of 0.10 mg L^{-1}; b) Saturation concentration of 0.12 mg L^{-1}; c) Saturation concentration of 0.13 mg L^{-1}; and d) Saturation concentration of 0.14 mg L^{-1}.

Table 3 shows the equations that describe the behavior of the residual ozone concentration related to the decomposition period of the gas in the flour, in compliance with the response linear plateau.

The greatest degree of adjustment of the decomposition kinetics model was obtained by a first-order system, in which the decay rate constants at saturation concentrations of 0.10, 0.12, 0.13 and 0.14 mg L^{-1} were 0.24, 0.23, 0.23 and 0.22 min^{-1}, respectively (Table 4).

The half-life times of ozone in the flour at saturation concentrations of 0.10, 0.12, 0.13 and 0.14 mg L^{-1} were 2.92, 3.00, 3.06 and 3.11 min, respectively, considering the first-order kinetics.

A first-order kinetic model has been used to determine the decay rate of ozone in different products (HARDIN et al. 2010; ALENCAR et al., 2011). In this study, nearly no variation in the kinetic behavior of ozone gas in wheat flour was observed with increasing ozone concentration. The average decay rate was 0.23 ± 0.008 min^{-1}, and the average half-life time was 3.02 ± 0.081 min. In comparison to these values, the decay rate and half-life time of ozone gas in peanut grains was 0.094 min^{-1} and up to 7.7 min, respectively (ALENCAR et al., 2011).

TABLE 3. Regression equations fitted to the data of the residual ozone concentration as a function of the decomposition period of the gas and their respective determination coefficients.

Saturation concentration (mg L^{-1})	Intervals of decomposition period (min)	Equation	Determination coefficient (r^2)
0.10	$x_i < 5.1472$	$\hat{y} = 0.0976 - 0.016\,x_i$	0.97
	$5.1472 \le x_i \le 9$	$\hat{y} = 0.0152$	
0.12	$x_i < 5.7550$	$\hat{y} = 0.1142 - 0.016\,x_i$	0.90
	$5.7550 \le x_i \le 9$	$\hat{y} = 0.0211$	
0.13	$x_i < 5.6929$	$\hat{y} = 0.1356 - 0.02\,x_i$	0.98
	$5.6929 \le x_i \le 10$	$\hat{y} = 0.0206$	
0.14	$x_i < 5.4235$	$\hat{y} = 0.139 - 0.022\,x_i$	0.96
	$5.4235 \le x_i \le 10$	$\hat{y} = 0.0212$	

x_i =decomposition period (min). $\hat{y}$ =residual ozone concentration (mg L^{-1}).

When ozonizing corn grains at a temperature of 23.5 °C and wheat grains at a temperature of 22.5 °C, HARDIN et al. (2010) observed decay rate constants of 5.8 x 10^{-5} and 5.5 x 10^{-5} min^{-1} and half-lives of 3.42 and 3.50 min, respectively. The decay rates of peanut, corn, and wheat grains were lower than the decay rate of wheat flour, but their half-lives were higher. Thus, the observed decay rate constant of ozone gas and its half-life confirm that, in addition to the temperature factor (ALENCAR et al., 2011), the ozonation process exhibits different behavior according to the type of product. Because wheat flour has a greater surface area than wheat grains, the reaction area is higher, which potentially results in a higher decay rate and shorter half-life time.

TABLE 4. Decomposition kinetics models of ozone in wheat flour.

Saturation concentration (mg L^{-1})	Models	Integrated and linearized equations	Determination coefficient (r^2)
0.10	Zero order	$C = 0.084 - 0.009t$	0.84
	First order	$\ln C = -2.357 - 0.237t$	0.91
	Second order	$\frac{1}{C} = 4.571 + 7.548t$	0.89
0.12	Zero order	$C = 0.102 - 0.011t$	0.87
	First order	$\ln C = -2.168 - 0.23t$	0.90
	Second order	$\frac{1}{C} = 4.214 + 5.895t$	0.87
0.13	Zero order	$C = 0.116 - 0.012t$	0.86
	First order	$\ln C = -2.033 - 0.226t$	0.92
	Second order	$\frac{1}{C} = 2.706 + 5.504t$	0.91
0.14	Zero order	$C = 0.115 - 0.012t$	0.81
	First order	$\ln C = -2.084 - 0.222t$	0.85
	Second order	$\frac{1}{C} = 4.889 + 5.311t$	0.81

Studies of ozone gas reaction kinetics are important for the implementation of the ozonation process in milling industries once the behavior of ozone in flour is characterized. In addition, ozone rapidly decomposes into oxygen and consequently does not leave residues in the products, which is a desirable characteristic for the implementation of this new technology in various food sectors.

CONCLUSIONS

With increasing ozone concentration, less time is required to saturate wheat flour. The kinetics for ozone decomposition can be represented by a first-order model with a decay rate constant of 0.23 ± 0.008 min^{-1} and a half-life time of 3.02 ± 0.081 min.

ACKNOWLEDGMENTS

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