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Drying kinetics of Chinese garlic (Allium tuberosum) and its effect on color

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ABSTRACT

Dehydrated garlic is an important component both for culinary and medicinal purposes. However, there is a scarcity of studies that characterizes its drying kinetics. Thus, the objective of this work was to study the drying kinetics of Chinese garlic (Allium tuberosum), as well as to analyze the color effect resulting from each treatment. The garlic bulbs were cut into thin slices with a width of 2 and 3 mm, subjected to the drying air temperature of 35, 45, 55 and 70 °C in a mechanical dryer of a fixed layer with forced convection. Was performed a non-linear regression analysis by the Quasi-Newton method, for adjustment to 11 mathematical models to the experimental data of drying. The Midilli equation was the mathematical model that best characterized all the drying temperatures, for the experimental data. The diffusion coefficient presented values between 1.46 x 10-11 and 7.32 x 10-11 m2.s-1. The increase of the drying air temperature caused the dimming of the samples with a reduction of the L* coordinate and reduction of the yellow of the samples according to the coordinate results h*. The temperature of 70 °C was detrimental to the maintenance of the Chinese garlic coloration.

Keywords: Mathematical modeling; Quality; Post-harvest

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1 - INTRODUCTION

Medicinal and aromatic plants have shown significant importance in the daily lives of people around the world, being used in a variety of ways. Garlic can be used to prepare tea, to prevent health, and especially to season various types of gastronomic dishes. Derived from the Celtic word "all", which means burner or abrasive, the genus *Allium* is one of the most important spices in Brazilian cuisine (MAITI and GEETHA, 2005).

According to the National Association of Garlic Producers, ANAPA (2019), the cultivation of garlic in Brazil is directly linked to manual operation, generating about 4 handworkers per hectare planted. This characteristic of garlic producers strengthens family farming in 13 of the 26 Brazilian states and keeps the domestic industry active.

The decrease in moisture content is a fundamental process for maintaining the quality and stability of the sensory and nutritional attributes of agricultural products since they are harvested in the field with a high moisture content (ZHANG *et al*., 2017; ARAL & BESE, 2016; NAIDU *et al*., 2016; GONELI *et al*., 2014a). Food drying can be defined as a simultaneous process of heat and mass transfer between the product and the drying air, which consists of the removal of excess water contained in it through evaporation (BROOKER *et al*., 1992).

Characteristics of the drying process, such as, particularities of the material, relative humidity, temperature, and air speed, are conditioning factors to this process. That is, they cause direct variations in the drying curves obtained, which are described using mathematical modeling (COSTA *et al*., 2018; SOUSA *et al*., 2018; LIU *et al*., 2017; SONMET *et al*., 2017).

According to Andrade and Borém (2008), through the mathematical simulation of the drying curves, it is possible to infer the dimensioning of the equipment used, the optimization and the determination of the viability of the commercial application of the processes used. Since through the drying time of a certain quantity of products, it is possible to estimate the energy expenditure, which reflects on the cost of processing and may influence its final price.

Besides, in the last years in which an analysis of agricultural products was studied (ZHANG *et al*., 2014), as an important factor for commercialization. It is possible to determine the quantitative form, by colorimetry, eliminating the subjectivity of human visual perception, with the use of specific equipment, such as spectrophotometers and colorimeters (SANDOVAL *et al*., 2018).

Currently the CIELAB color system is the most used, in which the color description is based on three parameters: L, a*, b*. L represents the brightness, which ranges from 0 (absolute black color) to 100 (absolute white color), a* measures green (-a*) or red (+ a*) and b*, which represents blue (-b*) or yellow (+b*). The parameter C (chroma, saturation) expresses the intensity of the color while h (Hue) tones angulation. The pitch angle h starts on the +a* axis and is given in degrees, where 0 would be +a* (red), 90 would be +b* (yellow), 180 would be –a* (green) and 270 would be –B* (blue) (Moura *et al*., 2014; Clydesdale; Ahmed, 1978).

Given the importance of knowledge of the drying kinetics of agricultural products, it is noted that the literature makes no mention of studies on drying kinetics and their effect on the color of Chinese garlic in the proposed form. Therefore, the present work aimed to determine the drying kinetics of Chinese garlic dried in layers 2 and 3 mm thick, adjusting different mathematical models to the experimental data, selecting the one that best represents the phenomenon, as well as studying the effect of the kinetics drying time in the color of the product.

2 - MATERIAL AND METHODS

The experiment was conducted at the Agricultural Products Processing Laboratory (LPPA) at the Federal University of Lavras (UFLA), in Lavras (MG). Chinese garlic (*Allium tuberosum*) purchased in the Lavras retail market was used as raw material.

At first, the initial moisture content of the garlic bulbs was determined, being 1.86 $kg.kg^{-1}$ dry base (bs) by the method established by the Adolfo Lutz Institute (1985), with a temperature of 105 ± 3 ºC, up to weight constant, in three repetitions.

The Chinese garlic bulbs were peeled and cut into thin slices 2 and 3 mm thick. For drying, a mechanical dryer with a fixed layer with forced convection was used, consisting of 6 perforated, square trays, with sides equal to 0.35 m and depth of 0.40 m. The trays were on a "plenum", which has the function of standardizing the hot drying air. The drying air temperatures were controlled at 30, 45, 55, and 70 ºC. The speed of the drying air, measured with a rotating blade anemometer, was approximately 0.33 $m.s^{-1}$. The experiment consisted of three replicates, each weighing ± 0.03 kg, dried at different temperatures and cutting thicknesses, all starting with the same moisture content: 1.86 $kg.kg^{-1}$ dry base (db). During the process, the samples were weighed initially at smaller intervals, every 10 minutes and later at more spaced intervals, every 20 minutes, until they reached a hygroscopic balance, at which point the weight became constant. The dryer temperatures were monitored with a Datalogger, model LG820-UM-851, connected directly to the garlic layers, in addition to the temperature and relative humidity being also controlled.

In the mathematical models (Table 1) adjusted to the experimental drying data, non-linear regression analysis was performed, by the Quasi-Newton method, in the computer program Statistica 5.0®. To determine the degree of adjustment at each drying temperature, the relative average error was considered, adopting a 5% level of significance.

Table 1 - Mathematical models applied to the drying curves

Model name	Model equation	Equation number
Two-term model	$MR = a \cdot \exp(-k_0 \cdot t) + b \cdot \exp(-k_1 \cdot t)$	(1)
Two term Exponential	$MR = a \cdot \exp(-k \cdot t) + (1-a)\exp(-k \cdot a \cdot t)$	(2)
Modified Henderson and Pabis	$MR = a \cdot \exp(-k \cdot t) + b \cdot \exp(-k_0 \cdot t) + c \cdot \exp(-k_1 \cdot t)$	(3)
Henderson and Pabis	$MR = a \cdot \exp(-k \cdot t)$	(4)
Midilli	$MR = a \cdot \exp(-k \cdot t^n) + b \cdot t$	(5)
Newton	$MR = \exp(-k \cdot t)$	(6)
Page	$MR = \exp(-k \cdot t^n)$	(7)
Thompson	$MR = \exp\{[-a-(-a^2 + 4 \cdot b \cdot t)^{0.5}] \cdot (2 \cdot b)^{-1}\}$	(8)
Verma	$MR = -a \cdot \exp(-k \cdot t) + (1-a)\exp(-k_1 \cdot t)$	(9)
Wang and Sing	$MR = 1 + a \cdot t + b \cdot t^2$	(10)
Valcam	$MR = a + b \cdot t + c \cdot t^{1.5} + d \cdot t^2$	(11)

where,

MR: moisture ratio;

t: drying time (h);

k, k_o e k_1: drying constants;

a, b, c, d, n: model coefficients.

To determine the moisture content ratios of garlic during drying, equation 12 was used:

$$MR = \frac{M - Me}{Mi - Me} \quad (12)$$

where:

MR: moisture ratio (dimensionless);

M: moisture content at time (kg of water. Kg of dry matter^{-1});

Mi: initial moisture content of the product (kg of water. Kg of dry matter^{-1});

Me: equilibrium moisture content of the product (kg of water. Kg of dry matter^{-1}).

The effective diffusion coefficient of the garlic slices, for the different drying conditions of 35, 45, 55, and 70 ºC, was calculated using equation 13. It is an analytical solution for the second Fick's Law, with an approximation of 8 terms and considering a flat geometric shape of the product.

$$MR = \frac{M - Me}{Mi - Me} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \pi^2 Di \frac{t}{4L^2}\right] \quad (13)$$

where,

Di: effective diffusion coefficient (m2.s-1);

L: product thickness (m);

t: drying time (s);

n: number of terms in the model.

For the calculation of equilibrium moisture content (Me), equation 14 was used, described by the model determined by Amâncio (2018):

$$M_e = \exp\left(\left(-6{,}5898\ RH - T^{0{,}4757} + \left(\frac{T-RH}{RH}\right)^{0{,}4757}\right)\right)^{-0{,}1004} \quad (14)$$

where,

Me: moisture content of the product (b.s.);

RH: relative humidity of the drying air (decimal);

T: Temperature of the drying air (°C).

The drying kinetics analysis has the representativeness of the experimental data in the models, the observed values were compared with the estimated data, the percentage of relative average error (P), and estimated average error (SE) was verified, according to the following equation (RYAN, 2009).

$$P = \frac{100}{n} \sum \frac{|Y - Y_0|}{Y} \quad (15)$$

$$SE = \sqrt{\sum \frac{(Y - Y_0)^2}{GLR}} \quad (16)$$

where,

Y - value observed experimentally;

Y0 - value calculated by the model;

n - number of experimental observations;

GLR - model degrees of freedom.

The rate of water reduction was determined by the amount of water that a product loses per unit of the product's dry matter per unit time, according to equation 17 (CORRÊA at al., 2001).

$$WRR = \frac{Wa_o - Wa_i}{D_M(t_i - t_o)} \quad (17)$$

where,

WRR: water reduction rate (kg kg^{-1} h^{-1});

Wao: total water body before the current one (kg);

Wai: current total water body (kg);

Dm: dry matter (kg);

to: total drying time before the current one (h);

ti: total current drying time (h).

The quantification of the color was done by the direct reflectance reading of the coordinates L *, a *, b *, in reflectance spectrophotometer model Minalta CR300. Equation 19 was used to obtain the hue angle (MOURA *et al*., 2014).

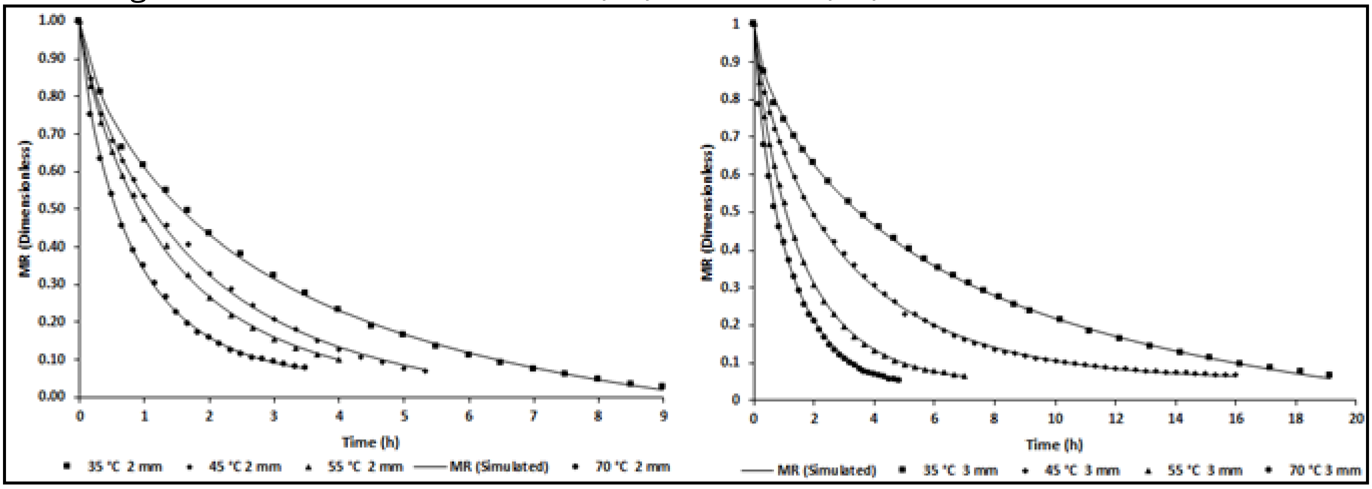
$$h = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (18)$$

The experimental design used for calorimetry analysis was in randomized blocks with three replications, in which all variables were subjected to analysis of variance by the Scott-knott test, with 5% significance, using the SISVAR software, version 5.5.

3 - RESULTS AND DISCUSSION

Figure 1A presents the results of the drying kinetics of garlic in thicknesses of 2 mm and Figure 1B the results for drying thicknesses of 3 mm. Both thicknesses for drying air temperatures of 35, 45, 55, and 70 °C. It can be seen that the drying time decreases with the increase of the air temperature and with the reduction of the initial moisture content, as expected.

Figure 1 - Ratio of moisture versus time for different drying air temperatures, for Chinese garlic with a thickness of 2 mm (1A) and 3 mm (1B)



A. **B.**

The increase in temperature reduces the viscosity of water, directly influencing the resistance of the fluid to flow and the decrease in viscosity facilitates the diffusion of water molecules in the capillaries of the product (ALVES *et al*., 2013). The drying time decreased with the increase in air temperature when the average times needed to complete the process for the Chinese garlic at 2 and 3 mm were 9.00; 5.33; 4.00; 3.5 h and 19.16; 16.00; 7.00 and 4.8 h for temperatures of 35, 45, 55 and 70 °C, respectively.

Table 2 shows the best results of the estimates related to the analysis of the drying kinetics models adjusted for Chinese garlic. The drying constant (k) can be used as an approximation to describe the drying temperature effect and is related to the effective drying diffusivity in which the liquid diffusion controls the drying process (MADAMBA *et al*., 1996). Table 2 presents the values of (k) and (n) for the Midilli model. The (k) values increase as there is an increase in the drying temperature in the different treatments, in addition to being greater in the thickness of thinner layers, of 2 mm, except for the temperature of 70 ºC. The values of (n) also increase as you work with higher drying temperatures.

The diffusion coefficients are presented at the same table, which have magnitudes between 1.46 x 10^{-11} and 7.32 x 10^{-11} $m^2.s^{-1}$, for the temperature range of 35 to 70 ºC. Which are in accordance with values indicated for an efficient drying of agricultural products, in the range of 10^{-11} to 10^{-9} m^2 s^{-1}. Cagnin *et al*. (2017) found values close to those of this study, also working with drying garlic (*Allium sativum L.*) at temperatures of 40, 50 and 60 ºC.

Table 2 - Parameters obtained from the models adjusted to the drying data of Chinese garlic, in thicknesses of 2 and 3 mm, for different temperatures of drying air and diffusion coefficient.

Temp (ºC)	**Thickness (mm)**	**Equation**	**a**	**k**	**b**	**N**	**Def (x10^{-11})**
35	2	MIDILLI	0.9963	0.4817	-0.0090	0.7362	1.4627
35	3	MIDILLI	0.9880	0.2619	-0.0011	0.7448	1.3344
45	2	MIDILLI	0.9894	0.6073	-0.0028	0.8078	1.9365
45	3	MIDILLI	0.9900	0.4483	-0.0028	0.7997	3.0074
55	2	MIDILLI	0.9965	0.6934	0.0022	0.8096	2.0692
55	3	MIDILLI	0.9980	0.6881	0.0016	0.8086	4.6542
70	2	MIDILLI	0.9928	1.0000	0.8069	0.0132	3.0212
70	3	MIDILLI	0.9893	1.0200	0.0068	0.7723	7.3194

The identification of the most satisfactory applied model concerning the values collected experimentally is made based on the coefficient of determination and relative average error. According to Teixeira *et al*. (2012), adjustments in which R^2 is less than 0.90 and P greater than 10 do not ideally represent the data, with the first the closer to 1 and the second to 0, the better the adequacy to the analyzed phenomenon.

Among the mathematical models applied for the experimental data of humidity and time ratio, the most representative was that of Midilli, in most treatments, with the best adjustment in the different temperatures and thicknesses of the garlic. With the exception of the cut thickness of 3 mm, where at temperatures of 35 and 45 ºC the modified Henderson and Pabis model presented better adjustments. The parameters of determination coefficients (R2), relative mean errors (P) and estimated mean error (SE) were tested for each applied mathematical model corresponding to the temperatures (35, 45, 55 and 70 ºC) of the two thicknesses of 2 and 3 mm, as shown in Table 3. The Midilli model was chosen for the adjustment of the experimental curves due to the simplicity of the equation and because it is widely used in the drying of agricultural products.

Table 3 - Determination parameters, relative average errors, and estimated drying data for Chinese garlic, in thicknesses of 2 and 3 mm, for different drying air temperatures

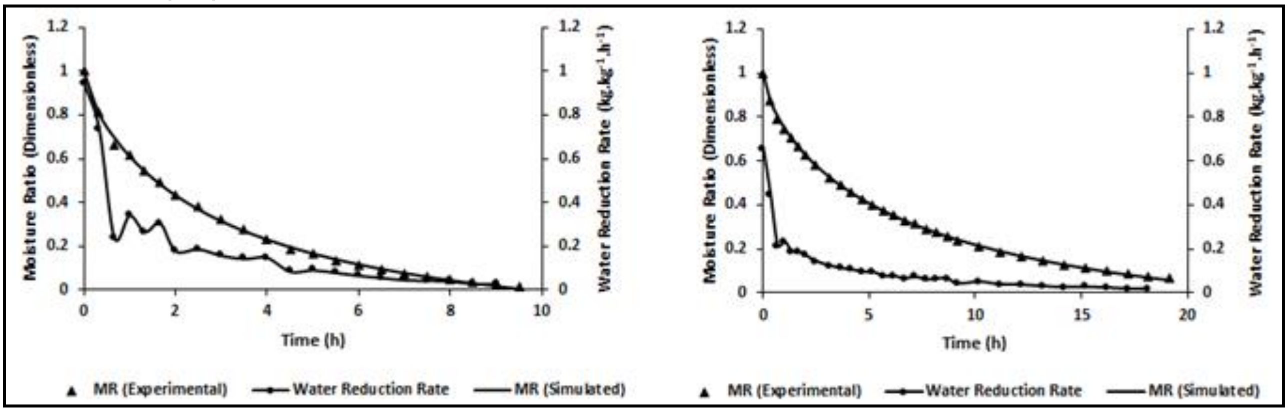
Models	Temperature (° C) and Cutting Thickness (mm)											
	35 °C; 2 mm			45 °C; 2 mm			55 °C; 2 mm			70 °C; 2 mm		
	R^2	P	SE	R^2	P	SE	R^2	P	SE	R^2	P	SE
Two-term model	0.9924	10.1299	0.1768	0.9931	5.3359	0.0617	0.9920	11.9293	0.1863	0.9760	26.7174	0.3697
Modified Henderson & Pabis	0.9924	10.1299	0.1768	0.9931	5.3359	0.0617	0.9920	11.9293	0.1863	0.9760	26.7174	0.3697
Henderson & Pabis	0.9924	10.1299	0.1768	0.9931	5.3359	0.0617	0.9920	11.9293	0.1863	0.9760	26.7174	0.3697
Midilli	0.9989	6.2770	0.1328	0.9992	3.1522	0.0454	0.9994	2.6664	0.0344	0.9994	2.1212	0.0264
Newton	0.9848	11.6756	0.1371	0.9822	12.3752	0.1486	0.9834	18.8215	0.2641	0.9626	34.5732	0.4529
Page	0.9957	20.5824	0.4175	0.9982	4.7987	0.0744	0.9993	3.5965	0.0525	0.9971	10.0797	0.1515
Thompson	0.9920	25.0530	0.5003	0.9952	7.5944	0.1149	0.9981	3.2106	0.0390	0.9978	7.2373	0.1005
Verma	0.9924	10.1299	0.1768	0.9931	5.3359	0.0617	0.9920	11.9293	0.1863	0.9760	26.7174	0.3697
Wang & Sing	0.9225	63.7851	1.3689	0.9466	22.3304	0.3361	0.9340	31.6053	0.4637	0.8348	55.7694	0.7256
Valcam	0.9963	9.5147	0.1956	0.9978	3.6044	0.0550	0.9986	2.6522	0.0348	0.9968	5.1206	0.0686
Two-term Exponential	0.9973	6.4104	0.2552	0.9984	1.7566	0.0221	0.9982	6.4231	0.1134	0.9880	20.5359	0.3045
Models	**Temperature (° C) and Cutting Thickness (mm)**											
	35 °C; 3 mm			**45 °C; 3 mm**			**55 °C; 3 mm**			**70 °C; 3 mm**		
	R^2	**P**	**SE**	**R^2**	**P**	**SE**	**R^2**	**P**	**SE**	**R^2**	**P**	**SE**
Two-term model	0.9997	1.1684	0.0140	0.9974	4.7686	0.0609	0.9884	17.5518	0.2629	0.9889	15.2276	0.2208
Modified Henderson & Pabis	0.9999	0.6154	0.0091	0.9999	0.7415	0.0117	0.9884	17.5518	0.2629	0.9889	15.2276	0.2208
Henderson & Pabis	0.9885	7.4802	0.0973	0.9782	23.4796	0.3316	0.9884	17.5518	0.2629	0.9889	15.2276	0.2208
Midilli	0.9997	1.3426	0.0242	0.9995	1.8526	0.0230	0.9997	1.4901	0.0176	0.9993	3.5310	0.0442
Newton	0.9624	16.5854	0.2124	0.9522	34.8475	0.4499	0.9778	25.1727	0.3471	0.9777	23.0781	0.3077
Page	0.9983	4.6257	0.0787	0.9979	8.1566	0.1237	0.9988	6.1040	0.1017	0.9992	4.2325	0.0581
Thompson	0.9937	8.5600	0.1422	0.9978	5.7037	0.0731	0.9987	3.9256	0.0536	0.9976	4.0353	0.0506
Verma	0.9885	7.4802	0.0973	0.9782	23.4796	0.3316	0.9884	17.5518	0.2629	0.9889	15.2276	0.2208
Wang &	0.9057	27.0072	0.4187	0.8412	49.4506	0.6484	0.9112	39.2290	0.5453	0.8991	42.8968	0.6050

Sing												
Valcam	0.9966	3.9809	0.0621	0.9972	4.2941	0.0568	0.9989	2.8792	0.0408	0.9975	4.2180	0.0555
Two term Exponential	0.9920	6.4104	0.0808	0.9830	21.5274	0.3111	0.9959	11.3810	0.1890	0.9966	9.0283	0.1504

Cagnin *et al*. (2017) dried garlic (*Allium sativum L.*) at different temperatures (40, 50 and 60 °C), and obtained the best-simulated adjustments of the humidity ratio to the experimental ones also from the model of Midilli, Verma, and Logarithm at temperatures of 40, 50 and 60 °C, respectively. Other studies used the drying equation proposed by Midilli to determine the corresponding curves for different agricultural products. Martinazzo *et al*. (2007), drying lemon grass leaves, concluded that the mathematical model proposed by Midilli was the one that best adjusted the experimental data. Resende *et al*. (2010a), in the research of mathematical modeling for the description of the drying kinetics of adzuki beans (*Vigna angularis*), concluded that among the models analyzed, Midilli and Henderson, and Modified Pabis presented the best adjustments for the description of the drying kinetics of the adzuki beans. Furtado *et al*. (2010) studied the drying of seriguela pulp by the foam layer method and found that the mathematical models of Midilli and Kucuk were the ones that best described the drying behavior.

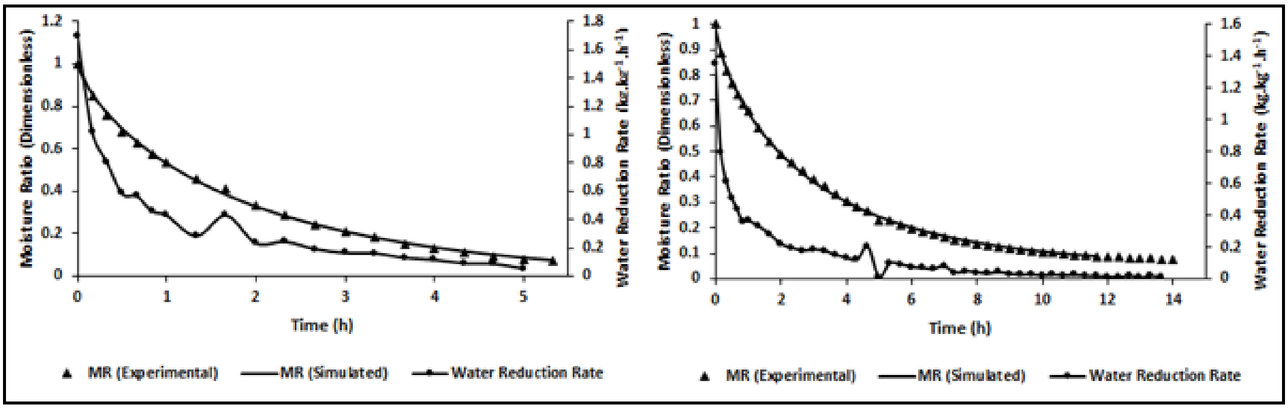
The drying curves at different air temperatures for Chinese garlic, with cut thicknesses of 2 and 3 mm, related to the values simulated by the Midilli model, are shown in Figures 2A to 5B. The adequate adjustment of the Midilli model is evidenced by the proximity of the experimental values about the curve estimated by the model in all the studied conditions. After modeling, the water reduction rate was analyzed, using the proposed equation to describe the loss of water per unit of dry matter per unit of time.

Figure 2 - Curves of moisture ratio, experimental and simulated, and water reduction rate for the temperature of 35 ºC of the drying air in the cutting thicknesses 2 mm (2A) and 3 mm (2B)



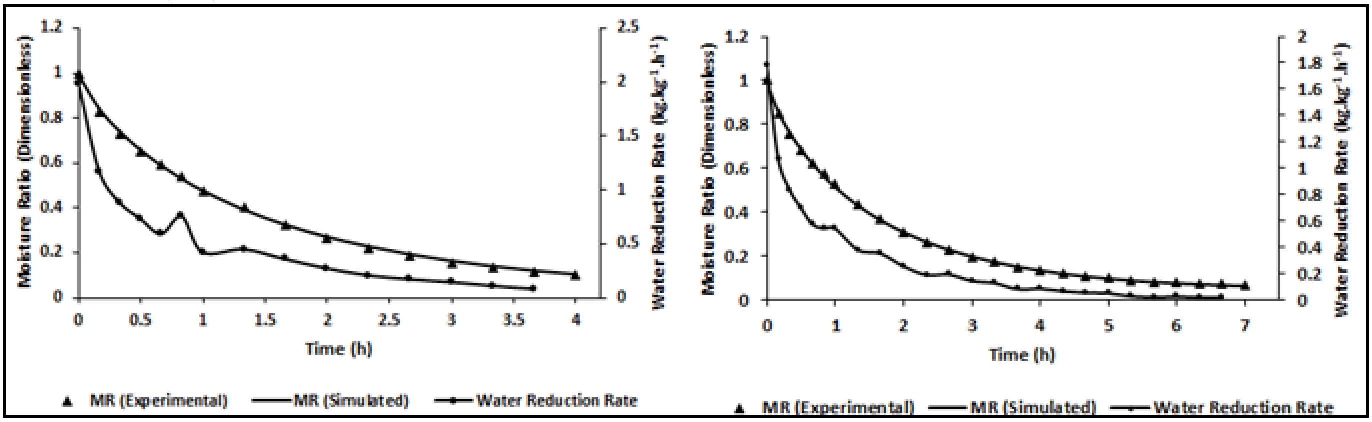
A. **B.**

Figure 3 - Curves of moisture ratio, experimental and simulated, and water reduction rate for the temperature of 45 ºC of the drying air in the cutting thicknesses 2 mm (3A) and 3 mm (3B)



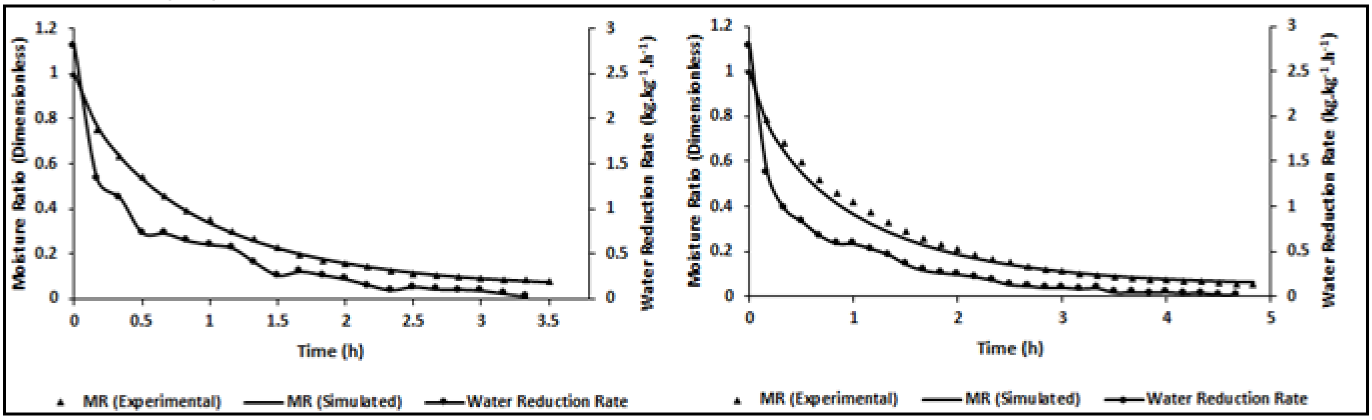
A. **B.**

Figure 4 - Curves of moisture ratio, experimental and simulated, and water reduction rate for the temperature of 55 ºC of the drying air in the cutting thicknesses 2 mm (4A) and 3 mm (4B)



A. **B.**

Figure 5 - Curves of moisture ratio, experimental and simulated, and water reduction rate for the temperature of 55 ºC of the drying air in the cutting thicknesses 2 mm (5A) and 3 mm (5B)



Looking at figures 2A to 5B, it is possible to observe that the water reduction rate was more pronounced at the beginning of drying, for all temperatures. This is because the drying of the product occurs, preferably, from the surface to the interior, promoting the removal of excess free water, so that at the end of the process the water is more strongly adhered to the dry matter. Thus, the rate of water reduction is noticeably higher in the first hour for all treatments, a phenomenon reported by Doymaz (2011).

After drying, it is observed in Table 4 that the variation in the temperature of the drying air caused the samples to darken by 2 and 3 mm, with a decrease in the L * coordinate, with consequent darkening of the samples. The brightness of the product demonstrated through L * was changed at a temperature of 55 °C for garlic with a thickness of 3 mm and 70 °C in both thicknesses of the product, with the material darkening, with the reduction of this coordinate, at these higher drying temperatures.

Table 4 - Results of L and H of the analysis of the color of Chinese garlic, for cut thicknesses of 2 and 3mm, after drying at different temperatures

Temperature	L		H	
	2mm	3mm	2mm	3mm
35°C	77.81 b	79.32 b	87.49 b	88.91 b
45°C	78.70 b	79.99 b	86.74 b	89.11 b
55°C	77.51 b	75.41 a	87.19 b	87.27 b
70°C	74.09 a	74.40 a	80.58 a	82.44 a
CV (%)	1.91		2.23	

* The values with the same letter in the rows and columns, referring to each constant, do not differ by 5%, using the Scott-knott test.

The values related to the hue angle (h), came from the data collected from the coordinates a * and b *. The temperature variation of the drying air affected the final color of the product, at higher temperatures. The drying carried out at 35 and 45 °C had no significant difference according to the statistical test applied, regardless of the thickness of the garlic. It was observed that the changes occurred only at higher temperatures. The occurrence of this phenomenon is a negative aspect since it can show the denaturation of allicin, which is one of the most important chemical compounds present in garlic (YIN & CHENG, 2003).

4 - CONCLUSION

The Midilli model showed the most satisfactory values, in most treatments, to represent the drying kinetics of Chinese garlic cut in thicknesses of 2 and 3 mm, with R^2 values greater than 0.99 and P values less than 10, at temperatures of 35, 45, 55 and 70 ° C.

The adequate adjustment presented by the Midilli model results in a better representation of the phenomenon in other applications, such as for the dimensioning of equipment or drying processes, under the conditions used in this research.

The diffusion coefficient showed values between 1.46×10^{-11} and 7.32×10^{-11} $m^2 s^{-1}$.

The samples submitted to drying at 70 °C, with thicknesses of 2 and 3 mm respectively, were dark and this is a negative factor in the final quality of the product since there was a decrease in the constant L*, as well as the decay of the product hue angle, which shows the greater intensity of the yellow color in the product.

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