EFFECT OF DRYING KINETICS ON COLOR OF "DEDO DE MOÇA" CHILI PEPPERS (*Capsicum baccatum*)

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ABSTRACT

This study aimed to assess the drying kinetics of red and yellow chili peppers, "dedo-de-moça" variety, at different temperatures (35, 45, 55, and 70 ºC) and model this phenomenon mathematically. We also evaluated the effect of these drying air temperatures on pepper fruit color. Pepper fruits were dried in a forced-air circulation dryer. Ten mathematical models were fitted to the experimental data by nonlinear regression analysis. After drying, pepper samples were analyzed for the following colorimetric parameters: lightness (L*), chroma or saturation (c), and hue angle (h), in order to determine the influence of drying air temperature on fruit coloration. Our findings showed that the higher the air temperature, the faster the drying process. Midilli model fitted well to all temperature data and best represented the drying kinetics of "dedo-de-moça" chili peppers. Moreover, fruit color was affected by the drying air temperatures, in which the higher the drying air temperature, the greater the color variation.

INTRODUCTION

Chili peppers are currently grown on family farms and have been responsible for bringing jobs and income to rural areas. Socioeconomically, chili pepper cultivation allows the settling of small farmers and respective families in rural areas and leads to seasonal labor hiring during harvest time (Veras et al., 2012). Another important market is processed and industrialized pepper, which includes dehydrated pepper fruits. This market is underestimated due to the great diversity of products and number of regionally active small companies (Henz & Ribeiro, 2008).

Chili peppers have vitamins, flavonoids, carotenoids, and other secondary metabolites with antioxidant properties, which reduce the risk of cancer or other chronic degenerative diseases. In addition, they have ascorbic acid and beta-carotene with proven pharmacological effects such as cholesterol reduction and appetite suppression (Veras et al., 2012). "Dedo-de-moça" is a variety of *Capsicum baccatum* highly perishable, so it needs to undergo processes to extend its shelf life and improve its handling, transport, and storage conditions. One example of such processes is fruit drying (Veras et al., 2012).

Drying is the most widely used process to ensure farm product quality and stability. This is because it reduces moisture content and hence biological activity and chemical and physical changes during storage (Silva & Rodovalho, 2012; Martinazzo et al., 2007). This process is among the conservation techniques used to maintain the desired quality for plant-origin products harvested with high moisture content (Almeida et al., 2013; Goneli et al., 2014). Storing products with high moisture level leads to growth of microorganisms, which induce fermentation and toxin-contamination thereof, which depreciate and hinders their marketing.

Drying curves show a set of information that is critical for process designing and equipment sizing. These data help determine the time needed to dry a given volume. Hence, this time can be used to estimate energy consumption and process costs, thus affecting the final price of the product (Vilela & Artur, 2008).

There is a lack of studies in the literature on drying kinetics and their effect on "dedo-de-moça" fruit color. Thus, this study aimed to evaluate the drying kinetics of "dedo-de-moça" pepper fruits, fit different mathematical models to the experimental data, and select the best one, besides evaluating its effect on fruit color.

MATERIAL AND METHODS

The study was developed at the School of Engineering at Universidade Federal Fluminense, Niterói-RJ, Brazil.

"Dedo-de-Moça" chili peppers (Capsicum baccatum) from São Paulo state, purchased from the Centro de Abastecimento do Estado da Guanabara (CADEG-RJ, Guanabara State Supply Center) were used in the experiment. We endeavored to select fruits with the same visual ripening characteristics, in terms of color and shape. These fruits were always obtained from the same sales point. Then, the samples were packaged in plastic bags and transported for about 1 hour at room temperature to the laboratory, wherein they were stored in airtight containers under refrigeration, until the beginning of the experiment.

We cut the pepper fruits with a stainless-steel knife lengthwise in four parts to obtain 1-cm-thick flat pieces. Then, these materials were dried in a lab stationary dryer at air temperatures of about 35, 45, 55, and 70 °C, under air circulation heated by a set of lamps. This lab dryer was designed and manufactured by the research team itself, and it had an accuracy of ± 0.1 °C. Mean relative air humidity was 63.15% and mean ambient temperature 23 °C. A digital thermo-hygrograph was used to measure ambient air temperature and relative humidity. Relative humidity inside the dryer was measured using GRAPSI® software.

A rotary vane anemometer was used to monitor drying airspeed at the fan inlet, which was kept constant at about 1 $m.s^{-1}$ throughout drying. Moisture loss was monitored by periodic weighing of samples (every 0.5 hours) from the start of testing, using GEHAKA BK600 precision scale. After, weighing was done at regular intervals until reaching constant weight. We determined moisture content of pepper fruit samples using the laboratory oven method at 105±1°C for 24 hours through the gravimetric method, according to analytical standards of the Adolfo Lutz Institute (1985).

Data gathered during drying were used to plot a drying curve as a function of time. The parameters for the fitted mathematical models were estimated by nonlinear modeling (Quasi-Newton method), using the STATISTICA 5.0 software. Table 1 lists the ten empirical and semi-empirical equations (Corrêa et al., 2007; Doymaz, 2006; Mohapatra & Rao, 2005; Lahsasni et al., 2004; Midilli et al., 2002; Panchariya et al., 2002; Ozdemir & Devres, 1999) used to fit models for drying kinetics to experimental data (Sousa et al., 2015; Sousa et al., 2014; Goneli et al., 2014; Siqueira et al., 2013).

TABLE 1. Mathematical models used to predict the drying kinetics of agricultural products.

Model name	Model equation	Eq. n°
Page	$MC=\exp(-kt^n)$	(1)
Approximation of Diffusion	$MC=a\exp(-kt)+(1-a)\exp(-kbt)$	(2)
Two Term	$MC=a\exp(-k_0 t)+b\exp(-k_1 t)$	(3)
Two Term Exponential	$MC=a\exp(-kt)+(1-a)\exp(-kat)$	(4)
Henderson and Pabis	$MC=a\exp(-kt)$	(5)
Modified Henderson and Pabis	$MC=a\exp(-kt)+b\exp(-k_0 t)+c\exp(-k_1 t)$	(6)
Logarithmic	$MC=a\exp(-kt)+c$	(7)
Midilli	$MC=a\exp(-kt^n)+bt$	(8)
Thompson	$MC=\exp((-a(a^2+4bt)^{0.5})/2b)$	(9)
Verna	$MC=a\exp(-kt)+(1-a)\exp(-kt)$	(10)

In which,

MC – product moisture content, dimensionless;

t - drying time, h;

k, k_0, k_1 - drying coefficients, h^{-1},

a, b, c, n – model constants, dimensionless.

Moisture contents (MC) during drying at different temperatures were calculated as follows:

$$MC = (U - U_e)/(U_i - U_e) \qquad (11)$$

In which,

U - product moisture content, decimal db;

U_i - initial product moisture content, decimal db,

U_e - equilibrium product moisture content, decimal db.

Equilibrium moisture content (Ue) was estimated by [eq. (12)], described by the model (determined by Andrade).

$$U_e = \exp\left(\left(-3.7576\,RH - T^{0.2733} + \left(\frac{T - RH}{RH}\right)^{0.2733}\right)\right)^{-0.2978} \qquad (12)$$

In which,

U_e - equilibrium product moisture content, db;

RH – drying-air relative humidity, decimal,

T – drying-air temperature, °C.

Nature of drying kinetics models was evaluated by comparing experimental data with estimates of each model in order to check to mean relative error (MRE), standard error (SE), and chi-square test (χ^2), according to with the following equations, respectively (Ryan, 2009).

$$P = \frac{100}{n}\sum\frac{|Y - Y_0|}{Y} \qquad (13)$$

$$SE= \sqrt{\sum \frac{(Y- Y_0)^2}{DF}} \qquad (14)$$

$$\chi^2= \sum \frac{(Y- Y_0)^2}{DF} \qquad (15)$$

In which,

Y – experimentally observed value, dimensionless;

Y_0 – model calculated value, dimensionless;

n - number of experimental observations,

DF - degrees of freedom of the model.

For Goneli et al. (2014) and Teixeira et al. (2012), the capacity of a model to describe physical processes faithfully is inversely proportional to the standard deviation (SD) of estimate. Model fit quality considers the magnitudes of determination coefficient (R^2), mean relative error (MRE), and standard error (SE).

According to Corrêa et al., (2001), water removal rate (WRR) is defined as the amount of water lost by a given product per unit of dry matter and unit of time, as in [eq. (16)].

$$WRR= (Ma_o - Ma_i)/(M_s \ (t_i - t_o)) \qquad (16)$$

In which,

WRR - water removal rate (1 kg water per kg product per hour), in kg. kg^{-1}. h^{-1};

Ma_o - total previous water mass, in kg;

Ma_i - total current water mass, in kg;

M_s - dry matter, in kg;

t_o - total previous drying time, in h,

t_i - total current drying time, in h.

Fruit color was assessed by direct reflectance reading of coordinates L *, a *, b * using reflectance spectrophotometer (BYK-GARDNER Color-view 9000) connected to a microcomputer with OnColor for Windows software 5.4.7.9. For each analysis, seven repetitions were performed.

Currently, the CIELAB color system is the most widely used for the characterization of colors in human perception. In this system, a* ranges from green (-a*) to red (+a*), b* from blue (-b*) to yellow (+b*), and L* (lightness) from 0 (black) to 100% (white) (Régula, 2004; Autran & Gonçalez, 2006; Guiné et al., 2010). Color differences between two samples in the same situation, or a single sample in two different situations, are commonly assessed by calculating hue angle (h) and chroma (C) (Moura et al., 2014; Oliveira et al. al., 2012).

Chroma is zero in the center of the color axis and increases with distance. Hue angle starts at the a* axis and is expressed in degrees. The h is zero when +a* (red), 90 ° is defined as +b* (yellow), 180° is -a* (green), and 270°, -b * is blue (Moura et al., 2014). However, these coordinates are not independent variables and should not be analyzed directly.

$$h= \tan^{-1}\left(\frac{b^*}{a^*}\right) \qquad (17)$$

$$C= \left[(a^*)^2+(b^*)^2\right]^{\frac{1}{2}} \qquad (18)$$

RESULTS AND DISCUSSION

Figure 1 (a and b) show the drying curves at different air temperatures for yellow and red "dedo de moça" pepper, respectively. The graphs show that drying time decreases with increasing air temperature.
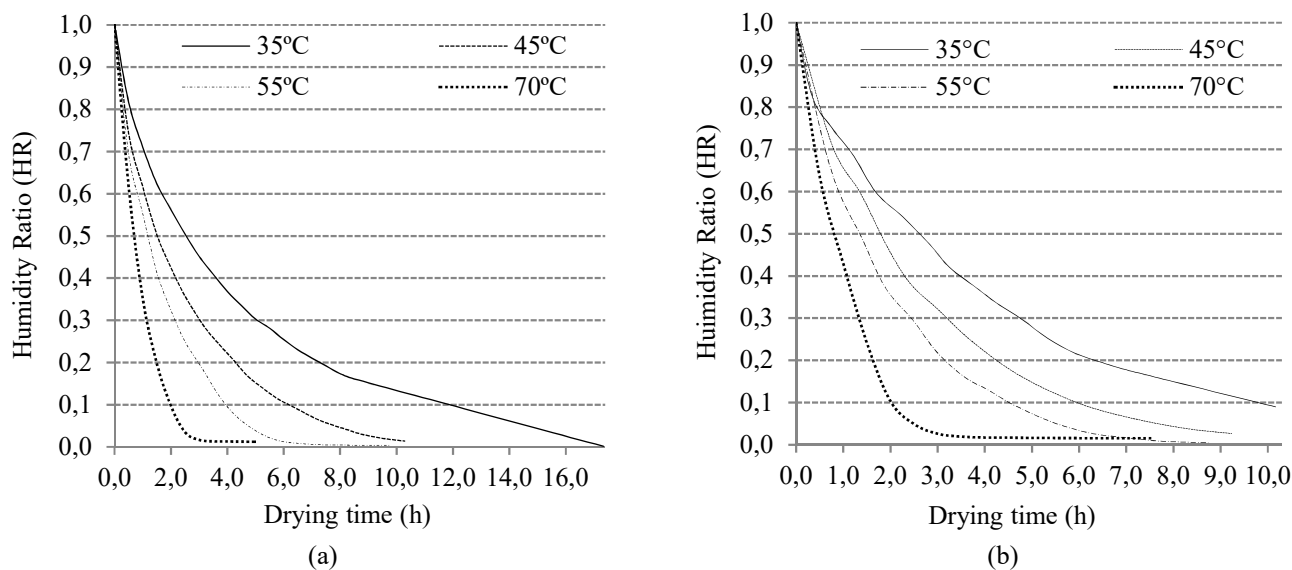

(a)

(b)

FIGURE 1. Moisture ratio as a function of time at different drying air temperatures for red (a) and yellow (b) "dedo de moça" chili peppers.

Drying kinetics was modeled using the models in Table 1, determining their respective parameters, coefficients of determination (R^2), mean relative error (P), mean estimated error (SE), and chi-square test (χ^2). Tables 2 to 5 below show the parameters of the models fitted to the drying kinetics of red and yellow "dedo de moça" chili peppers for each drying temperature.

TABLE 2. Parameters of the models fitted to the drying data of red and yellow "dedo de moça" chili peppers at drying air temperature of 35ºC.

Model	a	b	c	k	k0	k1	N	R² (%)	P (%)	SE (decimal)	χ² (decimal)
Yellow											
(1)				0.3337			0.7943	99.85	0.64	0.0160	0.0003
(2)	0.1853	0.1204		1.6232				99.92	0.67	0.0087	0.0001
(3)	0.4624	0.4624			0.2255	0.2255		98.91	4.00	0.0608	0.0037
(4)	0.1718			1.1776				99.77	1.73	0.0433	0.0019
(5)	0.9248			0.2255				98.91	4.00	0.1052	0.0111
(6)	0.3083	0.3083	0.3083	0.2255	0.2255	0.2255		98.91	4.00	0.0471	0.0022
(7)	0.8964		0.0409	0.2513				99.05	3.35	0.0630	0.0040
(8)	1.0003	-0.0031		0.3390			0.7510	99.99	0.32	0.0042	0.0000
(9)	0.1421	0.0826						91.50	11.21	0.2663	0.0709
(10)	0.1000			0.2480				97.75	6.71	0.1509	0.0228
Red											
(1)				0.3329			0.8313	99.57	3.80	0.0666	0.0044
(2)	0.1008	0.0121		19.2378				99.95	1.59	0.0166	0.0003
(3)	0.4684	0.4684			0.2452	0.2452		99.33	3.11	0.0481	0.0023
(4)	0.1011			2.3185				99.67	2.21	0.0587	0.0034
(5)	0.9368			0.2452				99.33	3.11	0.0833	0.0069
(6)	0.3123	0.3123	0.3123	0.2452	0.2452	0.2452		99.33	3.11	0.0373	0.0014
(7)	0.9061		0.0390	0.2693				99.40	2.80	0.0557	0.0031
(8)	0.9849	-0.0058		0.3190			0.7924	99.72	3.39	0.0308	0.0009
(9)	0.2376	0.2343						90.00	25.65	0.3209	0.1030
(10)	0.1000			0.2665				98.32	6.47	0.1315	0.0173

TABLE 3. Parameters of the models fitted to the drying data of red and yellow "dedo de moça" chili peppers at drying air temperature of 45ºC.

Model	a	b	c	k	k0	k1	N	R² (%)	P (%)	SE (decimal)	χ² (decimal)
Yellow											
(1)				0.4827			0.8489	99.84	13.07	0.0447	0.0020
(2)	0.8619	11.0486		0.3499				99.96	7.22	0.0165	0.0003
(3)	0.4723	0.4723			0.3846	0.3846		99.40	7.06	0.0501	0.0025
(4)	0.1479			2.3592				99.93	7.43	0.0301	0.0009
(5)	0.9446			0.3846				99.40	7.06	0.0867	0.0075
(6)	0.3149	0.3149	0.3149	0.3846	0.3846	0.3846		99.40	7.06	0.0388	0.0015
(7)	0.9340		0.0198	0.4103				99.47	13.75	0.0577	0.0033
(8)	0.9982	-0.0046		0.4862			0.7849	99.98	2.80	0.0086	0.0001
(9)	0.1410	0.0437						87.60	93.16	0.3937	0.1550
(10)	0.1000			0.4094				98.97	10.06	0.1134	0.0129
Red											
(1)				0.4017			0.9688	99.90	5.45	0.0350	0.0012
(2)	0.9624	82.4723		0.3730				99.93	4.93	0.0206	0.0004
(3)	0.4936	0.4936			0.3825	0.3825		99.89	3.30	0.0211	0.0004
(4)	0.7029			0.4325				99.88	4.77	0.0386	0.0015
(5)	0.9872			0.3825				99.89	3.30	0.0366	0.0013
(6)	0.3291	0.3291	0.3291	0.3825	0.3825	0.3825		99.89	3.30	0.0164	0.0003
(7)	0.9879		-0.0013	0.3811				99.89	2.74	0.0258	0.0007
(8)	0.9969	-0.0019		0.4037			0.9384	99.93	3.43	0.0171	0.0003
(9)	0.1472	0.0484						85.07	98.78	0.4239	0.1797
(10)	0.1000			0.3875				99.87	2.53	0.0398	0.0016

TABLE 4. Parameters of the models fitted to the drying data of red and yellow "dedo de moça" chili peppers at drying air temperature of 55ºC.

Model	a	b	c	k	k0	k1	N	R² (%)	P (%)	SE (decimal)	χ² (decimal)
Yellow											
(1)				0.6131			0.9355	99.66	16.62	0.0567	0.0032
(2)	0.0717	0.0256		21.1809				99.79	15.36	0.0318	0.0010
(3)	0.4887	0.4887			0.5713	0.5713		99.61	12.95	0.0350	0.0012
(4)	0.6152			0.7129				99.56	15.38	0.0646	0.0042
(5)	0.9773			0.5713				99.61	12.95	0.0606	0.0037
(6)	0.3258	0.3258	0.3258	0.5713	0.5713	0.5713		99.61	12.95	0.0271	0.0007
(7)	0.9852		-0.0115	0.5533				99.62	9.82	0.0421	0.0018
(8)	0.9986	-0.0160		0.5905			0.8025	99.95	4.46	0.0130	0.0002
(9)	0.1713	0.0519						81.92	105.99	0.4120	0.1697
(10)	0.1000			0.5851				99.53	11.95	0.0663	0.0044
Red											
(1)				0.5304			0.9740	99.85	16.64	0.0396	0.0016
(2)	0.0414	0.0432		11.5156				99.88	16.74	0.0245	0.0006
(3)	0.4950	0.4950			0.5131	0.5131		99.84	14.47	0.0232	0.0005
(4)	0.8951			0.5241				99.83	13.94	0.0419	0.0018
(5)	0.9900			0.5131				99.84	14.47	0.0403	0.0016
(6)	0.3300	0.3300	0.3300	0.5131	0.5131	0.5131		99.84	14.47	0.0180	0.0003
(7)	0.9966		-0.0105	0.4974				99.86	7.23	0.0267	0.0007
(8)	0.9985	-0.0049		0.5342			0.9053	99.95	6.43	0.0128	0.0002
(9)	0.1460	0.0368						82.90	159.30	0.4195	0.1760
(10)	0.1000			0.5179				99.83	13.81	0.0419	0.0018

TABLE 5. Parameters of the models fitted to the drying data of red and yellow "dedo de moça" chili peppers at drying air temperature of 70ºC.

Model	a	b	c	k	k0	k1	N	R² (%)	P (%)	SE (decimal)	χ² (decimal)
Yellow											
(1)				1.0520			1.1509	99.95	6.69	0.0188	0.0004
(2)	0.6095	1.0000		1.0757				99.60	17.63	0.0365	0.0013
(3)	0.5075	0.5075			1.0899	1.0899		99.63	16.85	0.0286	0.0008
(4)	1.0000			1.0757				99.60	17.63	0.0516	0.0027
(5)	1.0150			1.0899				99.63	16.85	0.0495	0.0025
(6)	0.3383	0.3383	0.3383	1.0899	1.0899	1.0899		99.63	16.85	0.0221	0.0005
(7)	1.0626		-0.0581	0.9434				99.95	4.57	0.0116	0.0001
(8)	0.9998	-0.0073		1.0199			1.0985	99.98	3.95	0.0057	0.0000
(9)	0.2082	0.0533						69.14	119.74	0.4585	0.2102
(10)	0.1000			1.0757				99.60	17.63	0.0516	0.0027
Red											
(1)				0.9237			1.1678	99.57	12.85	0.0532	0.0028
(2)	70.7046	1.0077		1.5143				99.56	12.94	0.0361	0.0013
(3)	0.5072	0.5072			0.9687	0.9687		99.11	23.32	0.0440	0.0019
(4)	1.6679			1.2451				99.57	13.99	0.0532	0.0028
(5)	1.0144			0.9687				99.11	23.32	0.0762	0.0058
(6)	0.3381	0.3381	0.3381	0.9687	0.9687	0.9687		99.11	23.32	0.0341	0.0012
(7)	1.1489		-0.1523	0.7159				99.83	7.65	0.0235	0.0006
(8)	0.9986	-0.0430		0.7920			0.9756	99.83	8.91	0.0193	0.0004
(9)	0.1748	0.0454						70.57	119.63	0.4381	0.1919
(10)	0.1000			0.9557				99.07	23.98	0.0778	0.0060

According to Teixeira et al., (2012), and Mohapatra & Rao (2005), models showing an unsuitable fit to the experimental data have a mean relative error (P) greater than 10% and are unable to adequately represent the analyzed phenomenon, and their R^2 should be near one.

After evaluating the results in Tables 2 to 5, we could observe that the Midilli model was the one that best fitted the drying kinetics of "dedo-de-moça" yellow chili pepper at 35, 45, 55, and 70 ºC, showing greater R^2 and lower P, SE, and χ^2 values.

As for the red "dedo de moça" chili pepper, Tables 2 to 5 show that the data of drying kinetics were satisfactorily fitted by the approximation of diffusion model at 35 ºC, the modified Henderson and Pabis model at 45 ºC, and the Midilli model at 55 and 70 ºC. Therefore, these models were the ones that best represent the drying phenomenon, with higher R^2 and lower P, SE, and χ^2 values.

As a result of ease of use and satisfactory fit, the Midilli model may be used to represent the drying kinetics of yellow and red "dedo de moça" chili peppers. As shown in Tables 2 to 5, this model had R^2 above 99.72%, and P, SE, and χ^2 values below 8.91%, 0.0308, and 0.0009, respectively, for all the analyses.

We analyzed the drying curve of yellow and red "dedo-de-moça" chili peppers to observe their drying behavior at each studied temperature, as seen in Figures 2 to 5 below. After that, we fitted the experimental data to different mathematical models that represent the drying phenomenon so that coefficients for drying kinetics equations could be obtained.

The following graphs show the simulated and experimental moisture ratios obtained by the best fit models, showing how well they represent the drying kinetics phenomenon.
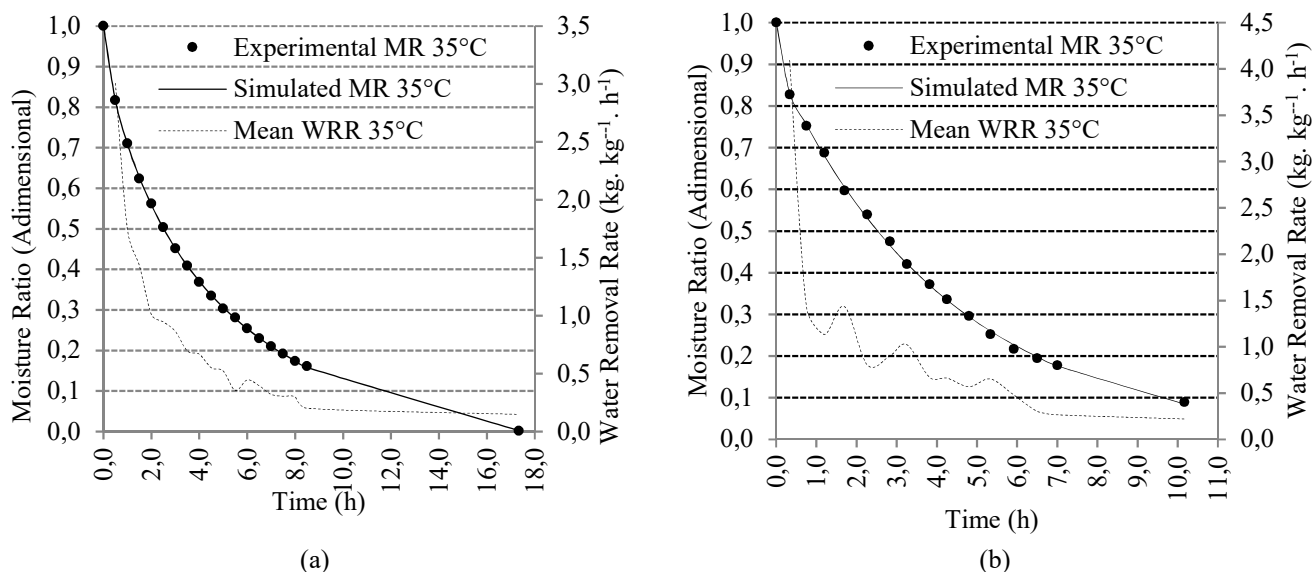

(a)   (b)

FIGURE 2. Experimental and simulated moisture ratio curve and water removal rate at 35 °C for yellow (a) and red (b) "dedo de moça" chili peppers.
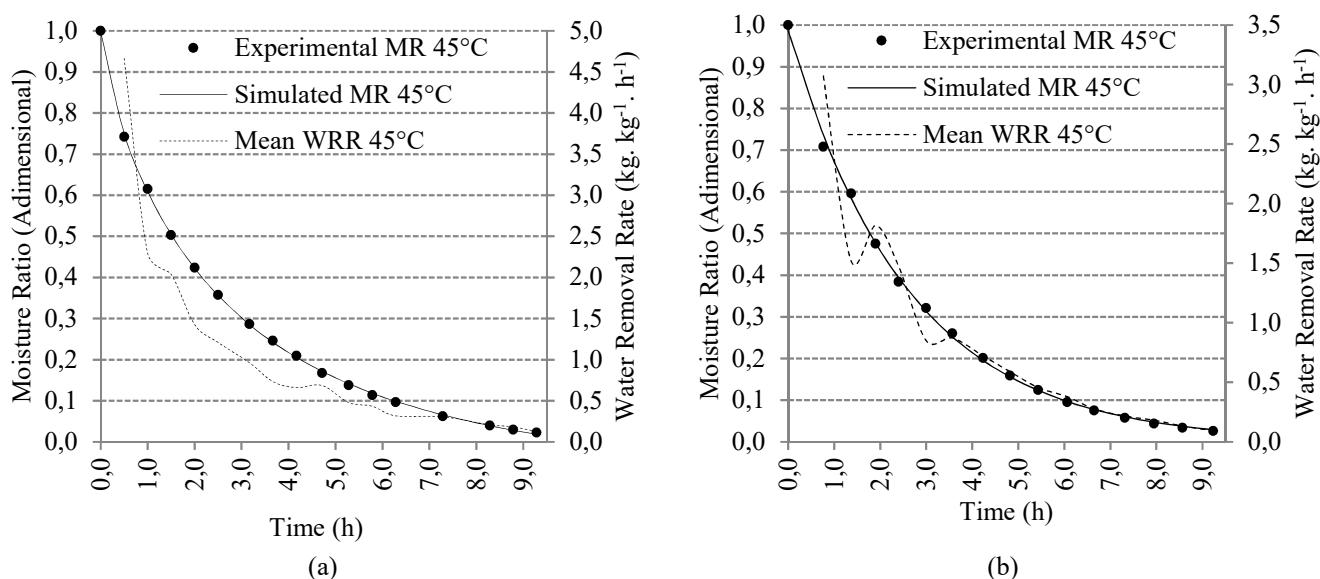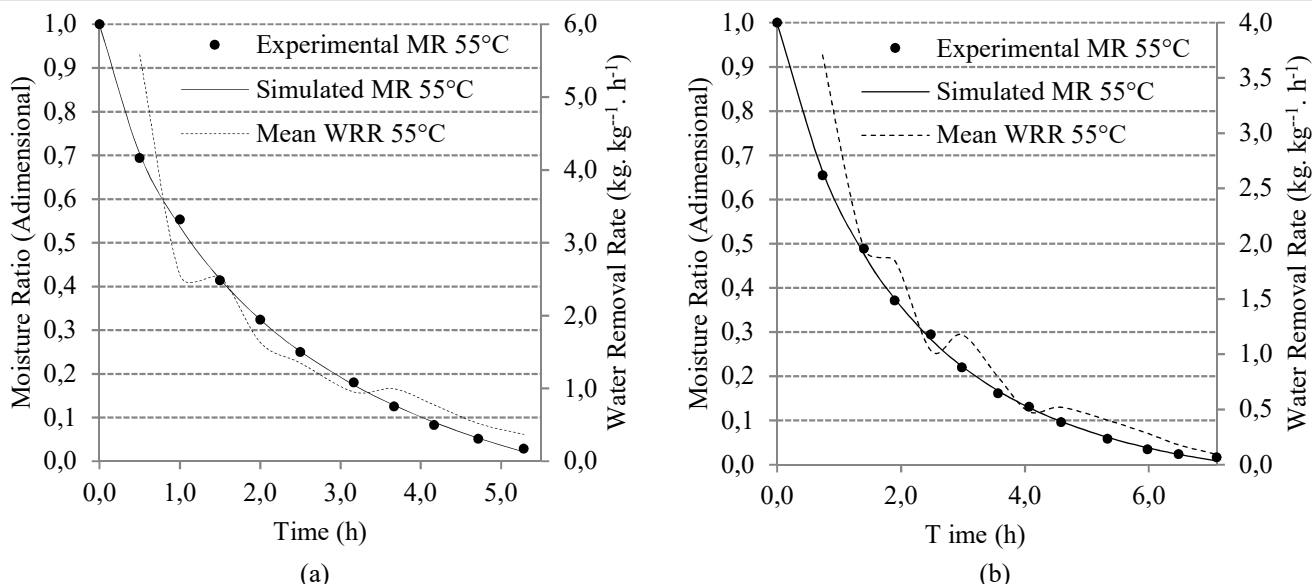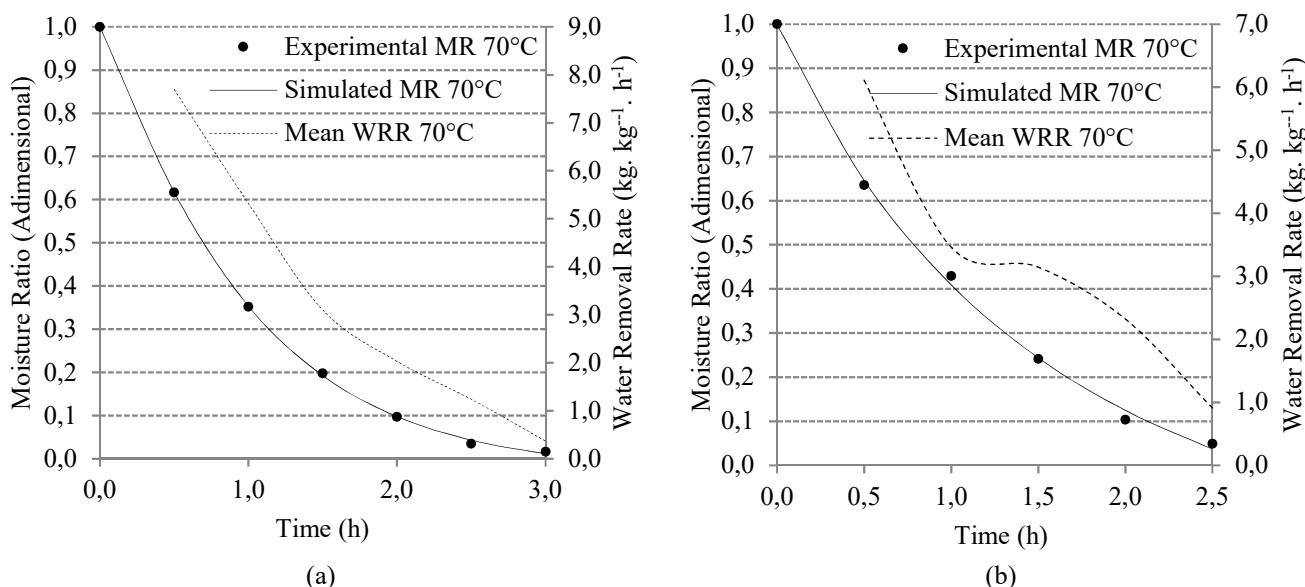

(a)   (b)

FIGURE 3. Experimental and simulated moisture ratio curve and water removal rate at 45 °C for yellow (a) and red (b) "dedo de moça" chili peppers.

FIGURE 4. Experimental and simulated moisture ratio curve and water removal rate at 55 °C for yellow (a) and red (b) "dedo de moça" chili peppers.

FIGURE 5. Experimental and simulated moisture ratio curve and water removal rate at 70°C for yellow (a) and red (b) "dedo de moça" chili peppers.

Together with experimental and simulated moisture ratio for the model fitted to the phenomenon, we also analyzed the water removal rate to describe water loss per unit dry matter and time. Through water removal data, we observed that drying was homogeneous without peaks or abrupt falls for both yellow and red "dedo-de-moça" chili peppers at all drying air temperatures. Abrupt changes in this parameter show failures in the drying process, e.g. in air temperature control.

Table 6 shows that changes in drying air temperature promoted lighter sample colors due to an increase in L* coordinate, i.e. an increase in drying air temperatures caused an increase in lightness and, hence, lighter pepper colors.

TABLE 6. Results of lightness (L*), redness (a*), yellowness (b*), chroma (C), and hue angle (h) of color analysis of red "dedo de moça" chili pepper.

Temperature (°C)	L*	a*	b*	C	h
70	42.51 a	32.85 a	26.59 a	42.26 a	38.99 a
55	41.63 ab	31.72 ab	25.57 a	40.77 ab	38.83 a
45	40.10 b	29.72 b	21.19 b	37.19 c	35.49 b
35	38.01 c	33.43 a	19.69 b	38.81 bc	30.52 c
	CV% = 2.72	CV% = 2.96	CV% = 4.39	CV% = 2.94	CV% = 4.51

Chroma (c) increased significantly with increasing drying air temperature, saturating or intensifying red "dedo-de-moça" chili peppers during drying, with the highest value at 70 °C.

Drying air temperature had a significant effect on hue angle (h). Intense red on sample surface was predominantly due to low h values. An increase in intense red saturation indicates chroma intensity (c) and hue angle (h). Therefore, the closer to zero, the greater the red color intensity. The lower the hue angle, the more intense the red color, and the lower the effect of drying air temperature on red color loss of red "dedo-de-moça" chili peppers. Thus, we conclude that a drying air temperature of 70 °C has a negative effect on the maintenance of original red color of "dedo-de-moça" chili peppers.

CONCLUSIONS

Midilli model shows a satisfactory fit to all drying air temperatures studied here; therefore, it can be used to represent drying kinetics of yellow and red "dedo-de-moça" chili peppers.

An increase in drying air temperature lightened the red color of pepper samples with reduced lightness (L*). A drying air temperature of 70 °C was detrimental to the maintenance of the original red color of "dedo-de-moça" chili peppers. Thus, based on our findings of pepper colorimetry and drying, temperatures below 55 ºC are recommended for the drying process of "dedo-de-moça" chili peppers.

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