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Mathematical modeling and thermodynamic properties in the drying of citron watermelon seeds[1]

Modelagem matemática e propriedades termodinâmicas na secagem de sementes de melancia africana

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HIGHLIGHTS:
The increase in drying temperature increases lipids and total sugar.
The temperatures have lower effect on the drying rate after a certain drying time.
The k constant of the Two Terms model increases as a function of the drying air temperature for watermelon seeds.

ABSTRACT: Citron watermelon is an agricultural product of excellent economic potential. Its seeds are widely used for oil extraction, serving as an energy source, showing nutritional characteristics that make them a suitable product to be studied. Thus, the objective was to characterize citron watermelon seeds regarding their physicochemical composition, in addition to determining drying kinetics, fitting mathematical models to the data, and determining the effective diffusivity coefficients and thermodynamic properties. The seeds were dried in a convective dryer, varying the drying temperature, with air velocity of 1.0 m s^{-1}. With the increase in drying temperature, there were reductions in moisture content, water activity (a_w), ash concentration, total titratable acidity, lipids and reducing sugar. Citron watermelon seeds are rich in lipids and ash, have low sugar concentration and low acidity; their drying kinetics was very well described by the Two Terms and Approximation of Diffusion models, followed by the models of Midilli and Page, which resulted in acceptable fits. Effective diffusivity accompanied the increase in drying temperature, and this behavior was well fitted by an Arrhenius-type equation. Enthalpy and entropy variations were reduced with drying temperature, with increments in Gibbs free energy.

Key words: *Citrullus lanatus* var. citroides, agricultural residues, sustainability, unconventional food, effective diffusivity

RESUMO: A melancia africana é um produto agrícola de excelente potencial econômico. Suas sementes são muito utilizadas para extração de óleo, servindo como fonte energética, demonstrando características nutricionais que a habilitam como produto a ser estudado. Assim, objetivou-se caracterizar quanto à composição físico-química, as sementes de melancia africana, além de determinar a cinética de secagem, ajustar modelos matemáticos aos dados, determinar os coeficientes de difusividade efetiva e propriedades termodinâmicas. As sementes foram submetidas à secagem em secador convectivo, variando-se a temperatura de secagem, com velocidade do ar de 1,0 m s^{-1}. Com o aumento da temperatura de secagem diminuiu o teor de água, atividade de água, teor de cinzas, acidez total titulável, lipídios e açúcar redutor. As sementes de melancia africana são ricas em lipídios e cinzas, tem baixos teores de açúcares e baixa acidez; as cinéticas de secagem foram muito bem descritas pelos modelos Dois Termos e Aproximação da Difusão, seguidos pelos modelos de Midilli e Page, que resultaram em ajustes aceitáveis. A difusividade efetiva acompanhou o aumento da temperatura de secagem, e este comportamento foi satisfatoriamente ajustado por equação do tipo Arrhenius. As variações de entalpia e entropia foram reduzidas com a temperatura de secagem, com aumentos da energia livre de Gibbs.

Palavras-chave: *Citrullus lanatus* var. citroides, resíduos agrícolas, sustentabilidade, alimentos não convencionais, difusividade efetiva

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Introduction

Citron watermelon (*Citrullus lanatus* var. citroides) belongs to the Cucurbitaceae family and has high potential for use in arid and semi-arid regions as a forage resource (Santos et al., 2017). It is used to feed animals in various regions of the world and can also be used in human food. During citron watermelon processing, large amounts of residues are generated and discarded in the form of rinds and seeds (Mallek-Ayadi et al., 2018). These residues have aroused interest due to their important nutritional properties, and the seeds can be used as an appetizer or for oil extraction.

Agro-industrial residues have high moisture content and limited shelf life. Due to this high perishability, it is necessary to use methods that reduce biological and biochemical activities. The first option for conservation of seeds is the drying, which aims to reduce the moisture content to values that enable their preservation for long periods. Drying also diversifies the forms of use, enabling the transformation into flour and use for the preparation of bakery products.

In the line of research on raw materials of unconventional consumption, several studies have been carried out to investigate mathematical modeling and determine the thermodynamic properties in the drying of seeds obtained from fruits such as *Hass avocado* (Avhad & Marchetti, 2016), *Cucumis melo* (Silva et al., 2018), *Jatropha curcas* L. (Keneni et al., 2019), *Citrullus lanatus* (Siqueira et al., 2020), among others. The thermodynamic properties can be used to assess the energy required to remove water from the product during the dehydration process, as well as to verify the partial vapor pressure of the water and to quantify the maximum energy released during the process.

In the case of citron watermelon, studies on its characterization and behavior during drying are insufficient or non-existent. Therefore, the objective was to characterize the citron watermelon seeds, subject them to drying at temperatures of 50, 60, 70 and 80 °C, fit mathematical models to the experimental data of drying kinetics, and calculate the effective diffusivity coefficients and thermodynamic properties.

Material and Methods

The study was carried out in the region around latitude 7° 12’ 52.67” S, longitude 35° 54’ 35.51” W, and altitude of 510.85 m, in the year 2020. The raw material used was seeds of citron watermelon purchased in the region around the latitude 7° 02’ 52” S, longitude 35° 55’ 51” W, at an altitude of 695 m, harvested in the ripe stage and transported to the Laboratory of Processing and Storage of Agricultural Products, at the Federal University of Campina Grande, PB, Brazil. The selection was carried out manually to eliminate the fruits that showed physical damage.

The selected fruits were washed under running water and then immersed in sodium hypochlorite solution at 100 ppm for 30 min. The citron watermelons were fractionated into smaller sections, and the pulp with seeds was separated manually from the rind. Pulping was performed in a stainless-steel horizontal pulping machine (Itametal®, Compacta model), which allowed the separation of seeds and pulp. The seeds were washed under running water and placed in trays for evaporation of surface water for two hours.

For fresh seeds, the following analyses were performed, in triplicate, according to the analytical procedures of the Adolfo Lutz Institute (IAL, 2008): moisture content, by the gravimetric method in an oven at 105 °C, until reaching constant weight; ash concentration, by incineration in muffle furnace at 550 °C, with results expressed in percentage (w/w); total acidity, by titrimetry with 0.1 M NaOH; and pH, determined with pH meter previously calibrated with pH buffer solutions 7.0 and 4.0.

Lipid concentration was determined by extraction with cold solvent mixture, according to the method described by Bligh & Dyer (1959). Water activity (a_w) was measured using an Aqualab hygrometer, 3TE model, Decagon Devices, at 25 °C. Total sugar was determined by the methodology described by Yemm & Willis (1954), in which the samples were analyzed in spectrophotometer at 620 nm, and quantified based on the standard glucose curve. Reducing sugars were determined by the methodology of Miller (1959), using 3,5-dinitrosalicylic acid (DNS) as an oxidizing agent, with readings in spectrophotometer (Coleman, 35 D, Santo André, SP, Brazil) at 540 nm. Non-reducing sugars were determined by the difference between the values of total sugars and reducing sugars.

The seeds were distributed in screened baskets (15 x 12 cm) and dried in a convective dryer, at temperatures of 50, 60, 70 and 80 °C and air velocity of 1.0 m s^{-1}. Drying kinetics was determined by weighing the baskets with the samples at regular intervals of 5, 10, 20, 30 and 60 min, until reaching equilibrium, and then the dry mass was determined after drying in the oven at 105 °C, according to the Adolfo Lutz Institute (IAL, 2008). The experimental data of drying kinetics were used to calculate the moisture content ratios of the samples, according to Eq. 1.

$$RX = \frac{X - X_e}{X_i - X_e} \tag{1}$$

where:

RX - moisture content ratio of the sample (dimensionless);
X - moisture content of the sample at a given drying time (d.b.);
X_i - initial moisture content of the sample (d.b.); and,
X_e - equilibrium moisture content of the sample (d.b.).

The nonlinear regression models (Table 1) of Newton, Thompson, Modified Page, Page, Henderson and Pabis, Two-Term Exponential, Logarithmic, Approximation of Diffusion, Two Terms and Midilli were fitted to the experimental data by the Quasi-Newton method, with the statistical computer program Statistica 7.7®.

The criteria used to assess the fitting quality of the models were the coefficient of determination (R^2), mean squared deviation (MSD) and the chi-square (χ^2), according to Eqs. 12, 13 and 14, respectively.

Table 1. Nonlinear regression models fitted to the drying kinetics data

Models	Equations	
Newton	$RX = \exp(-k.t)$	(2)
Thompson	$RX = \exp\left(\frac{-a-(a^2+4bt)^{0,5}}{2b}\right)$	(3)
Modified Page	$RX = \exp[-(k.t)^n]$	(4)
Page	$RX = \exp(-k.t^n)$	(5)
Henderson and Pabis	$RX = a\exp(-k.t)$	(6)
Two-Term Exponential	$RX = a.\exp(-k.t) + (1-a)\exp(-k.a.t)$	(7)
Logarithmic	$RX = a\exp(-k.t) + c$	(8)
Approximation of Diffusion	$RX = a.\exp(-k.t) + (1-a).\exp(-k.b.t)$	(9)
Two Terms	$RX = a.\exp(-k_0.t) + b.\exp(-k_1.t)$	(10)
Midilli	$RX = a.\exp(-k.t^n) + b.t$	(11)

RX - Moisture content ratio, dimensionless; a, b, k, n, q - Parameters of the models; t - Drying time, min

$$R^2 = 1 - \left(\frac{\sum_{i=1}^{n}\left(RX_{pred,i} - RX_{exp,i}\right)^2}{\sum_{i=1}^{n}\left(RX_{exp,i} - RX_{pred,i}\right)^2}\right) \quad (12)$$

$$MSD = \left[\frac{1}{n}\sum_{i=1}^{n}\left(RX_{pred,i} - RX_{exp,i}\right)^2\right]^{\frac{1}{2}} \quad (13)$$

$$\chi^2 = \frac{1}{n-N}\sum_{i=1}^{n}\left(RX_{exp,i} - RX_{pred,i}\right)^2 \quad (14)$$

where:

R^2 - coefficient of determination;
MSD - mean squared deviation;
χ^2 - chi-square;
$RX_{pred,i}$ - moisture content ratio predicted by the model;
$RX_{exp,i}$ - moisture content ratio obtained experimentally;
n - number of observations; and,
N - number of model constants.

Moisture content data (d.b.) of the seeds at each dehydration time were used to calculate the drying rates, according to Eq. 15.

$$TX = \frac{X_{t+dt} - X_t}{dt} \quad (15)$$

where:

TX - drying rate (kg kg^{-1} min^{-1});
X_{t+dt} - moisture content at t + dt (kg of water per kg of dry matter);
X_t - moisture content at a specific time (d.b.); and,
t - drying time (min).

The liquid diffusion equation (Eq. 16) with three-term approximation, considering the geometric shape of the seeds as similar to that of an infinite flat plate (average seed diameter of 0.00323 m), was fitted to drying kinetics data at temperatures of 50, 60, 70 and 80 °C. Uniform initial water distribution and absence of thermal resistance were considered in the calculation of effective diffusivity.

$$RX = \frac{X - X_e}{X_i - X_e} = \frac{8}{\pi^2}\sum_{n=0}^{3}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2 D_{ef}\frac{t}{4L^2}\right] \quad (16)$$

where:

D_{ef} - effective diffusivity (m^2 s^{-1});
n - number of terms of the equation;
L - characteristic dimension, half thickness (m); and,
t - time (s).

The relationship between the effective diffusivity and drying temperatures of the seeds was described by the Arrhenius-type equation (Eq. 17).

$$D_{ef} = D_{ef_0}\exp\left(-\frac{Ea}{RT}\right) \quad (17)$$

where:

D_{ef0} - pre-exponential factor (m^2 s^{-1});
E_a - activation energy (kJ mol^{-1});
R - universal gas constant (0.008314 kJ mol^{-1} K^{-1}); and,
T - absolute temperature (K).

The thermodynamic properties (variations of enthalpy, entropy and Gibbs free energy) of the drying process of the seeds at temperatures of 50, 60, 70 and 80 °C were quantified using the method described by Jideani & Mpotokwana (2009), according to Eqs. 18, 19 and 20.

$$\Delta H = Ea - RT \quad (18)$$

$$\Delta S = R\left[\ln\left(D_{ef_0}\right) - \ln\left(\frac{k_B}{h_p}\right) - \ln(T)\right] \quad (19)$$

$$\Delta G = \Delta H + T\Delta S \quad (20)$$

where:

ΔH - specific enthalpy (kJ mol^{-1});
ΔS - specific entropy (kJ mol^{-1} K);
ΔG - Gibbs free energy (kJ mol^{-1});
K_B - Boltzmann constant (1.38 × 10^{-23} J/K);
h_p - Planck constant (6.626 × 10^{-34} J s^{-1}); and,
T - absolute temperature (K).

The data generated by the physical-chemical characterization of watermelon seeds in two states, fresh and dehydrated at temperatures of 50, 60, 70 and 80 °C were subjected to analysis of variance and the Tukey test at $p \leq 0.05$ through the Assistat program, version 7.7 beta (Silva & Azevedo, 2016).

Results and Discussion

Table 2 shows the results of the physicochemical characterization of citron watermelon seeds in both states, fresh and dehydrated at temperatures of 50, 60, 70 and 80 °C.

Table 2. Physicochemical characterization of citron watermelon seeds in two states, fresh and dehydrated at temperatures of 50, 60, 70 and 80 °C

Variables (d.b.)	Fresh	50	60	70	80
		(°C)			
Moisture content (%)	54.15 ± 0.38 a	4.37 ± 0.09 b	3.42 ± 0.06 c	1.58 ± 0.07 d	0.81±0.02 e
Water activity (a_w)	0.986 ± 0.001 a	0.340 ± 0.001 b	0.328 ± 0.002 c	0.309 ± 0.003 d	0.293 ± 0.09 e
Total titratable acidity (%)	0.21 ± 0.00 a	0.20 ± 0.00 a	0.19 ± 0.00 a	0.18 ± 0.00 a	0.19 ± 0.00 a
pH	5.60 ± 0.07 b	7.10 ± 0.02 a	6.98 ± 0.04 a	6.86 ± 0.04 a	6.81 ± 0.02 a
Ash concentration (%)	1.67 ± 0.04 b	2.29 ± 0.07 a	2.38 ± 0.05 a	2.29 ± 0.04 a	2.29 ± 0.09 a
Lipids (%)	9.41 ± 0.31 d	28.93 ± 0.19 c	30.57 ± 0.27 b	29.88 ± 0.17 b	34.20 ± 0.09 a
Total sugar (g per 100 g)	0.17 ± 0.03 e	8.87 ± 0.03 b	8.35 ± 0.00 c	8.94 ± 0.01 a	8.25 ± 0.00 d
Reducing sugars (g per 100 g)	0.108 ± 0.00 a	0.09 ± 0.09 b	0.07 ± 0.07 c	0.05 ± 0.05 d	0.04 ± 0.04 d
Non-reducing sugars (g per 100 g)	0.06 ± 0.00 e	8.34 ± 0.04 b	7.86 ± 0.00 c	8.45 ± 0.01 a	7.80 ± 0.00 d

Means followed by the same letter do not differ by the Tukey test at $p \leq 0.05$; The means are followed by standard deviation

Drying increments the ash concentration, pH, lipids and total sugars of the flours, concentrating most solid constituents. Exposure to heat caused reductions in moisture content, water activity and, among solids, in reducing sugars, when compared to fresh seeds. Degradation of nutritional properties caused by heat is usually compensated by the concentration resulting from the reduction of liquid concentration. In some cases, however, there may be volatilization of thermolabile substances or conversion into other compounds, causing changes in nutritional values, and even reduction. Two changes are often observed during the convective drying process: shrinkage and thermal degradation of the product. Therefore, it results in products that undergo greater changes by heat treatment, due to the type of heat transfer by conduction (Téllez-Pérez et al., 2014).

The mean value of the moisture content found was 54.15% (dry basis, d.b.), similar to that reported by Souza et al. (2019), 55.29%, when studying the nutritional and chemical properties of common watermelon (*Citrullus lanatus*) seeds. In other fruit seeds, Almeida et al. (2018) found moisture contents of 56.57 and 60.33% in seeds of two species of jabuticaba, *Myrciaria grandifolia* and *Myrciaria jabuticaba*, respectively. The moisture content of the flours is within the standards established by Brazilian legislation, which establishes a maximum value of 15% for flours obtained from fruits and seeds (Brasil, 2005b).

The water activity value was reduced to about one third in the drying at 50 °C in comparison to the fresh material, gradually decreasing with the increase in drying temperature. The reduction of water activity to values below 0.4 makes the flours suitable for safe storage, as long as this free moisture content is maintained.

The total titratable acidity of the seeds, 0.21%, is within the expected range for seeds, which are materials of low acidity. Drying temperatures did not have a significant effect on total titratable acidity, keeping the values both between samples dried at different temperatures and between them and the fresh sample. Almeida et al. (2018) reported acidity values of 0.45 and 0.72% for *Myrciaria grandifolia* and *Myrciaria jabuticaba*, respectively. According to Zhang et al. (2013), the maintenance of acids present in materials subjected to drying can be promoted by the inactivation of enzymes that degrade the product.

The pH increased with drying in comparison to the fresh sample, remaining close to neutrality in the dried materials, with non-significant variations between temperatures. Mendes et al. (2013) explain that this is due to the strong buffering power of citric acid and the lower water activity promoted by drying. When comparing the pH of citron watermelon seed flours with that of other types of flours, it is possible to find values such as that of guava seed flour, of 5.98 (Silveira et al., 2016).

The average ash concentration of the flours obtained by drying, 2.31%, exceeds that of the fresh sample by about 0.64%, being higher than that established for refined wheat flour, which must contain a maximum of 1.4% ash, and similar to that of whole wheat flour, 2.5%, according to Normative Instruction No. 8 of June 2, 2005 (Brasil, 2005a).

The lipid concentration of the fresh sample, of almost 10%, exceeds those of most traditionally consumed grains, such as beans, rice and maize. The increase in lipid concentration can be attributed to the loss of seed mass, due to the degradation of high molecular weight compounds, such as starch and non-starchy carbohydrates. For cucurbits, Kulaitiene et al. (2018) evaluated seeds of Lithuanian cultivars and found values from 47.24 to 47.43%. With drying, the lipid concentration of flours increased compared to the fresh sample, increasing about 20% in the sample obtained at 50 °C up to approximately 25% in the flour obtained at 80 °C, with the increments accompanying the largest reductions in moisture content at the highest temperatures. In a study conducted by Souza et al. (2019), the lipids of fresh watermelon seeds showed a value of 11.06% and, after drying at a temperature of 50 °C, the authors found an increase to 24.75%.

The total sugar concentration, with a value of 0.17 g per 100 g of sample, is close to that observed in melon (*Cucumis melo* L.) seeds by Silva et al. (2018), who found results of 0.19 g per 100 g of fresh sample. In addition to the increase in total and non-reducing sugars with drying, there were statistical differences between the samples obtained at different temperatures, and the temperature of 70 °C resulted in higher concentration of the two parameters, possibly as the one that represented the best combination of water elimination and lower thermal degradation.

Figure 1 shows the average drying rates of citron watermelon seeds at temperatures from 50 to 80 °C. At temperatures from 60 °C, it is possible to note periods of virtually constant rates until 30 min of process, when the falling rate behavior begins.

The increments in drying temperature resulted in an increase in the rate of water evaporation from the seeds, but with similar curves, mainly from 60 to 80 °C. Beigi (2015)

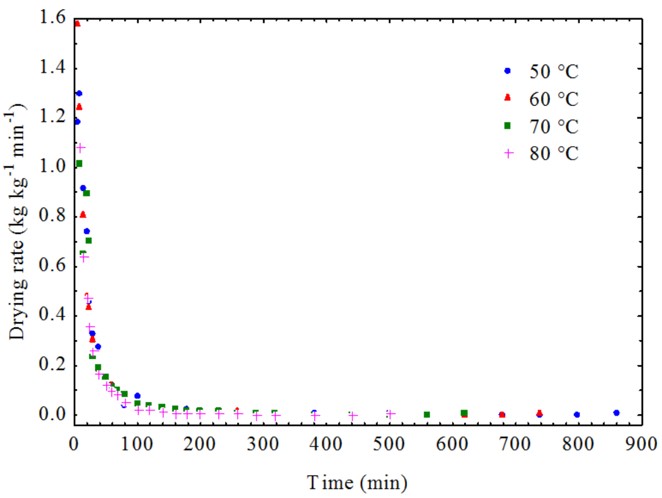

Figure 1. Drying rate of citron watermelon seeds as a function of drying time at different drying temperatures

explained that the higher drying rates are due to the higher gradient of water pressure at higher temperatures, which enables a faster evaporation of the liquid phase in a shorter time interval. At the initial times of drying of agricultural products, usually, after an initial induction period, there is a phase characterized by increased temperature of the material, with constant drying rates. As the process continues, from a certain time, the drying rates enter the falling rate period, indicating an increasingly slower water removal. Temperature increments lead to an increase in the potential for heat and mass transfer during this process, resulting in an increase in the drying rate and, consequently, a decrease in process time. Several authors have studied such behaviors in the drying of fruit seeds, such as avocado seeds (Avhad & Marchetti, 2016) and papaya seeds (Chielle et al., 2016).

Table 3 shows the parameters, coefficients of determination (R^2), mean squared deviations (MSD) and chi-squares (χ^2) of

Table 3. Parameters, coefficients of determination (R^2), mean squared deviations (MSD) and chi-squares (χ^2) of the nonlinear regression models fitted to the drying kinetics data of citron watermelon seeds at temperatures of 50, 60, 70 and 80 °C

Models	T (°C)	Parameters				R^2	MSD	χ^2
Newton		K						
	50	0.0321				0.9798	0.0372	0.0014
	60	0.0344				0.9550	0.0533	0.0029
	70	0.0409				0.9680	0.0453	0.0021
	80	0.0595				0.9613	0.0466	0.0023
Thompson		a	b					
	50	0.0029	0.0042			0.9611	0.0518	0.0029
	60	0.0037	0.0050			0.9830	0.0329	0.0011
	70	0.0023	0.0039			0.9752	0.0398	0.0017
	80	0.0109	0.0129			0.9868	0.0272	0.0008
Modified Page		k	n					
	50	0.0298	0.9481			0.9821	0.0351	0.0013
	60	0.0287	0.8888			0.9661	0.0463	0.0023
	70	0.0365	0.9218			0.9733	0.0413	0.0018
	80	0.0530	0.9162			0.9675	0.0428	0.0019
Page		k	n					
	50	0.0741	0.7533			0.9926	0.0226	0.0006
	60	0.1181	0.6331			0.9960	0.0159	0.0003
	70	0.1147	0.6781			0.9939	0.0197	0.0004
	80	0.1784	0.6244			0.9969	0.0130	0.0002
Henderson and Pabis		a	k					
	50	0.9481	0.0298			0.9821	0.0351	0.0013
	60	0.8888	0.0287			0.9661	0.0463	0.0023
	70	0.9218	0.0365			0.9733	0.0413	0.0018
	80	0.9162	0.0530			0.9675	0.0428	0.0019
Two-Term Exponential		a	k					
	50	0.2937	0.0788			0.9904	0.0257	0.0007
	60	0.2400	0.1064			0.9782	0.0372	0.0015
	70	0.2628	0.1144			0.9846	0.0314	0.0010
	80	0.2547	0.1748			0.9811	0.0326	0.0012
Logarithmic		a	k	c				
	50	0.9361	0.0334	0.0310		0.9898	0.0265	0.0008
	60	0.8791	0.0341	0.0396		0.9785	0.0369	0.0015
	70	0.9103	0.0420	0.0357		0.9838	0.0322	0.0012
	80	0.9060	0.0607	0.0324		0.9781	0.0351	0.0014
Approximation of Diffusion		a	k	b				
	50	0.7899	0.0478	0.1511		0.9995	0.0046	0.0000
	60	0.6428	0.0744	0.1372		0.9994	0.0057	0.0000
	70	0.7218	0.0715	0.1501		0.9991	0.0077	0.0001
	80	0.6592	0.1261	0.1452		0.9996	0.0055	0.0000
Two Terms		a	k0	b	k1			
	50	0.2146	0.0073	0.7916	0.0486	0.9996	0.0055	0.0000
	60	0.3537	0.0101	0.6411	0.0732	0.9995	0.0056	0.0000
	70	0.2758	0.0107	0.7205	0.0708	0.9991	0.0077	0.0001
	80	0.3399	0.0183	0.6585	0.1256	0.9996	0.0055	0.0000

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Continuation of Table 3

Models	T (°C)	Parameters				R^2	MSD	χ^2
		a	k	n	b			
Midilli	50	1.0272	0.0805	0.7391	0.0000	0.9935	0.0211	0.0005
	60	1.0176	0.1222	0.6296	0.0000	0.9965	0.0148	0.0002
	70	1.0174	0.1183	0.6752	0.0000	0.9945	0.0188	0.0004
	80	1.0083	0.1796	0.6254	0.0000	0.9972	0.0125	0.0001

the nonlinear regression models fitted to the experimental data of drying of citron watermelon seeds at temperatures from 50 to 80 °C. The coefficients of determination (R^2) were higher than 0.95 for all models and all drying temperatures. The Two Terms model had the highest coefficients of determination ($R^2 > 0.9991$), sharing with the Approximation of Diffusion model the lowest MSD and χ^2, resulting in almost equivalent fitting parameters.

When comparing the magnitude of R^2, only the Page, Approximation of Diffusion, Two Terms and Midilli models showed R^2 values ≥ 0.99 at all temperatures, while Newton, Thompson, Modified Page, Henderson and Pabis, Two-Term Exponential and Logarithmic models showed R^2 in many cases lower than 0.97.

Chaji & Hedayatizadeh (2017), studying the drying kinetics of watermelon seeds at temperatures of 40, 50 and 60 °C and air velocities of 0.5, 1.0 and 1.5 m s^{-1}, concluded that all models fitted to the experimental drying data (Newton, Page, Modified Page, Henderson and Pabis, Logarithmic, Two Terms, Two-Term Exponential, Midilli, Verma, Silva, and Modified Henderson and Pabis) and promoted satisfactory fits, since they showed $R^2 > 0.990$ and MSD < 0.021. Chielle et al. (2016) dried papaya (*Carica papaya* L.) seeds at temperatures from 40 to 100 °C and air velocities from 1.0 to 3.0 m s^{-1} and reported that the drying rate was directly proportional to the temperature increase and little influenced by drying air velocity. The authors also found that the Lewis and Two-Term Exponential models showed good fits to the experimental drying data of the seeds, with $R^2 >$ 0.990 and MSD < 0.001.

The parameters a and b (constant of proportionality between the drying rate and the moisture ratio) of the Diffusion Approximation model did not show a defined behavior with the increase in temperature (50 to 80 °C). However, it can be seen that the drying constant values k increased, in general, with increasing temperature. The k parameter, which corresponds to the drying rate constant in the models used, tends to increase with increasing drying temperature, as higher temperatures lead to higher drying rates, and the material reaches equilibrium moisture content in a shorter process time (Corrêa et al., 2010). Similar results were found in the drying kinetics of passion fruit seeds by Santos et al. (2018), who found that the k parameter increased with increasing temperature.

Figure 2 shows the curves from 50 to 80 °C fitted by the Two Terms model. It is possible to identify a more pronounced effect of temperature in the curve referring to 80 °C, which stands out from the curves relative to temperatures from 50 to 70 °C. It is also possible to observe low dispersion of the experimental values in relation to the fitting curves, resulting from the high values of R^2 and low values of MSD and χ^2.

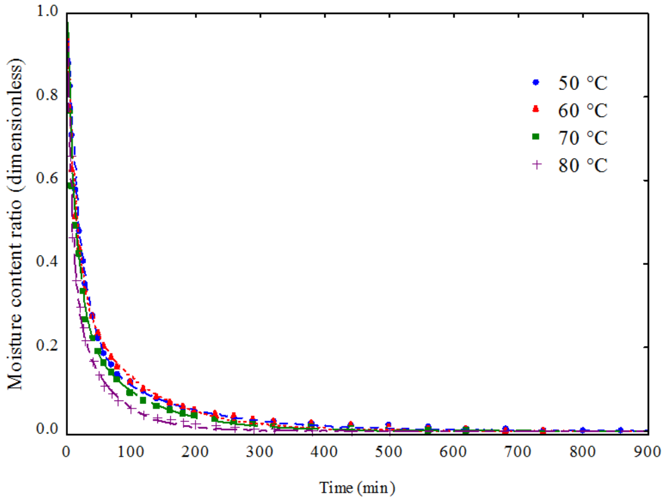

Figure 2. Moisture content ratio of citron watermelon seeds as a function of drying time described by the Two Terms model, at drying temperatures from 50 to 80 °C

Effective diffusivity

Table 4 shows the effective diffusivity coefficients obtained in the drying of citron watermelon seeds at temperatures from 50 to 80 °C. Diffusivity values increased with the increase in drying air temperature by about 89% between the temperatures of 50 and 80 °C, and all values were within the range frequently reported for foodstuffs, which is from 10^{-11} to 10^{-9} m^2 s^{-1} (Madamba et al., 1996). Chaji & Hedayatizadeh (2017), studying the drying kinetics of watermelon seeds, found values of effective diffusivity ranging from 3.009×10^{-10} to 6.805×10^{-11} m^2 s^{-1} and activation energy between 37.11 and 56.63 kJ mol^{-1}. Silva et al. (2018), studying the drying of watermelon seeds, observed increase in diffusivity with the increase in drying temperature, obtaining values of 1.553×10^{-10}, 1.709×10^{-10}, 1.917×10^{-10} and 2.091×10^{-10} m^2 s^{-1} for temperatures of 35, 40, 45 and 50 °C, respectively.

Figure 3 shows the values of the effective diffusivity (D_{ef}), represented in the form of 'ln Def' as a function of the inverse of absolute temperature (1/T), for the drying of citron watermelon seeds. It can be observed that dependence is satisfactorily described by the Arrhenius-type equation, with values showing a linear behavior and R^2 of 0.8737.

From Figure 3, the activation energy (E_a) was quantified based on the slope of the line. Thus, Eq. 21 presents the

Table 4. Mean values of effective diffusivity (D_{ef}) and the coefficients of determination (R^2) obtained in the drying of citron watermelon seeds at temperatures from 50 to 80 °C

Temperatures (°C)	D_{ef} (m^2 s^{-1})	R^2
50	4.21×10^{-10}	0.9829
60	4.44×10^{-10}	0.9783
70	5.38×10^{-10}	0.9812
80	7.97×10^{-10}	0.9790

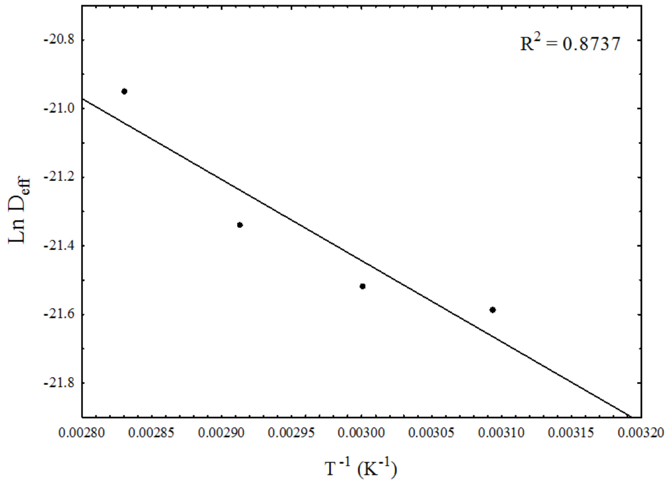

Figure 3. Effective diffusivity by Arrhenius-type equation for the drying of citron watermelon seeds

effective diffusivity as a function of temperature based on the Arrhenius-type equation.

$$D_{ef} = 6.098 \times 10^{-7} \exp\left(-\frac{19.78}{RT}\right) \quad (21)$$

The activation energy is related to the amount of energy needed to trigger the water diffusion process, so the lower the activation energy, the greater the effective diffusivity of the product's water, that is, the lower the energy needed to transform liquid free water into vapor (Martins et al., 2015). In this study, the drying process of citron watermelon seeds showed activation energy of 19.78 kJ mol^{-1}, a value that is within the range frequently reported in foodstuffs, which is from 12.7 to 110 kJ mol^{-1} (Zogzas et al., 1996). Higher value was reported by Silva et al. (2018) for melon seeds, 55.81 kJ mol^{-1}.

Thermodynamic properties

Table 5 presents the thermodynamic properties of the drying process, variations of enthalpy, entropy and Gibbs free energy, at temperatures from 50 to 80 °C in the drying of citron watermelon seeds. Enthalpy variation decreased with the increase in drying temperature, being between 16.8449 and 17.0943 kJ mol^{-1}, which indicates that a smaller amount of energy is required for drying to occur at higher temperatures. Similar behavior was reported by Costa et al. (2016), who found values of 34.74, 34.66, 34.58 and 34.50 kJ mol^{-1} for enthalpy variations of jabuticaba residues, at drying temperatures of 40, 50, 60 and 70 °C, respectively. Entropy behaved similarly to enthalpy, with reduction in the values as temperature increased, ranging from -0.3645 at 50 °C to -0.3653 kJ mol^{-1} K^{-1} at 80 °C.

Table 5. Mean values of the thermodynamic properties of the drying process of citron watermelon seeds at temperatures from 50 to 80 °C

Temperature (°C)	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
50	17.0943	-0.3645	134.8986
60	17.0112	-0.3648	138.5453
70	16.9280	-0.3650	142.1946
80	16.8449	-0.3653	145.8463

ΔH - Enthalpy; ΔS - Entropy; ΔG - Gibbs free energy

A proportional increase in the values of Gibbs free energy is observed with increasing drying air temperature. Maia et al. (2019) justified that the increase in the work performed to make sorption sites available increases the capacity to transfer water molecules from the product to the drying air. This phenomenon was expected, since the drying process was not spontaneous, characterizing the endothermal reaction.

Conclusions

1. Citron watermelon seeds are rich in lipids and have low concentrations of simple sugars.
2. Constant drying rates occurred in short periods, close to or less than 30 min.
3. Two Terms and Approximation of Diffusion models showed excellent description of the drying kinetics of citron watermelon seeds, followed by Midilli and Page models.
4. The effective diffusivity increases with the drying temperature, with the relationship satisfactorily fitted by Arrhenius-type equation.
5. The increase in drying temperature decreases enthalpy and entropy and increases Gibbs free energy.

Literature Cited

Almeida, E. S. de; Silva, R. J. N. da; Gonçalves, E. M. Total phenolic compounds and physicochemical characteristics of jabuticaba fruit. Gaia Scientia, v.12, p.81-89, 2018.

Avhad, M.; Marchetti, J. Mathematical modelling of the drying kinetics of Hass avocado seeds. Industrial Crops and Products, v.91, p.76-87, 2016. https://doi.org/10.1016/j.indcrop.2016.06.035

Beigi, M. Hot air drying of apple slices: dehydration characteristics and quality assessment. Heat and Mass Transfer, v.52, p.435-1442, 2015. https://doi.org/10.1007/s00231-015-1646-8

Bligh, E. G.; Dyer, W. J. A rapid method of total lipid extraction and purification. Canadian Journal of Biochemistry and Physiology, v.37, p.911-917, 1959. https://doi.org/10.1139/y59-099

Brasil. Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa nº 8, de 2 de junho de 2005. Regulamento técnico de identidade e qualidade da farinha de trigo. Diário Oficial [da] República Federativa do Brasil, Brasília, DF, n.105, p.91, 3 jun. 2005a.

Brasil. Ministério da Saúde. Agência Nacional de Vigilância Sanitária (ANVISA) Resolução RDC nº 263 de 22 de setembro de 2005. Dispões sobre o Regulamento Técnico para produtos de cereais, amidos, farinhas e farelos. Diário Oficial [da] República Federativa do Brasil, Brasília, DF, 2005b.

Chaji, H.; Hedayatizadeh, M. Quality assessment and kinetics of dehydrated watermelon seeds: Part 1. Engineering in Agriculture, Environment and Food, v.10, p.1-8, 2017. https://doi.org/10.1016/j.eaef.2017.01.006

Chielle, D. P.; Bertuol, D. A.; Meili, L.; Tanabe, E. H.; Dotto, G. L. Convective drying of papaya seeds (*Carica papaya* L.) and optimization of oil extraction. Industrial Crops and Products, v.85, p.221-228, 2016. https://doi.org/10.1016/j.indcrop.2016.03.010

Corrêa, P. C.; Oliveira, G. H. H.; Botelho, F. M.; Goneli, A. L. D.; Carvalho, F. M. Mathematical modeling and determination of thermodynamic properties of coffee (*Coffea arabica* L.) during the drying process. Revista Ceres, v.57, p.595-601, 2010. https://doi.org/10.1590/S0034-737X2010000500005

Costa, C. F.; Corrêa, P. C.; Vanegas, J. D. B.; Baptestini, F. M.; Campos, R. C.; Fernandes, L. S. Mathematical modeling and determination of thermodynamic properties of jabuticaba peel during the drying process. Revista Brasileira de Engenharia Agrícola e Ambiental, v.20, p.576-580, 2016. https://doi.org/10.1590/1807-1929/agriambi.v20n6p576-580

Instituto Adolfo Lutz (São Paulo). Métodos físico-químicos para análise de alimentos. São Paulo: Instituto Adolfo Lutz, 2008. 1020p.

Jideani, V. A.; Mpotokwana, S. M. Modeling of water absorption of botswana bambara varieties using Peleg's equation. Journal of Food Engineering, v.92, p.182-188, 2009. https://doi.org/10.1016/j.jfoodeng.2008.10.040

Keneni, Y. G.; Hvoslef-Eide, K.; Marchetti, J. M. Mathematical modelling of the drying kinetics of *Jatropha curcas* L. seeds. Industrial Crops and Products, v.132, p.12-20, 2019. https://doi.org/10.1016/j.indcrop.2019.02.012

Kulaitiene, J.; Černiauskienė, J.; Jarienė, E.; Danilčenko, H.; Levickienė, D. Antioxidant activity and other quality parameters of cold pressing pumpkin seed oil. Notulae Botanicae Horti Agrobotanici Cluj-Napoca, v.46, p.161-166, 2018. https://doi.org/10.15835/nbha46110845

Madamba, P. S.; Driscoll, R. H.; Buckle, K. A. The thin-layer drying characteristics of garlic slices. Journal of Food Engineering, v.29, p.75-97, 1996. https://doi.org/10.1016/0260-8774(95)00062-3

Maia, R. B.; Santos, S. G. F. dos; Queiroz, J. S.; Rodovalho, R. S.; Silva, D. P. Morgado, V. N. de M. Drying kinetics and thermodynamic properties of pigeon pea beans. Científica, v.47, p.164-174, 2019. https://doi.org/10.15361/1984-5529.2019v47n2p164-174

Mallek-Ayadi, S.; Bahloul, N.; Kechaou, N. Chemical composition and bioactive compounds of *Cucumis melo* L. seeds: Potential source for new trends of plant oils. Process Safety and Environmental Protection, v.113, p.68-77, 2018. https://doi.org/10.1016/j.psep.2017.09.016

Martins, E. A. S.; Lage, E. Z.; Goneli, A. L. D.; Hartmann Filho, C. P.; Lopes, J. G. Drying kinetics of *Serjania marginata* Casar leaves. Revista Brasileira de Engenharia Agrícola e Ambiental, v.19, p.238-244, 2015. https://doi.org/10.1590/1807-1929/agriambi.v19n3p238-244

Mendes, G. R. L.; Freitas, C. H. de F.; Scaglioni, P. T.; Schmidt, C. G.; Furlong, E. B. Conditions for osmotic dehydration of oranges and functional properties of the product. Revista Brasileira de Engenharia Agrícola e Ambiental, v.17, p.1210-1216, 2013. https://doi.org/10.1590/S1415-43662013001100012

Miller, G. L. Use of dinitrosalicylic acid reagent for determination of reducing sugar. Analytical Chemistry, v.31, p.426-428, 1959. https://doi.org/10.1021/ac60147a030

Santos, H. H.; Rodovalho, R. S.; Silva, D. P. da; Morgado, V. N. de M. Drying kinetics of passion fruit seeds. Científica, v.46, p.49-56, 2018. https://doi.org/10.15361/1984-5529.2018v46n1p49-56

Santos, R. M.; Melo, N. F. de; Fonseca, M. A. J. da; Queiroz, M. A. A. Combining ability of forage watermelon (*Citrullus lanatus* var *citroides*) germplasm. Revista Caatinga, v.30, p.768-775, 2017. https://doi.org/10.1590/1983-21252017v30n325rc

Silva, I. L.; Silva, H. W. da; Camargo, F. R. T. de; Farias, H. F. L. de; Freitas, E. de F. M. Drying and diffusivity of melon seeds. Revista de Ciências Agrárias, v.41, p.309-315, 2018. https://doi.org/10.19084/RCA17278

Silva, F. A. S.; Azevedo, C. A. V. The Assistat Software Version 7.7 and its use in the analysis of experimental data. African Journal of Agricultural Research, v.11, p.3733-3740, 2016. https://doi.org/10.5897/AJAR2016.11522

Silveira, M. L. R.; Santos, C. O.; Penna, N. G.; Sautter, C. K.; Rosa, C. S.; Bertagnolli, S. M. M. Technological use of guia seeds (*Psidium guajava* L.) as flour in the preparation of biscuits. Boletim Centro de Pesquisa de Processamento de Alimentos, v.34, p.1-20, 2016. https://doi.org/10.5380/cep.v34i2.53178

Siqueira, V. C.; Mabasso, G. A.; Quequeto, W. D.; Silva, C. R. da; Martins, E. A. S.; Isquierdo, E. P. Drying kinetics and effective diffusion of watermelon seeds. Research, Society and Development, v.9, p.1-17, 2020. https://doi.org/10.33448/rsd-v9i4.2887

Souza, A. V. C.; Oliveira, B. S.; Hey, G. B. S.; Witt, S. H.; Balbi, M. E.; Campos, F. R. Chemical and chemical analysis of watermelon (*Citrullus lanatus*, Curcubitaceae) seeds and fixed oil. Visão Acadêmica, v.20, p.18-28, 2019. https://doi.org/10.5380/acd.v20i1.66842

Téllez-Pérez, C.; Sobolik, V.; Montejano-Gaitán, J. G.; Abdulla, G.; Allaf, K. Impact of swell-drying process on water activity and drying kinetics of moroccan pepper (*Capsicum annum*). Drying Technology, v.33, p.131-142, 2014. https://doi.org/10.1080/07373937.2014.936556

Yemm, E. W.; Willis, A. J. The estimation of carbohydrates in plant extracts by anthrone. Biochemical Journal, v.57, p.508-515, 1954. https://doi.org/10.1042/bj0570508

Zhang, X.; Shen, L.; Li, F.; Meng, D.; Sheng, J. Arginase induction by heat treatment contributes to amelioration of chilling. Postharvest Biology and Technology, v.79, p.1-8, 2013. https://doi.org/10.1016/j.postharvbio.2012.12.019

Zogzas, N. P.; Maroulis, Z. B.; Marinos-Kouris, D. Moisture diffusivity data compilation in food stuffs. Drying Technology, v.14, p.2225-2253, 1996. https://doi.org/10.1080/07373939608917205