ISSN 2175-6813

Revista Engenharia na Agricultura

Viçosa, MG, DEA/UFV - DOI: 10.13083/reveng.v29i1.9935 V.28, p.535-548, 2020

MOISTURE ADSORPTION ISOTHERMS AND DRYING KINETIC OF PERSIAN CLOVER (*Trifolium resupinatum L.*) AND ARROWLEAF CLOVER (*Trifolium vesiculosum*) SEEDS

Gabriela Saldanha Soares[1], Scarlet Neves Tuchtenhagen[2], Luiz Antonio de Almeida Pinto[3] & Carlos Alberto Severo Felipe[4]

1 - Chemical Engineer, Msc, FURG/RioGrande – RS; E-mail: gabrielasoares_eq@yahoo.com.br

2 - Chemical Engineer, Undergraduate student, FURG/Rio Grande – RS; Email: scarlet.tuchtenhagen@gmail.com

3 - Chemical Engineer, Dr., FURG/Rio Grande – RS; E-mail: dqmpinto@furg.br

4 – Chemical Engineer, Dr., FURG/Rio Grande – RS; Email: severopeixoto@yahoo.com.br

Keywords:
Activation energy
Adsorption isotherms
Arrowleaf clover
Persian clover
Thin layer drying

ABSTRACT

The aim of this work was to obtain adsorption isotherms and to study the drying kinetics of persian clover (*Trifolium resupinatum L.*) and arrowleaf clover (*Trifolium vesiculosum*) seeds. The equilibrium moisture content and the moisture adsorption behavior were found by isotherms curves at 40, 45 and 50 ºC, and the Peleg model was the most suitable. The drying kinetics was determined by thin layer assays in an air parallel flow dryer at all three temperatures. In addition, the predominance of the falling drying rate period for the two species of seeds was observed, and the critical moisture content values were approximately of 0.20 and 0.25 $g_{water}\, g_{dry\ matter}^{-1}$ for persian clover and arrowleaf clover seeds, respectively. The effective diffusivity values were estimated in ranges of values of $3.61\times10^{-11} – 6.81\times10^{-11}$ m² s^{-1} for persian clover and $6.76\times10^{-11} – 1.15\times10^{-10}$ m²s^{-1} for arrowleaf clover seeds and the temperature effect was expressed by an Arrhenius relation. Thus, drying kinetics confirmed the greater difficulty in moisture removal from the arrowleaf clover seeds, compared to the persian clover seeds drying, in agreement with the results obtained through adsorption isotherms.

Palavras-chave:
Energia de ativação
Isotermas de adosrção
Trevo vesiculoso
Trevo persa
Secagem em camada fina

Isotermas de adsorção de umidade e cinética de secagem de sementes de trevo persa (*Trifolium resupinatum L.*) e trevo vesiculoso (*Trifolium vesiculosum*)

RESUMO

O objetivo deste trabalho foi obter as isotermas de adsorção e estudar a cinética de secagem de sementes de trevo persa (*Trifolium resupinatum L.*) e trevo vesiculoso (*Trifolium vesiculosum*). O conteúdo de umidade de equilíbrio e o comportamento da adsorção de umidade pelas sementes foram verificados em curvas de isoterma a 40, 45 e 50 ºC, e o modelo de Peleg foi o mais apropriado para este propósito. A cinética de secagem foi determinada por experimentos em camada delgada em um secador de fluxo paralelo nas três temperaturas citadas. Além disso, foi constatado o predomínio do período de secagem à taxa decrescente para as duas espécies de sementes, e o valor do conteúdo de umidade crítica foi de aproximadamente 0.20 e 0.25 $g_{água}\, g_{matéria\ seca}^{-1}$ para o trevo persa e para o tervo vesiculoso, respectivamente. Os valores de difusividade efetiva foram estimados no intervalo entre $3.61\times10^{-11} – 6.81\times10^{-11}$ m² s^{-1} para as sementes de trevo persa e $6.76\times10^{-11} – 1.15\times10^{-10}$ m²s^{-1} para o trevo vesiculoso, e o efeito da temperatura foi expresso pela relação de Arrhenius. Portanto, o estudo da cinética de secagem confirmou a maior dificuldade em remover a umidade das sementes de trevo vesiculoso, comparado à secagem de sementes de trevo persa, em concordância com os resultados obtidos por meio das isotermas de adsorção.

Recebido para publicação em 04/04/2020 • Aprovado em 14/12/2020 • Publicado em 24/12/2020

Nomenclature

A	Drying parameter (dimensionless)	R	Universal gases constant (kJ mol^{-1}K^{-1})
A	Thermodynamics constant of Eq. (4) (dimensionless)	R^2	Correlation coefficient (dimensionless)
a_w	Water activity (dimensionless)	$RMSE$	Root mean square error (dimensionless)
B	Thermodynamics constant of Eq. (4) (dimensionless)	T	Time (min)
C_B	Thermodynamics constant of Eq. (1) (dimensionless)	T	Temperature (ºC or K)
C_G	Thermodynamics constant of Eq. (2) (dimensionless)	t_c	Critical time (min)
d_p	Particle diameter (mm)	t_t	Transition time (min)
$Deff$	Effective diffusivity (m² s^{-1})	t_T	Total time (min)
D_0	Diffusion constant (m² s^{-1})	X_0	Initial moisture content ($g_{water}\, g_{dry\ matter}$)
E_a	Activation energy (kJ mol^{-1})	X_c	Critical moisture content ($g_{water}\, g_{dry\ matter}$)
K	Drying parameter (min^{-1})	X_e	Equilibrium moisture content ($g_{water}\, g_{dry\ matter}$)
k_b	Thermodynamics constant of Eq. (2) (dimensionless)	X_F	Final moisture content ($g_{water}\, g_{dry\ matter}$)
k_1	Thermodynamics constant of Eq. (3) (dimensionless)	X_m	Mean moisture content ($g_{water}\, g_{dry\ matter}$)
k_2	Thermodynamics constant of Eq. (3) (dimensionless)	X_{mo}	Monolayer moisture content ($g_{water}\, g_{dry\ matter}$)
L	Plate half-thickness (m)	X_R	Moisture ratio, $(X-X_e)/X_0-X_e)$ (dimensionless)
R	Drying rate (g.m^{-2}min^{-1})	X_{sat}	Saturation moisture content ($g_{water}\, g_{dry\ matter}$)
R_c	Constant drying rate (g m^{-2}min^{-1})	X_t	Transition moisture content ($g_{water}\, g_{dry\ matter}$)
N	Drying parameter (dimensionless)	Φ	Sphericity (dimensionless)
n_1	Exponent in 1st term of Eq. (3) (dimensionless)	ρ_p	Particle density (g.cm^{-3})
n_2	Exponent in 2nd term of Eq. (3) (dimensionless)	S	Superficial area (m^2.g^{-1})

INTRODUCTION

Regions of temperate climate support the cultivation of forage seeds, which planting is easy, has good resistance to heat and excess moisture, besides enriching the soil with nutrients (COELHO *et al*., 2002). In this context, two annual winter forage species of the genus *Trifolium*, the persian clover (*Trifolium resupinatum L.*) and the arrowleaf clover (*Trifolium vesiculosum*) stand out. They have high nutritional value (REIS, 2007) and are widely used in crop-livestock integration systems (BEVILAQUA; OLANDA, 2011). Therefore, the knowledge of drying kinetic and moisture sorption mechanisms of these species is very useful, given the possibility of drying these seeds on an industrial scale.

The drying operation aims to reduce the moisture content of the material by simultaneous heat and mass transfer between solid and air

(MOCELIN *et al*., 2013; MUJUMDAR, 2014). Moisture removal is strongly influenced by process variables and moisture transport mechanisms. This influence can be understood by determining the sorption isotherms and the drying kinetics of material samples (KIRANOUDS, 1997).

Sorption isotherms describe the behavior of the solid-liquid sorption systems, and they are useful for determining the driving force generated in moisture transport from the material to the drying medium (KAYA *et al*., 2007). Isotherms relate equilibrium moisture content to water activity at constant temperature and pressure and can be of two types: desorption (moisture loss) or adsorption (moisture increase) (RAO *et al*., 2005). Drying Kinetics is determined by the construction of the drying curves and its analysis is performed through models. Drying curves are basically divided into three periods in terms of moisture loss: a period of sample adaptation to the drying temperature, a constant rate period and a decreasing rate period (MUJUMDAR, 2014). One of the most common and efficient methods for obtaining the kinetics of a given material is thin layer drying (UDDIN *et al*., 2016).

Due to the absence of bibliographical information about the drying of persian clover and arrowleaf clover seeds, the aim of this paper was to obtain the adsorption isotherms and to study the kinetics of thin-layer drying of these species of seeds, fitting the models predicted of the literature to the experimental data.

MATERIAL AND METHODS

Materials

Persian clover (*Trifolium resupinatum L.*) and arrowleaf clover seeds (*Trifolium vesiculosum*) were used in this work (Figure 1). These seeds were provided by Brazilian Agricultural Research Corporation (EMBRAPA Temperate Climate – Pelotas/RS/Brazil).

Physical characterization of the seeds

The two seed species were characterized according to their mean diameter, sphericity, density and initial moisture. These physical characteristics, were compared by analysis of variance at 95% confidence ($p<0.05$), and all determinations were performed in triplicate.

The mean diameter of the seed was determined by sieving tests (using the Sauter definition), and the sphericity was determined by scanning electron microscopy (SEM) by measurement of the diameters inscribed and circumscribed, both according to the methodology described by Cremasco (2012). The particles density was determined by pycnometry assays using hexane (PEÇANHA, 2014). Finally, the seeds were kept in an oven (*De Leo*, DL-SE, Brazil) at 105 ºC for 24 h to determine the initial moisture content of the raw samples, according to the AOAC methodology (AOAC, 1995).

The surface area of seeds was also determined using a surface area analyser (Gemini VII 2390, Micromeritics, USA) through BET method.

Preparation of seeds for drying

Due to their low moisture content, before drying, the persian clover and arrowleaf clover seeds were moisturized in a thermostatic bath. The process consisted in placing the seeds (700 g) on a screen in a thermostatic capped bath (*Biomatic*, Brazil, capacity 32.4 L). The water volume was 16 L and the material was kept during 5 h until the water temperature was approximately 50 °C. Then the bath was switched off and the seeds remained in the equipment still capped for another 4 h. After

Figure 1. Seeds: (a) persian clover and, (b) arrowleaf clover

this period, samples were removed and submitted to moisture content analysis (AOAC, 1995).

Determination of equilibrium moisture content

Equilibrium moisture content values of the persian clover and arrowleaf clover seeds were determined by the static gravimetric method, in which diffusion is the only mechanism of mass transfer (HASSINI *et al*., 2015). The adsorption isotherms were obtained at temperatures of 40, 45 and 50 °C.

The experimental procedure consisted of inserting 1 (± 0,1) g of dry sample into hermetically sealed glass containers containing 20 mL of sulfuric acid solution in 11 different concentrations (0.20-0.70 kg kg^{-1}) with a variation of 0.05 kg kg^{-1}, in order to maintain water activity (a_w) between 0.050 and 0.899 (MORAES *et al*., 2008). Inside the containers, the seeds were deposited on a thin mesh attached to a support to avoid contact with the liquid solution and thus ensure only the gas diffusion of moisture. Azoxystrobin Pestanal (*Sigma-Aldrich*) diluted in 5 mL of acetonitrile was added to the seeds in vials containing acid solutions with water activity higher than 0.75, in order to avoid the fungi formation. The assays were performed in triplicate and, the containers were kept in an oven (*Nova Ética*, 400/ND, Brazil) with controlled temperature (40, 45 and 50 ºC) and weighed daily in a digital analytical balance (*Shimadzu*, AUY220), with accuracy of ± 0.0001 g, until they reached a constant weight (approximately 24 d). After reaching the equilibrium, the samples moisture contents were determined (AOAC, 1995). Then, the equilibrium moisture data, at each temperature, were plotted as a function of the water activity, at the corresponding concentrations of sulfuric acid solution.

Afterward, four isotherms models typically used for grains and seeds were fitted, through the non-linear regression, to determine the moisture adsorption behavior of the persian clover and arrowleaf clover seeds and their equilibrium moisture at each temperature. The models tested were BET (Equation 1), GAB (Equation 2), Peleg (Equation 3) and Oswin (Equation 4) (PARK *et al*., 2001; WANI *et al*., 2006; ZOMORODIAN *et al*., 2011; HASSINI *et al*., 2015; MONTE *et al*., 2018).

$$X_e = \frac{X_{mo} C_B a_w}{(1-a_w)(1-a_w+C_B a_w)} \tag{1}$$

$$X_e = \frac{X_{mo} C_G k_b a_w}{(1-k_b a_w)(1-k_b a_w+C_G k_b a_w)} \tag{2}$$

$$X_e = k_1 {a_w}^{n_1} + k_2 {a_w}^{n_2} \tag{3}$$

$$X_e = A\left(\frac{a_w}{1-a_w}\right)^B \tag{4}$$

Peleg (1993) also reported that, for the use of Equation 3, one must apply the restriction that $n_1 < 1$ and $n_2 > 1$, and the BET equation should only be applied to the monolayer region, with a_W of up to approximately 0.4. Thus, it was possible to obtain, besides the equilibrium moisture, the thermodynamic parameters for each model. The selection of the most appropriate model for the experimental data was performed by statistical analysis, coefficient of determination (R^2) and root mean square error (*RMSE*) (WILLMOTT *et al.*, 1985).

Drying Kinetics

The drying kinetics of the persian clover and arrowleaf clover seeds were studied by thin-layer drying experiments, and the assays were performed using an air parallel flow dryer. The experimental procedure consisted of placing a thin layer of the wet seeds (30-40 g) in rectangular trays of approximately 0.017 m², so that the air passed evenly over the sample. The drying air velocity was 2 m s^{-1} so that the effect of external resistance to mass transfer was negligible (ROBERTS *et al.*, 2008). All the assays were performed in triplicate, so that the three trays were placed inside the drying chamber and simultaneously withdrawn for weighing in a digital analytical balance (Marte, BL3200H, Brazil), with an accuracy of ± 0.01

g, at intervals of 2.5 min in the first 40 min, and after, every 5 min, until the weight seeds reached a constant value.

Afterward, the drying curves were plotted, presenting the drying rate (R) as a function of the moisture content of the sample (X_m) in dry basis, and the moisture ratio (X_R) as a function of the drying time. The moisture ratio curves were used to describe the drying process. The empirical models of Lewis (1921), Page (1949) and Henderson (1961) fitted to the experimental data according to Equations 5, 6 and 7, respectively.

$$X_R = \exp(-kt) \quad (5)$$

$$X_R = \exp(-kt^n) \quad (6)$$

$$X_R = a\exp(-kt) \quad (7)$$

The fit was performed by non-linear regression so that the drying parameters were obtained. In order to select the most suitable model for the experimental data and verify the quality of the fit, the coefficient of determination (R^2) and root mean square error (*RMSE*) were considered (WILLMOTT *et al.*, 1985).

The effective diffusivity of the two materials was determined by the Lewis model (Equation 5), by an analogy to the equation resulting from the model based on the second law of Fick for diffusion in the steady-state, satisfying the following considerations (Equation 8): infinite plate, uniform initial moisture distribution, drying by one side, air temperature and diffusion coefficient of sample are constant, negligible shrinkage, process without the interference of external resistances and large drying time (GEANKOPLIS, 1993; BARONI; HUBINGER, 1998; TASIRIN *et al.*, 2014).

$$X_R = \frac{8}{\pi^2}\exp\left[\frac{-\pi^2 D_{eff} t}{4L^2}\right] \quad (8)$$

The effect of temperature on the effective diffusivity was analyzed by Arrhenius equation (Equation 9), and through the linearization this equation, the slope results in the E_a/R and the intercept is the D_0 value (GEANKOPLIS, 1993; MONTE *et al.*, 2018).

$$D_{eff} = D_0\exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

RESULTS AND DISCUSSION

Physical characterization of the seeds

The results of the physical characterization of the seeds, such as mean diameter, sphericity, density and initial moisture content (dry basis) are shown in Table 1. In Figure 2 is shown the images by scanning electron microscopy (SEM) for the two seed species, the persian clover and the arrowleaf clover.

In Table 1 is shown that the sphericity and density results did not show significant differences between the two species ($p > 0.05$). However, it can be reported that the arrowleaf clover presented a larger diameter and surface area besides a rougher surface than the persian clover, being this last

Table 1. Physical characterization of the persian clover and arrowleaf clover seeds

Characteristic	Persian clover	Arrowleaf clover
Φ (dimensionless)	0.88 ± 0.01^a	0.88 ± 0.05^a
d_p (mm)	0.81 ± 0.04^b	1.22 ± 0.01^a
ρ_p (g cm^{-3})	2.01 ± 0.03^a	1.96 ± 0.04^a
X (%, d.b.)	9.96 ± 0.03^b	13.25 ± 0.02^a
S (m^2/g)	0,0541	0,0639

Mean values ± standard deviation (in triplicate, except S); d.b.: dry basis; d_p: particles mean diameter; X: moisture content of raw seeds before of moisturized; ϕ: sphericity; ρ_p: particle density. According to Tukey test, letters with different superscript in the same line indicate significant differences at 95% significance ($p<0.05$)

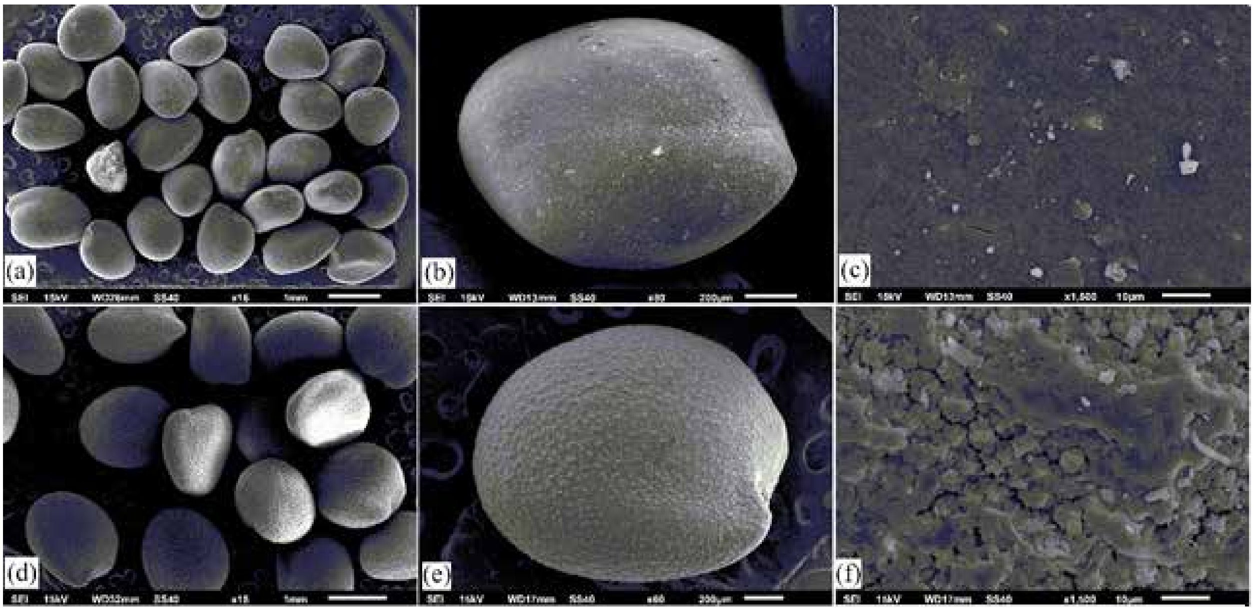

Figure 2. Scanning electron microscopy: (a), (b) e (c) persian clover seeds and its surface (×18, ×80, ×1500, respectively) and, (d), (e) e (f) arrowleaf clover seeds and its surface (×18, ×60, ×1500, respectively)

characteristic verified by Figure 2.

Determination of equilibrium moisture content

The equilibrium moisture contents of the persian clover and arrowleaf clover seeds were determined by adsorption isotherms at 40, 45 and 50ºC. Thus, semiempirical (BET and GAB) and empirical models (Peleg and Oswin) were fitted to the experimental data of equilibrium moisture (X_e) *versus* water activity. The drying parameters and the analysis statistical are shown in Table 2.

We can be observe in Table 2 that the semiempirical models of GAB and BET presented satisfactory values for the coefficient of determination. However, for the thermodynamics constants C_B and C_G, indicative of the sorption binding energy in the monolayer (RAO *et al.*, 2005; MONTE, 2018), the values obtained showed orders of magnitude far above what is common according to the literature, considering the adsorption and desorption isotherms of other seeds and foodstuffs (PELEG, 1993; HASSINI *et al.*, 2015; PARK *et al.*, 2001; CHEN, 2003; THYS *et al.*, 2010; COSTA *et al.*, 2015). Among the two empirical models tested, the Peleg model presented a better fit to the experimental data according to the statistical parameters. Considering this model, the R^2 values were ≥ 0.998 and those of *RMSE* between 0.001 and 0.003 for the two seed species. Since the Peleg model is quite simple and does not require the determination of the moisture content corresponding to the monolayer in the molecular domain, it can be used as an alternative for cases in which some models, such as GAB, are not compatible with certain aspects of the phenomena of moisture sorption. The Peleg model was also suitable for fitting the isotherms of some foodstuffs, such as: gelatin, coffee, wheat bran, pear and pine nut (PELEG, 1993; PARK *et al.*, 2001; THYS *et al.*, 2010).

In Figure 3 is illustrated the experimental data corresponding to the adsorption isotherms of the persian clover and arrowleaf clover seeds, at the three temperatures analyzed, and the fit of the Peleg model.

The isotherms for the two seed species showed a sigmoid shape, as observed for other seeds (CHEN, 2003; WANI *et al.*, 2006). Thus, the four-parameter, double-power Peleg model was more appropriate and was subsequently used to determine the equilibrium moisture content for each of the materials, at the corresponding drying temperature.

Table 2. Results of fitting of the adsorption isotherms of persian clover and arrowleaf clover seeds

Models and parameters	Persian clover			Arrowleaf clover		
	40 ºC	45 ºC	50 ºC	40 ºC	45 ºC	50 ºC
BET (Eq. (1)) (up to a_w = 0.4)						
X_{mo} (kg kg^{-1}, d.b.)	0.041	0.041	0.036	0.066	0.062	0.061
C_B	6.07×10^{6}	1.39×10^{7}	6.54×10^{7}	2.50×10^{7}	3.51×10^{6}	8.89×10^{7}
R^2	0.998	0.998	0.999	0.997	0.999	0.998
RMSE	0.009	0.011	0.005	0.010	0.006	0.010
GAB (Eq. (2))						
X_{mo} (kg kg^{-1}, d.b.)	0.040	0.049	0.039	0.069	0.062	0.065
C_G	1.01×10^{7}	1.29×10^{8}	8.07×10^{44}	2.23×10^{7}	1.57×10^{7}	6.72×10^{6}
K_b	0.451	0.511	0.640	0.608	0.748	0.656
R^2	>0.999	>0.999	0.991	0.998	>0.999	>0.999
RMSE	0.002	0.005	0.003	0.015	0.008	0.004
Peleg (Eq. (3))						
k_1	0.065	0.059	0.053	0.102	0.096	0.094
k_2	0.039	0.075	0.067	1.105	0.205	0.109
n_1	0.079	0.027	0.074	0.099	0.107	0.098
n_2	4.482	5.231	4.186	20.150	5.740	3.996
R^2	0.998	>0.999	0.998	>0.999	0.998	0.998
RMSE	0.002	0.001	0.001	0.001	0.003	0.003
Oswin (Eq. (4))						
A	0.066	0.068	0.059	0.103	0.107	0.102
B	0.110	0.121	0.186	0.163	0.247	0.198
R^2	0.992	0.965	0.978	0.914	0.961	0.986
RMSE	0.003	0.006	0.005	0.015	0.012	0.007

A, B: thermodynamics constants of Eq. (4); C_B: thermodynamics constant of Eq. (1); C_G, k_b: thermodynamics constants of Eq. (2); k_1, k_2: thermodynamics constants of Eq. (3); n_1, n_2: exponents of Eq. (3); R^2: coefficient of determination; *RMSE*: root mean square error; *T*: temperature; X_e: equilibrium moisture content; X_{mo}: monolayer moisture content

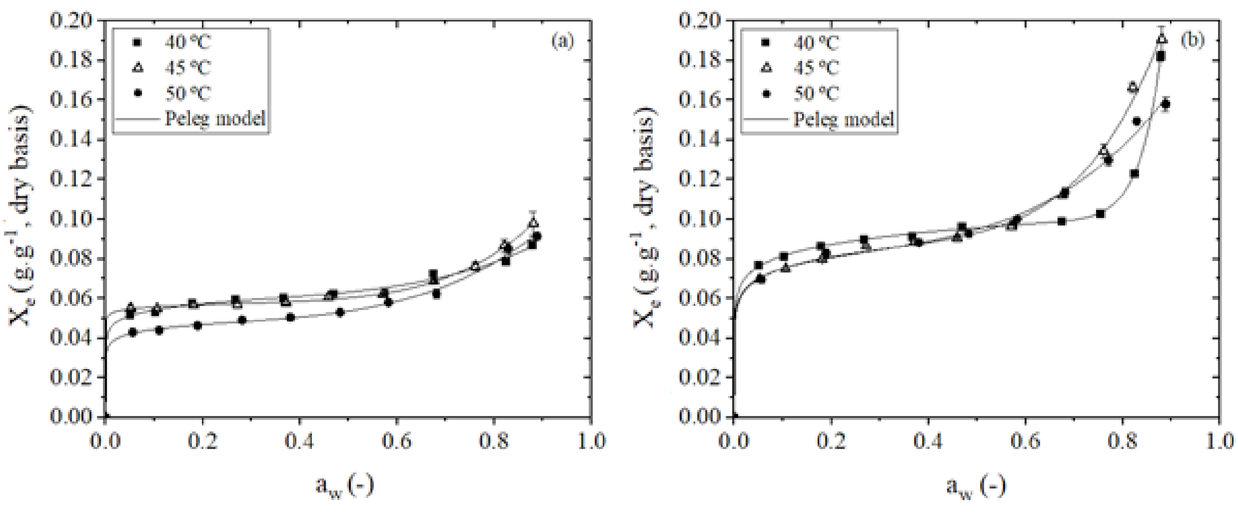

Figure 3. Experimental data and fit by the Peleg model for the adsorption isotherm of seeds, at different temperatures: (a) persian clover and, (b) arrowleaf clover

For the two seed species, we can observe the increase of the equilibrium moisture content with the water activity at constant temperature, that is a behavior also presented in isotherms of prickly pear seeds, watermelon seeds and nut seeds (WANI *et al*., 2006; THYS *et al*., 2010; HASSINI *et al*., 2015). The increase in temperature caused a decrease in the equilibrium moisture content for constant water activity. Similar result was also reported by other authors (CHEN, 2003; WANI *et al*., 2006; COSTA *et al*., 2015; ZEYMER *et al*., 2017), who indicate an increase of the solute solubility and the reduction of the attraction forces, making it difficult to retain water. This behavior is maintained until the isotherms intersection. After this time, the temperature no longer interferes with solubility and begins to change the material characteristics, leading to an increase in vapor pressure and, consequently, an increase in moisture content.

As for adsorption, we could observe that the arrowleaf clover seeds presented a higher moisture adsorption capacity, reaching up to approximately 20% (dry basis), in contrast to the persian clover seeds, which were able to absorb only about 10%. This difference is related to the physical characteristics of the two materials. The arrowleaf clover seeds have a more rugged surface (Figure 2) and a larger surface area in contact with the exterior, according to the results for this parameter (Table 1), in agreement with a larger monolayer region. These characteristics facilitate the moisture retention in solid inside the and lead to greater difficulty in the drying operation compared to the persian clover seeds. Furthermore, we could observe the approximation between the isotherms of 40 ºC and 45 ºC for the persian clover seeds and between 45 ºC and 50 ºC for the arrowleaf clover seeds, indicating a greater sensitivity to the temperature change for the last species.

Drying Kinetics

The drying kinetics of persian clover and arrowleaf clover seeds were determined by thin-layer drying experiments at air temperatures of 40, 45 and 50 °C, using a drying air velocity of 2 m s^{-1}. The initial moisture content values of the persian clover and arrowleaf clover seeds samples, after moisturized, were approximately of 28.11% and 42.10% (dry basis), respectively. This difference in moisture content values can be due to the arrowleaf clover presenting a greater capacity of moisture retention, which was verified by the adsorption isotherms. Through the experimental data it was possible to plot drying curves, showing the drying rate (R) as a function of the solid moisture content (X_m) (dry basis) and the moisture content ratio (X_R) as a function of the drying time. In Figure 4 is presented the drying rate *versus* seeds mean moisture content for the two species.

In Figure 4 is observed the existence of the constant rate and falling drying rate periods for the two seed species. Initially, the solids presented excessive initial moisture content, above their saturation moisture content (X_{sat}), so that at the beginning of the operation, evaporation and free

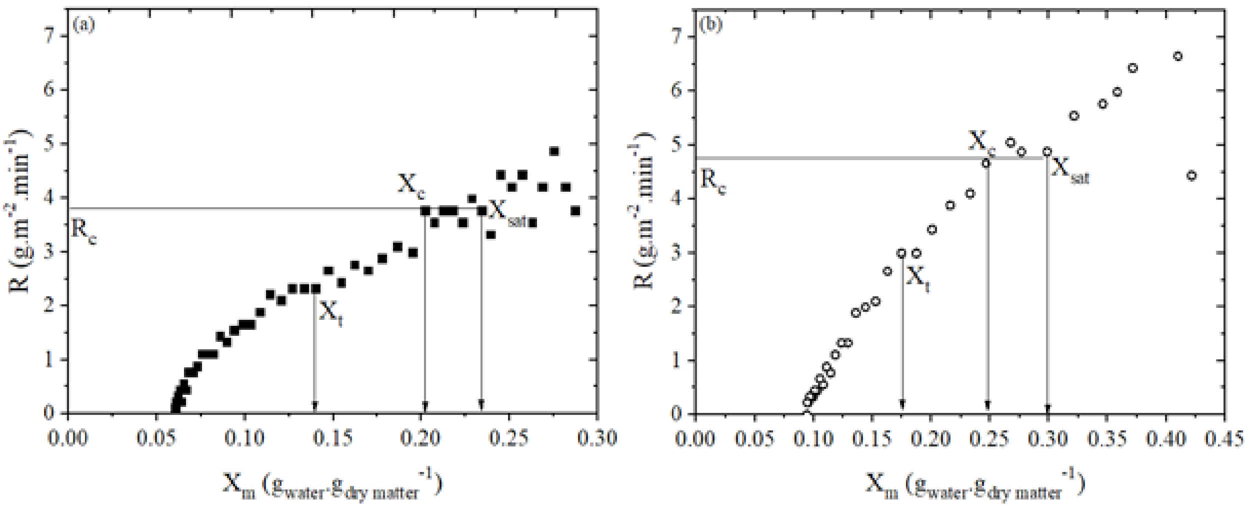

Figure 4. Drying rate *versus* mean humidity for seeds: (a) persian clover at 40 ºC and, (b) arrowleaf clover at 50 ºC

water drag occurred in the layers above the solid surface. After evaporation of the excess water, the evaporation of moisture on the solid surface began, with constant drying rate, until the reach of the critical moisture content (X_c). During this period the material is surrounded by a moisture film, which is withdrawn and replaced simultaneously by moisture migration from the solid interior to the surface (GEANKOPLIS, 1993; MUJUMDAR, 2014).

The critical moisture content values found for the persian clover and arrowleaf clover seeds were approximately of 0.20 and 0.25 $g_{water}\ g_{dry\ matter}^{-1}$, respectively, at the three temperatures analyzed (Figure 4). After reaching critical moisture content, the drying period at the falling rate began. This drying period was divided in two steps: the first, from X_c to X_t, which represents the moisture transport by liquid diffusion; and the second, from X_t to the drying end, corresponding to the gas diffusion process. Regarding the drying rate, we could verify that the constant rate (R_c) increased by more than 20% for the two seeds species, with each increase of 5 ºC. The increase in air temperature accelerated the removal of moisture from the seeds. Thus, both water evaporation from the seed surface and internal moisture transport by diffusion occurred more rapidly.

In addition, we could observe that the arrowleaf clover seeds presented a slower drying operation than the persian clover seeds, with lower drying rates and consuming more time. This result is due to the fact that arrowleaf clover seed has a higher moisture retention capacity than persian clover, which facilitated the entry of water during moisturized and contributed to the moisture removal from the material interior to become difficult as the operation progresses. This behavior proves that the temperature and the material characteristics are factors that strongly influence the drying kinetics, together with the air velocity, as reported by Uddin *et al*. (2016).

In Table 3 is presented a summary of the experimental data, showing the drying rate values and parameters related to the moisture contents in the periods mentioned previously and the final moisture content (X_F), as well as the critical time (t_c), transition time (t_t) and, the total drying time (t_T).

We can observe in Table 3 that, during the persian clover seeds drying, the constant rate step corresponded to around than 20% of the total drying time for all air temperatures. As for arrowleaf clover seeds, this period represented 33% of the total drying time at 40 °C, 29% at 45 °C and 24% at 50 °C. Thus, in all cases, the predominance of the falling rate period occurred. The preponderance of the falling rate period, or the total absence of the constant rate period, was also observed by other authors for grape seeds (ROBERTS *et al*., 2008), rapeseed (DUC *et al*., 2011), papaya seeds (MOCELIN *et al*., 2013) and pumpkin seeds (UDDIN *et al*., 2016).

Table 3. Drying parameters for persian clover and arrowleaf clover seeds in different temperatures

Parameter	Persian clover			Arrowleaf clover		
	40 ºC	45 ºC	50 ºC	40 ºC	45 ºC	50 ºC
X_{sat} ($g_{water}\ g_{dry\ matter}^{-1}$, d.b.)	0.23 ± 0.01	0.22 ± 0.01	0.23 ± 0.01	0.30 ± 0.01	0.29 ± 0.01	0.30 ± 0.01
X_c ($g_{water}\ g_{dry\ matter}^{-1}$, d.b.)	0.20 ± 0.01	0.19 ± 0.01	0.21 ± 0.01	0.25 ± 0.01	0.26 ± 0.01	0.25 ± 0.01
X_t ($g_{water}\ g_{dry\ matter}^{-1}$, d.b.)	0.14 ± 0.01	0.13 ± 0.01	0.12 ± 0.01	0.17 ± 0.01	0.18 ± 0.01	0.17 ± 0.01
X_F ($g_{water}\ g_{dry\ matter}^{-1}$, d.b.)	0.06 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.13 ± 0.01	0.12 ± 0.01	0.09 ± 0.01
R_c ($g\ m^{-2} min^{-1}$)	3.77 ± 0.03	4.69 ± 0.19	5.82 ± 0.03	3.11 ± 0.02	3.96 ± 0.45	4.77 ± 0.08
t_c (min)	38 ± 0.01	30 ± 0.01	15 ± 1.77	65 ± 3.54	50 ± 3.54	38 ± 0.01
t_t (min)	75 ± 0.01	60 ± 0.01	40 ± 1.77	115 ± 3.54	85 ± 0.01	60 ± 0.01
t_T (min)	195 ± 3.54	150 ± 0.01	105 ± 0.01	195 ± 0.01	170 ± 0.01	155 ± 0.01

Mean values ± standard deviation (in triplicate). d.b.: dry basis; R_c: constant drying rate; t_c: constant drying time; t_t: transition time; t_T: total time; X_c: critical moisture content; X_F: final moisture content; X_{sat}: saturation moisture content; X_t: transition moisture content

From the experimental data of moisture content (dry basis) X and the values of X_e obtained through the Peleg model, moisture content ratio (X_R) curves were plotted *versus* drying time for the two seed species. The Lewis, Page and Henderson-Pabis models were fitted to experimental data. In Figure 5 is represented the fit of models to the experimental data for the moisture ratio curve as a function of the drying time for each of the seed species. In Table 4 is shown the drying parameters obtained from the three models tested and their statistical parameters.

According to the results presented in Table 4, the equation that best described the drying operation for both species was the Page model. The best fit to the experimental data was confirmed by the highest values of R^2 (≥ 0.996). This result was also reinforced by the lower *RMSE* values, between 0.004 and 0.020, covering all the assays. The

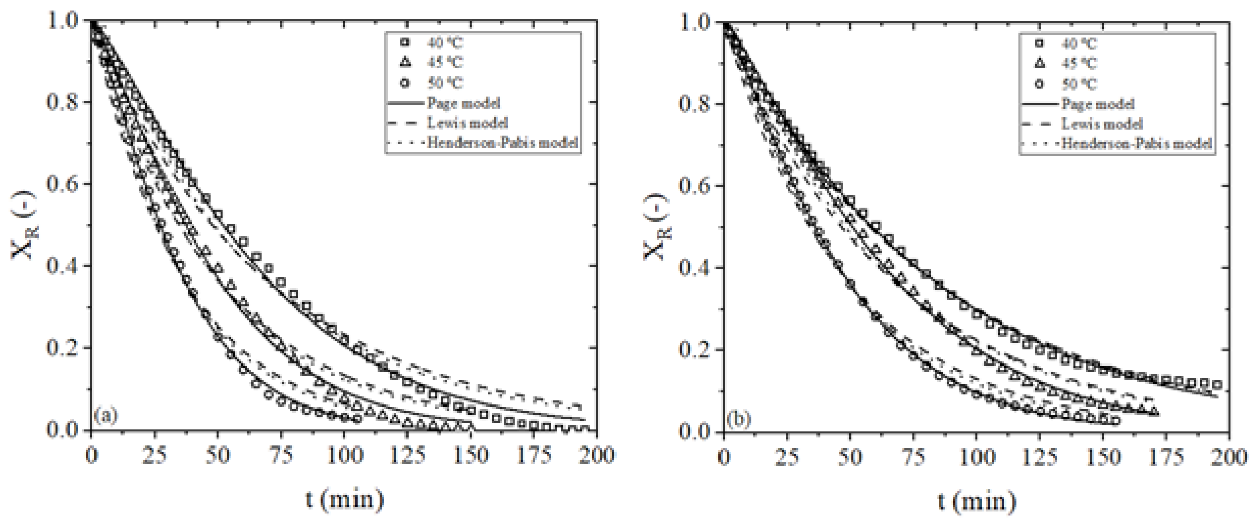

Figure 5. Lewis, Page and, Henderson-Pabis models fitted to experimental data of the ratio moisture *versus* drying time for: (a) persian clover seeds and, (b) arrowleaf clover seeds

Table 4. Drying parameters for Lewis, Page and, Henderson-Pabis models

Constants	Persian clover			Arrowleaf clover		
	40 ºC	45 ºC	50 ºC	40 ºC	45 ºC	50 ºC
Lewis (Eq. (5))						
K	0.014	0.020	0.027	0.012	0.015	0.020
R²	0.981	0.983	0.985	0.998	0.985	0.991
RMSE	0.046	0.043	0.038	0.014	0.034	0.031
Page (Eq. (6))						
K	0.005	0.008	0.012	0.010	0.005	0.010
N	1.254	1.239	1.234	1.050	1.231	1.194
R²	0.996	0.996	0.999	0.998	0.999	0.999
RMSE	0.020	0.020	0.012	0.011	0.010	0.004
Henderson-Pabis (Eq. (7))						
K	0.016	0.021	0.029	0.012	0.016	0.022
A	1.067	1.059	1.059	1.015	1.064	1.062
R²	0.987	0.987	0.990	0.998	0.991	0.995
RMSE	0.039	0.038	0.032	0.013	0.031	0.023

Page model was also suitable for drying kinetics of amaranth seeds (ABALONE *et al*., 2006) and rapeseed (DUC *et al*., 2011).

The results regarding the effective diffusivityare presented in Table 5, and its relation to the temperature is shown in Figure 6. A linear relationship between the effective moisture diffusivity and the air temperature was observed for persian clover and arrowleaf clover seeds, and it could be satisfactorily described by an Arrhenius-type equation. The coefficient of determination showed a higher temperature dependence for the persian clover seeds ($R^2 = 0.999$). Equations 10 and 11 represent the models of effective diffusivity as a function of temperature for the seeds of persian clover and arrowleaf clover seeds, respectively.

Table 5. Effective diffusivity for persian clover and arrowleaf clover seeds at differents. temperatures

T (ºC)	Persian clover	Arrowleaf clover
	Deff (m² s⁻¹)	*Deff* (m² s⁻¹)
40	3.61×10^{-11}	6.76×10^{-11}
45	4.99×10^{-11}	8.419×10^{-11}
50	6.81×10^{-11}	1.15×10^{-10}

Deff: effective diffusivity

$$D_{eff} = 2.84 \times 10^{-2} \exp\left(-\frac{6423.79}{T}\right) \quad (10)$$

$$D_{eff} = 1.87 \times 10^{-3} \exp\left(-\frac{5371.70}{T}\right) \quad (11)$$

The D_{eff} values are close to those presented by Doulia *et al*. (2000) for sunflower seeds and Clemente *et al*. (2014) for grape seeds, in the same temperature range. The results found for E_a were 53.41 kJ mol⁻¹ for persian clover seeds and 44.66 kJ mol⁻¹ for arrowleaf clover seeds, and they are within the range of values reported by other authors for other seeds, from 15 to 95 kJ mol⁻¹ (RAMALLO *et al*., 2001; CLEMENTE *et al*., 2014).

CONCLUSION

- The determination of the adsorption isotherms and the thin layer drying of the persian clover and arrowleaf clover seeds experiments allowed to determine the behavior of the solid-liquid sorption and the drying characteristics of these seeds.
- The Peleg model was more suitable for the determination of the equilibrium moisture content of the seed, due to the better R^2 and RMSE results. In addition, the arrowleaf clover presented a higher moisture adsorption capacity and a higher sensitivity to temperature than persian clover.
- The drying kinetics of both seeds showed

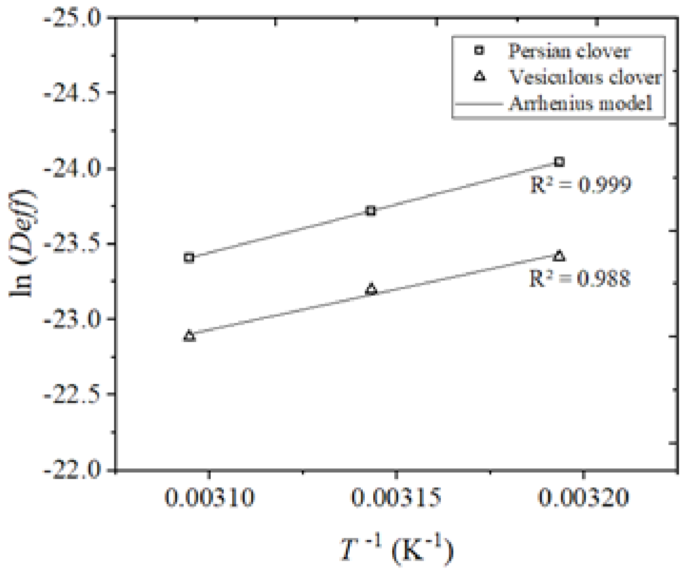

Figure 6. Arrhenius-type relationship between the effective diffusivity and temperature for persian clover and arrowleaf clover seeds

that these materials were composed by the periods of constant rate and falling rate, with a predominance of the falling rate. This result indicates that a diffusion phenomenon is the governing physical mechanism of moisture transfer in both seeds. The Page model was the most suitable to describe these characteristics.

- In addition, the influence of the drying temperature on the effective moisture diffusivity was described satisfactorily by an Arrhenius-type equation and the activation energy for moisture diffusion also was calculated, presenting values within the range reported in the literature for other seeds.

ACKNOWLEDGEMENTS

The authors thank CAPES (Coordination for the Improvement of Higher Education Personnel) and FAPERGS (Research Support Foundation of Rio Grande do Sul State) for the financial support. They also thank CEME-SUL/FURG (Electron Microscopy Center of South/Federal University of Rio Grande/RS/Brazil) for the scanning electron microscopy analysis and EMBRAPA Temperate Climate (Brazilian Agricultural Research Corporation) for seeds donation.

REFERENCES

AOAC. Official Methods of Analysis of the Association of Official Analytical Chemists, ed. 16, Association of Official Analytical Chemists: Washington, 1995.

ABALONE, R., GASTÓN, A., CASSINERA, A., LARA, M. A. Thin layer drying of amaranth seeds. **Biosystems Engineering**, v. 93, n. 2, p. 179-188, 2006.

BARONI, A.F., HUBINGER, M.D. Drying of onion: effects of pretreatment on moisture transport. **Drying Technology,** v. 16, n. 10, p. 2083-2094, 1998.

BEVILAQUA, G. A. P.; OLANDA, R. B. Sistema de produção de forragem e de sementes de trevo vesiculoso para a agricultura familiar. Pelotas, **Boletim de Pesquisa e Desenvolvimento/ Embrapa** Clima Temperado, 2011.

CHEN, C. Moisture sorption isotherms of pea seeds. **Journal of Food Engineering,** v. 58, n. 1, p. 45-51, 2003.

CLEMENTE, G., SANJUÁN, N., CÁRCEL, J.A., MULET, A. Influence of temperature, air velocity, and ultrasound application on drying kinetics of grape seeds. **Drying Technology,** v. 32, n. 1, p. 68-76, 2014.

COELHO, R. W., RODRIGUES, R. C., REIS, J. C. L. Rendimento de forragem e composição bromatológica de quatro leguminosas de estação fria. Pelotas. **Comunicado Técnico/Embrapa** Clima Temperado, 2002.

CREMASCO, M.A. Operações unitárias em sistemas particulados e fluidomecânicos. São Paulo: Blucher, 2012.

COSTA, L.M., RESENDE, O., OLIVEIRA, D.E.C., SOUSA, K.A. Isotermas e calor isostérico de sementes de *Buchenavia capitata* (Vahl) Eichler. **Revista Ciencia Agronômica,** v. 46, n. 3, p. 516-523, 2015.

DOULIA, D., TZIA, K., GEKAS, V. A knowledge base for the apparent mass diffusion coefficient (*Deff*) of foods. **International Journal of Food Properties,** v. 3, n. 1, p. 1-14, 2000.

DUC, L.A., HAN, J.W., KEUM, D.H. Thin layer drying characteristics of rapesed (*Brassica napus L.*). **Journal of Stored Products Research,** v. 47, n. 1, p. 32-38, 2011.

GEANKOPLIS, C. J. Transport processes and unit operations. Prentice-Hall: Englewood Cliffs, 1993.

HASSINI, L., BETTAIEB, E., DESMORIEUX, H., TORRES, S.S., TOUIL, A. Desorption isotherms and thermodynamic properties of prickly pear seeds. **Industrial. Crops and Products,** v. 67, p. 457-465, 2015.

HENDERSON, S.M., PABIS, S. Grain drying theory I: temperature effect on drying coefficient. **Journal of Agricultural Engineering Research,** v. 6, p. 169-174, 1961.

KAYA, A., AYDIN, O., DEMIRTAS, C., AKGÜN, M. An experimental study on the drying kinetics of quince. **Desalination,** v. 212, n. 1, p. 328-343, 2007.

KIRANOUDS, C.T., TSAMI, E., MAROULIS, Z.B., MARINOS-KOURIS, D. Drying kinetics of some fruits. **Drying Technology,** v. 15, n. 5, p. 1399-1418, 1997.

LEWIS, W.K. The rate of drying of solid materials. **The Journal of Industrial and Engineering Chemistry,** v. 13, n. 5, p. 427-432, 1921.

MOCELIN, B., OLIVEIRA JR., D.L., CHIELLE, D.P., TANABE, E.H., BERTUOL, D.A., SCHWAAB, M., MEILI, L. Mathematical modeling of thin layer drying of *Papaya* seeds in a tunnel dryer using particle swarm optimization method. **Particulate Science and Technology,** v. 32, n. 2, p. 123-130, 2013.

MONTE, M.L., SENNA, J., ARRIECHE, L.S., PINTO, L.A.A. Moisture sorption isotherms of chitosan-glycerol films: Termodynamic properties and microstruture. **Food Bioscience,** v. 22, p. 170-177, 2018.

MORAES, M.A., ROSA, G. S., PINTO, L.A.A. Moisture sorption isotherms and thermodynamics properties of apple fuji and garlic. **International Journal of Food Science and Technology,** v. 43, n. 10, p. 1824-1831, 2008.

MUJUMDAR, A.S. Handbook of industrial drying. New York: CRC Press, 2014.

PAGE, G.E. Factors influencing the maximum rates o fair drying shelled corn in thin layers. Purdue University: West Lafayette, 1949.

PARK, K.J., BIN, A., BROD, F.P.R. Obtenção das isotermas de sorção e modelagem matemática para a pêra Bartlett (*Pyrus sp.*) com e sem desidratação osmótica. **Ciência e Tecnologia de Alimentos,** v. 21, n. 1, p. 73-77, 2001.

PEÇANHA, R. Sistemas particulados: operações unitárias envolvendo partículas e fluidos. Rio de Janeiro: Elsevier, 2014.

PELEG, M. Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. **Journal of Food Process Engineering,** v. 16, p. 21-37, 1993.

RAO, M.A., RIZVI, S.S.H., DATTA, A.K. Engineering properties of foods. New York: Marcel Dekker Inc., 2005.

RAMALLO, L.A., POKOLENKO, J.J., BALMACEDA, G.Z., SCHMALKO, M.E. Moisture diffusivity, shrinkage, and apparent density variation during drying of leaves at high temperatures. **International Journal of Food Properties,** v. 4, n. 1, p. 163-170, 2001.

REIS, J. C. L. R. Origem e características de novos trevos adaptados ao Sul do Brasil. Pelotas. **Documento/Embrapa** Clima Temperado, 2007.

ROBERTS, J.S., KIDD, D.R., ZAKOUR, O.P. Drying kinetics of grape seeds. **Journal of Food Engineering,** v. 89, n. 4, p. 460-465, 2008.

TASIRIN, S.M., PUSPASARI, I., LUN, A.W., CHAI, P.V., LEE, W.T. Drying of kaffir lime leaves in a fluidized bed dryer with inert particles: kinetics and quality determination. **Industrial Crops and Products,** v. 61, p. 193-201, 2014.

THYS, R.C.S., NOREÑA, C.P.Z., MARCZAK, L.D.F., AIRES, A.G., CLADERA-OLIVERA, F. Adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) starch and thermodynamic analysis. **Journal.of Food Engineering,** v. 100, n. 3, p. 468-473, 2010.

UDDIN, Z., SUPPAKUL, P., BOOSUPTHIP, W. Effect of air temperature and velocity on moisture diffusivity in relation to physical and sensory quality of dried pumpkin seeds. **Drying Technology,** v. 34, n. 12, p. 1423-1433, 2016.

WANI, A.A., SOGI, D.S., SHIVHARE, U.S., AHMED, I., KAUR, D. Moisture adsorption isotherms of watermelon seed and kernels. **Drying Technology,** v. 24, n. 1, p. 99-104, 2006.

WILLMOTT, C.J., ACKLESON, S.G., DAVIS, R.E., FEDDEMA, J.J., KLINK, K.M., LEGATES, D.R., O'DONNELL, J., ROWE, C.M. Statistics for the evaluation of model performance. **Journal of Geophysical Research,** v. 90, n. 5, p. 8995-9005, 1985.

ZEYMER, J.S., CORRÊA, P.C., OLIVEIRA, G.H.H., BAPTESTINI, F.M., FREITAS, R.C.P. Desorption isotherms of *Lactuca sativa* seeds. **Revista Brasileira de Engenharia Agricola e Ambiental,** v.21, n. 8, p. 568-572, 2017.

ZOMORODIAN, A., KAVOOSI, Z., MOMENZADEH, L. Determination of EMC isotherms and appropriate mathematical models for canola. **Food Bioproducts Processing,** v. 89, n. 4, p. 407-413, 2011.