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Adsorption isotherms and thermodynamic properties of *Carthamus tinctorius* L. seeds[1]

Isotermas de adsorção e propriedades termodinâmicas de sementes de *Carthamus tinctorius* L.

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HIGHLIGHTS:

The Chung-Pfost model showed the best fit to describe the phenomenon of adsorption of safflower seeds.
For constant water activity, the values of the equilibrium moisture content decreased with increasing temperature.
The thermodynamic properties were influenced by the moisture content of the seeds.

ABSTRACT: Safflower is a crop of high economic value with high oil concentration in its seeds and great industrial versatility, besides various benefits to human health. As with other agricultural crops, it is common to store safflower to make it available in different periods of the year and, due to its hygroscopic characteristics, studies evaluating the effect of temperature and air relative humidity on its moisture content become relevant. Thus, the objective of the present study was to determine the water adsorption isotherms of safflower seeds and analyze their thermodynamic properties. Moisture contents of 6.5, 6.9, 7.3, 7.7, 8.3 and 9.1% (dry basis) were obtained by adsorption under controlled conditions of temperature (30 °C) and relative air humidity (90%). The adsorption isotherms were obtained by the indirect static method at different temperatures (10, 20, 30 and 40 °C). As temperature increased, for the same moisture content, there was an increase in water activity and, for constant water activity, the values of equilibrium moisture content decreased with increasing temperature. Chung-Pfost model showed the best fit to describe the phenomenon of hygroscopicity of safflower seeds. The thermodynamic properties were influenced by the moisture content of the seeds, reducing the energy necessary for water absorption in the product with the increase in adsorption, and the enthalpy-entropy theory was controlled by enthalpy.

Key words: equilibrium moisture content, hygroscopicity, oilseed

RESUMO: O cártamo é uma cultura de elevado valor econômico que possui alto teor de óleo nos grãos e grande versatilidade industrial com vários benefícios à saúde humana. Assim, como outras culturas agrícolas é comum o armazenamento do cártamo para disponibilização em diferentes épocas do ano, e devido suas características higroscópicas tornam-se relevantes estudos que avaliem o efeito da temperatura e da umidade relativa do ar no teor de água. Deste modo, objetivou-se neste estudo determinar as isotermas de adsorção de água das sementes de cártamo e analisar as propriedades termodinâmicas. Os teores de água de 6,5; 6,9; 7,3; 7,7; 8,3 e 9,1% (base seca) foram obtidos por adsorção em condições controladas de temperatura (30 °C) e umidade relativa do ar (90%). As isotermas de adsorção foram obtidas pelo método estático indireto em diferentes temperaturas (10, 20, 30 e 40 °C). Com o aumento da temperatura, para um mesmo teor de água, tem-se elevação da atividade de água e, para uma atividade de água constante, os valores do teor de água de equilíbrio diminuíram com o aumento da temperatura. O modelo de Chung-Pfost apresentou o melhor ajuste para descrever o fenômeno de higroscopicidade das sementes de cártamo. As propriedades termodinâmicas foram influenciadas pelo teor de água das sementes, reduzindo a energia necessária para a absorção de água no produto com o aumento da adsorção, sendo a teoria da compensação entalpia-entropia controlada pela entalpia.

Palavras-chave: teor de água de equilíbrio, higroscopicidade, oleaginosa

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Introduction

Safflower (*Carthamus tinctorius* L.) is a species cultivated for more than two millennia and has lately been commercially exploited in all continents. This crop is an alternative for oil production, with 32 to 40% oil concentration, for use in human food and industry for various purposes, besides having high drought tolerance and adaptability to different soil conditions (Bonamigo et al., 2013).

Due to the hygroscopic characteristics, the seeds tend to remain in balance with the temperature and relative humidity of the air, so they have a different behavior in the sorption isotherms (Isquierdo et al., 2020a). Lipid-rich seeds have lower moisture contents in comparison to starchy grains when stored under similar environmental conditions, because they adsorb less water, for being hydrophobic (Brooker et al., 1992). This characteristic is important to ensure and assist in the maintenance of seed quality during storage.

Mathematical models help predict the behavior during storage, using sorption isotherms, as they report the moisture content of the product under a given environmental condition with no need for performing costly and time-consuming tests. In addition, together with the weather forecast, it is possible to predict in a long period of time what may occur with the stored seeds, supporting the decision making of the professional in charge (Corrêa et al., 2016). The sorption isotherms and the other thermodynamic properties have been studied by several researchers (Goneli et al., 2016; Resende et al., 2017; Siqueira et al., 2018; Fonseca et al., 2020).

In view of the above, the objective of this study was to determine the water adsorption isotherms of safflower seeds and analyze their thermodynamic properties through the integral isosteric heat, differential entropy and Gibbs free energy for the studied conditions.

Material and Methods

The study was conducted in the Laboratory of Postharvest of Plant Products of the Instituto Federal de Educação, Ciência e Tecnologia Goiano - Rio Verde Campus, located in the municipality of Rio Verde, GO, Brazil (17° 80' S, 50° 90' W and altitude of 753 m). Safflower seeds provided by the California Oils Corporation company were used in the study. Their initial moisture content, equal to 6.5% (dry basis, d.b.), was determined by the oven method at 105 ± 3 °C for 24 hours, in two replicates (BRASIL, 2009).

The seeds were re-moistened in a B.O.D. (Box Organism Development) chamber with temperature of 30 °C and 90% relative air humidity until reaching moisture contents of 6.5, 6.9, 7.3, 7.7, 8.3 and 9.1% (d.b.).

The sorption isotherms of safflower seeds were determined using the indirect static method, and their water activity (a_w) was determined with the HygroPalm Aw1 device. For each moisture content, three samples of approximately 28.5 g were used, which were individually put in the device's container and placed in B.O.D. chamber regulated at temperatures of 10, 20, 30 and 40 °C.

The nonlinear regression models frequently used to represent the hygroscopicity of agricultural products were fitted to the experimental data, and their equations are presented in Table 1.

Table 1. Regression models used to predict the phenomenon of hygroscopicity of plant products

Model	Model designation	
$Xe = a - b \ln[-(T + c) \ln(a_w)]$	Chung-Pfost	(1)
$Xe = \exp[a - (b\,T) + (c\,a_w)]$	Copace	(2)
$Xe = (a\,b\,c\,a_w)/[(1 - c\,a_w)(1 - c\,a_w + b\,c\,a_w)]$	GAB	(3)
$Xe = [\exp(a - b\,T)/- \ln(a_w)]^{1/c}$	Modified Halsey	(4)
$Xe = a\,(a_w^{b/Tc})$	Sabbah	(5)
$Xe = \exp\{a - (b\,T) + [c \exp(a_w)]\}$	Sigma Copace	(6)
$Xe^* = (a + b\,T)/[a_w/(1 - a_w)]^{1/c}$	Modified Oswin	(7)
$Xe = [\ln(1 - a_w)/(a\,(T^b))]^{1/c}$	Cavalcanti Mata	(8)
$Xe = [\ln(1 - a_w)/(-a\,(T + b))]^{1/c}$	Modified Henderson	(9)
$Xe = [\ln(1 - a_w)/(-a\,(T + 273.16))]^{1/b}$	Henderson	(10)
$Xe = [1/[(1 - a_w)(1/a\,b + ((a - 1)/a\,b))]]$	BET	(11)

Xe - Equilibrium moisture content, % d.b.; a_w - Water activity, decimal; T - Temperature, °C; a, b, c - Coefficients that vary according to the product

Fitting of the nonlinear regression models was performed by the Gauss-Newton method. Model selection was carried out considering the significance of the regression coefficient by the t-test at $p \leq 0.01$, the magnitude of the coefficient of determination (R^2), the values of mean relative error (P) and mean estimated error (SE), Chi-square test (χ^2), and the behavior of the residual distribution. Mean relative and estimated errors and Chi-square test were calculated for each mathematical model using the following expressions, respectively:

$$P = \frac{100}{n} \sum \frac{\left|Y - \hat{Y}\right|}{Y} \tag{12}$$

$$SE = \sqrt{\frac{\sum (Y - \hat{Y})^2}{DF}} \tag{13}$$

$$\chi^2 = \sum \frac{\left|Y - \hat{Y}\right|^2}{DF} \tag{14}$$

where:

Y - experimental value;

Y - value estimated by the model;

n - number of experimental observations; and,

DF - degrees of freedom of the model (number of observations minus the number of parameters of the model).

The latent heat of vaporization of the water in the product (L) was calculated for each condition of hygroscopic equilibrium moisture content of the seeds and each temperature studied. For this, Eq. 17 was used to quantify the partial vapor pressure contained in porous systems (Othmer & Brown, 1940).

$$\mathrm{Ln}(Pv) = \frac{L}{L'} \mathrm{Ln}(Pvs) + C \tag{15}$$

where:

$$Pv = a_w Pvs \quad (16)$$

$$Pv = 0.61078\ 10^{\left(\frac{7.5\,T}{273.3+T}\right)} \quad (17)$$

$$L' = 2502.2 - 2.39T \quad (18)$$

where:

Pvs - saturation vapor pressure of free water, for a certain equilibrium temperature, T;

Pv - vapor pressure of free water, for determination of the equilibrium temperature, T;

L - latent heat of vaporization of the water contained in the product, kJ kg^{-1};

L' - latent heat of vaporization of free water, at equilibrium temperature, kJ kg^{-1}; and,

C - constant of integration.

The equation for water vaporization enthalpy presented by Rodrigues-Arias (Eq. 19) (Brooker et al., 1992) was fitted to the values of the L/L' ratio (Eq. 15), including the parameter "m" to improve the estimates of L/L' (Corrêa et al., 1998).

$$\frac{L}{L'} - 1 = a\exp\left(-b\ Xe^m\right) \quad (19)$$

where:

a, b, m - coefficients that depend on the product.

To quantify the latent heat of vaporization of the water contained in the seeds, for each temperature studied, Eqs. 19 and 20 were combined, which led to the following expression (Corrêa et al., 1998):

$$L = \left(2502.2 - 2.39T\right)\left[1 + a\exp\left(-b\ Xe^m\right)\right] \quad (20)$$

The thermodynamic parameters differential enthalpy, differential entropy, enthalpy-entropy relationship and Gibbs free energy, involved in the water adsorption process in safflower seeds, were calculated using Eqs. 21, 22, 23 and 24, respectively (Madamba et al., 1996; Nkolo Meze'e et al., 2008).

$$\ln\left(a_w\right) = \frac{\Delta h_{st}}{RT_a} - \frac{\Delta S}{R} \quad (21)$$

$$\Delta S = \frac{\Delta h_{st} - \Delta G}{T_a} \quad (22)$$

$$\Delta h_{st} = T_B\left(\Delta S\right) + \Delta G_B \quad (23)$$

$$\Delta G = R\ T_a \ln\left(a_w\right) \quad (24)$$

where:

Δh_{st} - differential enthalpy, kJ kg^{-1};

R - universal gas constant (8.314 kJ kmol^{-1} K^{-1}), equal to 0.4619 kJ kg^{-1} K^{-1} for water vapor;

T_a - absolute temperature, K;

ΔS - differential entropy of sorption, kJ kg^{-1} K^{-1};

T_B - isokinetic temperature, K;

ΔG_B - Gibbs free energy at isokinetic temperature, kJ kg^{-1}; and,

ΔG - Gibbs free energy, kJ kg^{-1}.

To validate the existence of chemical compensation, or enthalpy-entropy compensation theory, Krug test was applied to compare the isokinetic temperature (T_B) with the harmonic mean temperature (T_{hm}), whose approximate confidence interval (1-α; 100%), for the isokinetic temperature, was calculated according to Eqs. 25-28 (Krug et al., 1976a; 1976b).

$$T_{hm} = \frac{n}{\sum\left(\frac{1}{T}\right)} \quad (25)$$

$$T_b = \hat{T}_b \pm t_{m-2,\frac{\alpha}{2}}\sqrt{Var\ (T_b)} \quad (26)$$

where:

$$\hat{T}_b = \frac{\sum\left(\Delta h_{st} - \overline{\Delta h_{st}}\right)\left(\Delta S - \overline{\Delta S}\right)}{\sum\left(\Delta S - \overline{\Delta S}\right)^2} \quad (27)$$

$$Var(T_b) = \frac{\sum\left(\Delta h_{st}\,\overline{\Delta G_B} - \hat{T}_B \Delta S\right)^2}{\left(m-2\right)\left(\Delta S - \overline{\Delta S}\right)^2} \quad (28)$$

where:

n - number of temperatures used;

m - number of enthalpy-entropy data pairs;

Δh_{st} - average enthalpy, kJ kg^{-1};

Δs - average entropy, kJ kg^{-1} K^{-1};

ΔG_B - Gibbs free energy at the isokinetic temperature, kg kJ^{-1};

T_b - isokinetic temperature, K;

T_{hm} - harmonic mean temperature, K;

T_B - calculated isokinetic temperature, K;

t_{m-2} - tabulated value of Student's t; and,

α - approximate confidence interval, 95%.

Results and Discussion

There was increase in the water activity of safflower seeds as a function of the increase in air temperature and in their moisture content (Table 2), corroborating the results obtained by Zeymer et al. (2019), who evaluated the adsorption isotherms of paddy rice (*Oryza sativa* L.) grains for different air conditions.

GAB was the only model whose parameters were not all significant by t-test (Table 3). The Chung-Pfost, Copace, Modified Halsey, Modified Oswin, Sigma Copace and Modified Henderson models had coefficients of determination (R^2) greater than 99%, with the highest value (99.45%) for the Chung-Pfost model. It must be emphasized that the coefficient

Table 2. Average values of water activity in safflower seeds (decimal), obtained by the adsorption process, as a function of air temperature and moisture content

Moisture content (% d.b.)	Temperature (°C)			
	10	20	30	40
7.21	0.333	-	-	-
7.34	-	0.378	-	-
7.31	-	-	0.400	-
7.25	-	-	-	0.422
9.63	0.433	-	-	-
9.62	-	0.497	-	-
9.67	-	-	0.521	-
9.49	-	-	-	0.538
11.93	-	-	-	0.622
12.06	-	0.573	-	-
12.07	-	-	0.611	-
12.19	0.527	-	-	-
12.99	0.558	-	-	-
13.29	-	0.620	-	-
13.31	-	-	0.650	-
13.03	-	-	-	0.669

Table 3. Parameters of the adsorption isotherm models fitted to the experimental data of safflower seeds with their respective coefficients of determination (R^2), mean estimated errors (SE) and mean relative errors (P), Chi-square (χ^2) and trend of residual distribution

Models	Parameters	SE (decimal)	P (%)	χ^2 (decimal)	R^2 (%)	Residual distribution
Chung-Pfost	a = 23.1706** b = 3.6272** c = 117.0422**	0.069	0.677	0.0047	99.45	R
Copace	a = 1.1790** b = 0.0032** c = 1.560965**	0.088	0.885	0.0077	99.09	R
GAB	a = 3.659** b = -18.2981^{ns} c = 0.8135**	0.292	2.992	0.0855	89.96	B
Modified Halsey	a = 3.887411** b = 0.006902** c = 2.16336**	0.083	0.749	0.0070	99.18	R
Sabbah	a = 15.42607** b = 0.93362** c = 0.07015**	0.132	1.291	0.0175	97.95	R
Sigma Copace	a = 0.564856** b = 0.003199** c = 0.84816**	0.077	0.763	0.0060	99.25	R
Modified Oswin	a = 7.105151** b = -0.021172** c = 2.737047**	0.081	0.784	0.0066	99.22	R
Cavalcanti Mata	a = -0.017103** b = 0.1225** c = 1.769402**	0.103	0.997	0.0105	98.76	R
Modified Henderson	a = 0.0001** b = 148.8543** c = 1.7671**	0.092	0.936	0.0084	99.02	R
Henderson	a = 0.000081** b = 1.789511**	0.152	1.590	0.0230	97.18	R
BET	a = 52.29137** b = 0.34238**	0.776	7.190	0.6018	25.96	B

R - Random; B - Biased; ns, ** - Not significant and significant at $p \leq 0.01$ by t-test, respectively

of determination should not be used as the single and main statistical criterion for decision; instead, it is indicated as auxiliary in the decision making regarding the model to be used to represent the adsorption phenomenon.

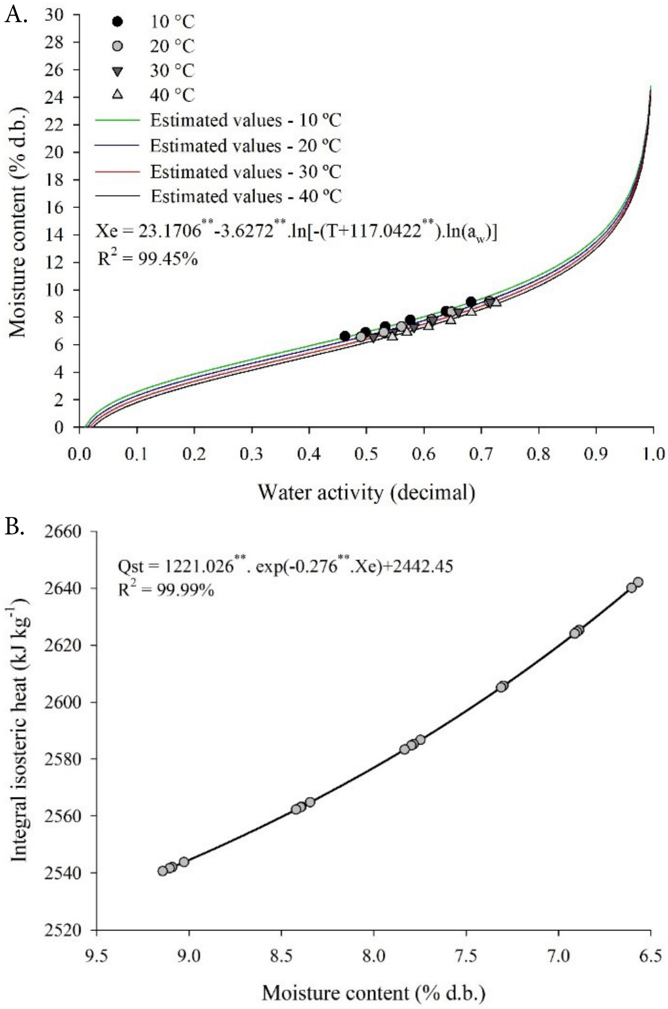
Among all the models analyzed, Chung-Pfost had the lowest values of mean estimated error (SE) and Chi-square (χ^2). The capacity of a model to adequately represent a process is inversely proportional to the values of its parameters, that is, the lower the values, the better the fit of the model in relation to the experimental data (Siqueira et al., 2013).

Regarding the mean relative error (P), the Chung-Pfost model also had the lowest value. All models analyzed showed mean relative errors lower than 10%, which according to Mohapatra & Rao (2005) is a reference value for using the model to represent the phenomenon in question.

Regarding the residual distribution (Table 3), only GAB and BET models showed biased distribution, while the others exhibited random distribution, indicating adequate fit to the experimental data.

Based on the statistical criteria adopted, all models showed good fit, but the Chung-Pfost model had more satisfactory results because, except for the mean relative error, all the others are complementary. Thus, this model was selected to represent the phenomenon of adsorption of safflower seeds.

By analyzing the isotherms (Figure 1A), it was found that, with the increase in temperature, for the same moisture content, water activity is increased. In addition, for a constant water activity, the values of the equilibrium moisture content



** - Significant at $p \leq 0.01$ by t-test

Figure 1. (A) Experimental values of equilibrium moisture content and adsorption isotherms estimated by the Chung-Pfost model, as a function of the water activity for four air temperatures and (B) experimental and estimated values of integral isosteric heat of adsorption as a function of the equilibrium moisture content for safflower seeds

decreased as the temperature increased, following the same trend observed in most agricultural products.

Several authors studying the hygroscopicity of seeds have also observed better fit to the experimental data with the Chung-Pfost model, such as Oliveira et al. (2013) for cotton (*Gossypium hirsutum* L.) seeds, Corrêa et al. (2016) for beet (*Beta vulgaris* L.) seeds, Ullmann et al. (2016) for sweet sorghum (*Sorghum bicolor* (L.) Moench) grains, Siqueira et al. (2018) for niger (*Guizotia abyssinica* Cass.) seeds, Fonseca et al. (2020) for sorghum (*Sorghum bicolor* (L.) Moench) grains and Isquierdo et al. (2020b) for passion fruit (*Passiflora alata* Curtis) seeds.

The increase in the equilibrium moisture content led to a reduction in the energy needed for water adsorption to occur in the product (Figure 1B), demonstrating a relationship of dependence between the integral isosteric heat and the moisture content of safflower seeds.

The estimated values of isosteric heat of safflower seeds ranged from 2,642.08 to 2,540.64 kJ kg^{-1} for the respective moisture contents between 6.57 and 9.14% (d.b.). It can be noted that, with the increase in moisture content, the value of isosteric heat tends to decrease. This occurs because the adsorption heat is a measure of the energy released in the sorption of water in the product (Rizvi, 1995), being considered an indication of the intermolecular forces of attraction between the sorption sites and the water vapor (Wang & Brennan, 1991), so the higher the moisture content of the product, the lower the adsorption heat due to the lower number of bonds between the sorption sites.

Oliveira et al. (2017), studying the isosteric heat of sucupira-branca (*Pterodon emarginatus* Vogel) fruits, observed similar behavior for the integral isosteric heat, which ranged from 3,477.54 to 15,375.89 kJ kg^{-1} within the moisture content range from 10.4 to 4.7% (d.b.), respectively. Also in Figure 1B, it is possible to note that the regression equation can be used to estimate the integral isosteric heat of adsorption for safflower seeds, as it has a high coefficient of determination (R^2).

The increase in moisture content leads to a reduction in the L/L' ratio, and the magnitudes are close to 1.0 for the highest values of moisture content in safflower seeds (Table 4). The same behavior has also been observed by several researchers, such as Corrêa et al. (1998), Oliveira et al. (2014a) and Resende et al. (2017), evaluating the latent heat of water vaporization of popcorn (*Zea mays* L.) seeds, 'tucumã-de-Goiás' (*Astrocaryum huaimi* Mart.) seeds and baru (*Dipteryx alata* Vogel) fruits, respectively.

Table 4. Equilibrium moisture content (Xe) of safflower seeds and latent heat of vaporization of the water contained in the product or latent heat of vaporization of free water (L/L')

Xe (% d.b.)	L/L'	Xe (% d.b.)	L/L'
6.57	1.0816	7.8300	1.0576
6.60	1.0808	8.3400	1.0500
6.89	1.0747	8.3900	1.0494
6.90	1.0745	8.4000	1.0493
6.91	1.0742	8.4200	1.0449
7.30	1.0667	9.0300	1.0414
7.31	1.0665	9.0900	1.0407
7.75	1.0589	9.1000	1.0405
7.78	1.0583	9.1400	1.0401
7.80	1.0582		

The latent heat of vaporization ranged from 2,680.97 to 2,502.36 kJ kg^{-1} for moisture contents between 6.57 and 9.14% (d.b.), and with the increase in the equilibrium moisture content there was a reduction in the energy necessary for water evaporation in safflower seeds (Figure 2A). It can also be noted that, as the temperature increases, for the same equilibrium moisture content, there is a reduction in the values of the latent heat of vaporization of the product. This property is mainly influenced by moisture content and temperature (Brooker et al., 1992).

Studies with passion fruit seeds (Isquierdo et al., 2020b) obtained water's latent heat of vaporization from 3,937.11 to 2,493.77 to kJ kg^{-1} with moisture contents from 2.17 to 13.69% (d.b.). For jatropha seeds (Oliveira et al., 2014b), the values varied from 2,762.92 to 2,495.56 kJ kg^{-1} for moisture contents ranging from 5.61 to 13.42% (d.b.). This variation in the values obtained for the different agricultural products may be related to their structure and chemical composition, besides the influence of air temperature and moisture content.

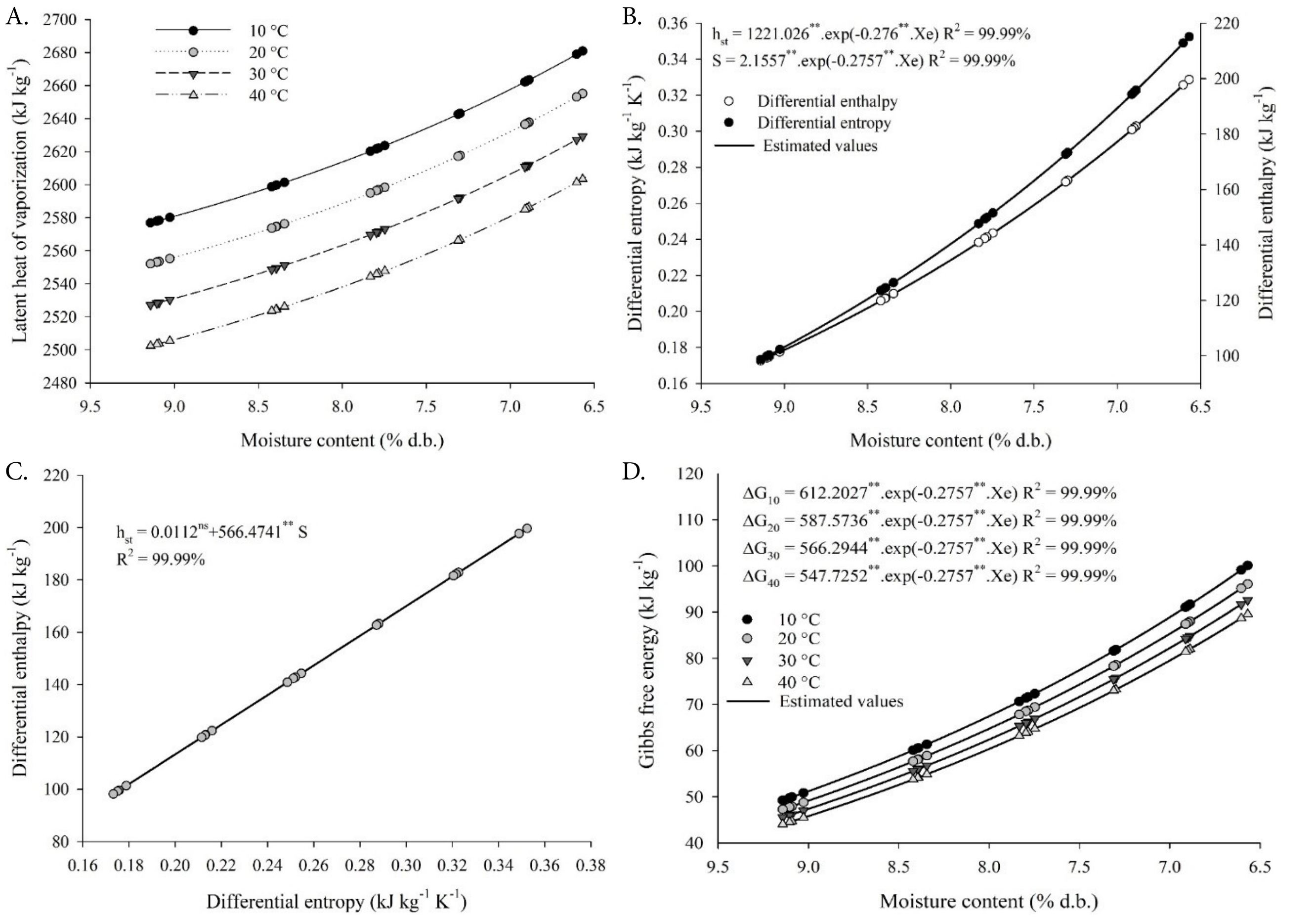
The differential entropy (S) and differential enthalpy (h_{st}) of adsorption showed similar trends for the moisture content range studied (Figure 2B). The elevation of moisture content promotes marked reduction in the differential entropy and enthalpy. The differential entropy of a material is proportional to the number of sorption sites available at a specific energy level (Madamba et al., 1996), indicating a state of mobility of water molecules in the product. In turn, differential enthalpy provides information on the process of interaction between water molecules and the sorbent.

The equations used are satisfactory to describe the differential enthalpy and entropy of the sorption of the safflower seeds, as they have highly significant parameters and high values of coefficient of determination.

The enthalpy-entropy relationship in the adsorption process of safflower seeds was adequately described by a linear regression, showing a high coefficient of determination (99.99%) (Figure 2C).

Due to the linearity between differential enthalpy and differential entropy, the enthalpy-entropy compensation theory can be considered valid for the phenomenon of adsorption in safflower seeds. Hence, the isokinetic temperature was compared with the harmonic mean temperature of the temperature range used in this study. The isokinetic temperature (T_B) was 566.47 K and the isokinetic temperature range was from 566.57 to 566.37 K. The calculated harmonic mean temperature (T_{hm}) was 292.35 K.

In the linear enthalpy-entropy compensation, when $T_B > T_{hm}$, the process is controlled by enthalpy; otherwise ($T_B < T_{hm}$), the process is controlled by entropy (Ryde, 2014). It can be observed that the harmonic mean had values lower than the range of isokinetic temperature, showing that the process is controlled by enthalpy. These results are consistent with those found by several researchers who have successfully applied the isokinetic theory to the sorption of the most diverse products (Hassini et al., 2015; Goneli et al., 2016; Oliveira et al., 2017; Resende et al., 2017; Silva et al., 2018; Campos et al., 2019).



ns, ** - Not significant and significant at $p \leq 0.01$ by t-test, respectively

Figure 2. (A) Experimental and estimated values of latent heat of water vaporization as a function of the equilibrium moisture content, (B) observed and estimated values of differential enthalpy and entropy of sorption, (C) enthalpy-entropy relationship for the water adsorption process and (D) Gibbs free energy as a function of the moisture content of safflower seeds for four air temperatures

Changes in Gibbs free energy during the water exchange between the product and the surrounding medium characterize the energy required to transfer water molecules from the state of vapor to a solid surface (sorbent) or vice versa (Nkolo Meze'e et al., 2008). Thus, with the increase in the moisture content of safflower seeds, there is a reduction in the amount of energy from the medium required for adsorption to occur (Figure 2D). In addition, the calculated values of Gibbs free energy increase with the reduction of temperature.

These equations can be satisfactorily used to predict Gibbs free energy values within the moisture content range between 6.57 and 9.14% (d.b.), due to the high values of the coefficient of determination (R^2) and high significance of its parameters.

Conclusions

1. Among the nonlinear regression models applied to the experimental data, the Chung-Pfost model showed the best fit and was selected to describe the adsorption isotherms of safflower seeds.

2. The thermodynamic properties were influenced by the moisture content of the seeds, reducing the energy needed for water adsorption to occur in the product, with the increase of adsorption, and enthalpy-entropy compensation theory was controlled by enthalpy.

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