

# Water adsorption isotherms and thermodynamic properties of germinated pumpkin seeds flours<sup>1</sup>

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**ABSTRACT** - The use of residues resulting from the processing of agricultural products is an widely studied topic, which is justified by the need to reduce costs and by the search for productive sustainability, which has as one of its principles the full use production, reducing waste and therefore increasing the amount of products extracted per unit of area. Residual seeds, resulting from the production of fruit pulps, are rich in nutrients and with the potential to be further improved by the application of germination, increasing the protein content and the content of bioactive compounds. However, in the germination process, the product acquires a high water content, requiring immediate drying and control of the water adsorption kinetics after dehydration. Therefore, the objective of this study was to determine the water adsorption isotherms of germinated seeds flours from pumpkins of three varieties at temperatures of 15, 25 and 35 °C, to obtain the most appropriate mathematical model to describe the hygroscopic behavior and to determine the thermodynamic properties of water adsorption, through the values of the integral isosteric heat, differential entropy, differential enthalpy and Gibbs free energy for the studied conditions. The GAB and Peleg models fit the experimental data well. With increasing water activity, there was a reduction in isosteric heat and entropy. The enthalpy-entropy compensation theory was confirmed. Gibbs free energy was negative for all temperatures, increasing with increasing equilibrium water content, demonstrating that it is a spontaneous process.

**Key words:** Integral isosteric heat. Cucurbits. Hygroscopic balance. Differential entropy. Gibbs free energy.

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## INTRODUCTION

Pumpkin is a fruit of the Cucurbitaceae family, rich in polysaccharides, vitamins, mineral salts and of expressive importance and production in Brazil: *Cucurbita maxima*, *Cucurbita moschata* and *Cucurbita pepo*, with emphasis, in each species, of the varieties Crown, Jacarezinho and Italian, respectively.

Pumpkin seeds are reservoirs of proteins, lipids, minerals and fibers, however, they are discarded during processing in the agro-industry. Simple and low-cost alternatives such as germination and drying can be applied to these seeds, giving them new nutritional attributes and an unprecedented product appeal.

The germination process can be used as a potential mechanism for the accumulation of bioactive compounds in edible seeds. The changes that occur in its composition contribute to the process of technological innovation and expansion of offers aimed at meeting consumer preferences (GAN *et al.*, 2017). Several studies have demonstrated that germination can increase the content of folic acid,  $\gamma$ -aminobutyric acid, phenolic compounds, and other bioactive substances in grains, as well as remove antinutritional factors such as enzyme inhibitors (LI *et al.*, 2019).

After subjected to imbibition, necessary for the germination process, the seeds contain a high water content, becoming perishable materials that require immediate drying. The drying process, in addition to ensuring the maintenance of the quality of the germinated seeds, favors their transformation into flour, expanding the possibilities of use and alternative for conservation (ARAÚJO *et al.*, 2017).

After drying, the water content needs to be kept at safe levels, which demands informations about the behavior of the adsorption isotherms. These informations are important in evaluating changes in water content under certain conditions of temperature and relative humidity of the environment, so that the shelf life of products can be predicted and adequate storage and packaging conditions can be determined (LAGO; NOREÑA, 2015).

The isotherm predicts the amount of water that a material can retain if exposed to an environment with certain conditions of water activity and temperature (SORMOLI; LANGRISH, 2015). Among the thermodynamic properties associated with hygroscopicity, the heat of absorption is commonly used to indicate the attractive forces of water vapor to the adsorption sites of agrifood products, while the differential entropy is proportional to the number of accessible adsorption sites at a fixed energy level (TAO *et al.*, 2018). Enthalpy-entropy compensation is

a valuable theory that is being widely used to evaluate various physico-chemical phenomena, such as water adsorption (CHENG; ZHANG; ADHIKARI, 2020).

In this context, the study of the adsorption behavior provides relevant information for the adequacy of procedures necessary to preserve the quality and stability of the product. Thus, the objective of the study was to determine the water adsorption isotherms of the germinated pumpkin seed flour at temperatures of 15, 25 and 35 °C, and to determine the thermodynamic properties of water adsorption, such as: integral isosteric heat, differential entropy, differential enthalpy and the Gibbs free energy.

## MATERIAL AND METHODS

The raw materials used were pumpkin seeds of the Crown (*Cucurbita maxima* Duchesne), Jacarezinho (*Cucurbita moschata* Duchesne) and Italian (*Cucurbita pepo* L.) varieties, obtained from ripe fruits produced in the vicinity of Campina Grande city, state of Paraíba, Brazil (geographical coordinates: latitude 7° 13' 50" S, longitude 35° 52' 52" W, altitude 551 m). The fruits were transported in polypropylene boxes to the Laboratory of Agricultural Products Storage and Processing (LAPPA), of the Agricultural Engineering Academic Unit (UAEA), of the Federal University of Campina Grande (UFCG), where they were sanitized, cut and had the seeds removed manually. Before submitting to the germination process, the seeds were washed in running water to remove traces of mucilage and of pulp.

The germination was carried using germitest paper (J. Prolab) with dimensions 28 x 38 cm and 65 g as substrate. The seeds were placed between two sheets of paper moistened with an amount of water 2.5 times the mass of the dry paper; then, the papers with the seeds were folded into rolls, placed in low density polyethylene bags and put in a BOD-type germination oven (CienlaB, CE 300/350) at 25 °C for 96 h.

The seeds germinated with radicles were crushed in a processor (Philco®, PMX600, 600 W), then the material was spread in mesh baskets, in a layer of 0.5 cm, and subjected to drying until reaching equilibrium using a convective dryer with speed of air of 1.0 m/s and temperature of 70 °C. During drying, the baskets were weighed at regular time intervals until constant mass.

The dry material was removed with a stainless steel spatula, and later crushed in a knife mill, obtaining the flours, which were placed in laminated packages until the moment of analysis.

The water adsorption isotherms of the flours were carried out at temperatures of 15, 25 and 35 °C according

to the special indirect static method proposed by Crapiste and Rotstein (1982). To measure the water activity, the Aqualab model 3TE hygrometer (Decagon) was used. The models of GAB, Halsey, Iglesias and Chirife, Kuhn, Oswin and Peleg (Table 1) were fitted to water adsorption data by nonlinear regression using the Quasi-Newton method of the Statistica 7.0 computer program.

The determination coefficient ( $R^2$ ) and the mean percent deviation (P) (Equation 7) were the criteria used to determine the best fit of the models to the data from the water adsorption isotherms.

$$P = \frac{100}{n} \sum_{i=1}^n \frac{X_{exp} - X_{pred}}{X_{exp}} \quad (7)$$

On what: P - mean percentage deviation (%);  $X_{exp}$  - values obtained experimentally;  $X_{pred}$  - values predicted by the model; n - number of experimental data.

The sorption net isosteric heat or sorption differential enthalpy ( $\Delta q_{st}$ ) was determined using the Clausius-Clayperon equation (Equation 8).

$$\frac{\partial \ln(a_w)}{\partial T} = \frac{q_{st}}{RT^2} \quad (8)$$

Integrating Equation 8 and assuming that the sorption net isosteric heat is independent of temperature, it was obtained the Equation 9.

$$\ln(a_w) = -\left(\frac{q_{st}}{R}\right)\frac{1}{T} + C \quad (9)$$

On what:  $a_w$  - water activity (dimensionless);  $\Delta q_{st}$  - sorption net isosteric heat (kJ kg); R - universal constant (8.314 J mol K for gases and 0.4619 kJ kg K for water vapor); T - absolute temperature (K); C - integration constant (dimensionless).

As it presented the best fit to the experimental data of the isotherms, the GAB model was used to

obtain the values of water activity for equilibrium water content between 3 to 40% db. With the  $a_w$  data, the Equation 9 was linearized. From the slope of the linear regression of  $\ln(a_w)$  versus  $1/T$ , considering different levels of equilibrium water content (3 to 40% db), it was obtained the sorption net isosteric heat ( $q_{st}$ ) values for each equilibrium water content.

The sorption integral isosteric heat ( $Q_{st}$ ) was obtained by adding the sorption net isosteric heat ( $q_{st}$ ) with the vaporization latent heat of free water (L). This sum was estimated according to Equation 10.

$$Q_{st} = q_{st} + L = a \cdot \exp(-b \cdot X_e) + L \quad (10)$$

On what:  $Q_{st}$  - sorption integral isosteric heat (kJ kg); L - vaporization latent heat of free water (kJ kg);  $X_e$  - equilibrium water content (% db); a and b - model coefficients.

The vaporization latent heat of free water (L) in kJ kg, necessary to calculate  $Q_{st}$ , was obtained through the average temperature (T) in the range under study, in °C, according to Equation 11.

$$L = 2502.2 - 2.386T \quad (11)$$

Gibbs free energy ( $\Delta G$ ) in kJ kg was calculated according to Equation 12:

$$\Delta G = RT \cdot \ln(a_w) \quad (12)$$

Equation 13 (ISQUIERDO *et al.*, 2020) of the exponential type was used to estimate the Gibbs free energy data:

$$\Delta G = a \cdot \exp(bX_e) \quad (13)$$

Changes in sorption differential entropy ( $\Delta S$ ) were calculated from the Gibbs Helmholtz equation, Equation 14:

$$S = \frac{q_{st} - G}{T} \quad (14)$$

**Table 1** - Mathematical models of water adsorption isotherms

Designation	Model	Number
GAB	$X_e = \frac{X_m C k a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$	(1)
Halsey	$x_e = \left[ \frac{-a}{\ln a_w} \right]^{\frac{1}{b}}$	(2)
Iglesias e Chirife	$x_e = A + \left[ B \left( \frac{a_w}{1 - a_w} \right) \right]$	(3)
Kuhn	$x_e = \left( \frac{A}{\log a_w} \right)^{+B}$	(4)
Oswin	$x_e = a \left( \frac{a_w}{(1 - a_w)} \right)^b$	(5)
Peleg	$X_e = K_1 a_w^{n_1} + K_2 a_w^{n_2}$	(6)

Where:  $X_e$  - equilibrium water content;  $a_w$  - water activity;  $X_m$  - water content in the molecular monolayer; C and K - parameters that depend on the temperature and nature of the product;  $K_1$ ,  $K_2$ ,  $n_1$ ,  $n_2$ , a and b - constants of the models

Where:  $\Delta S$  - sorption differential entropy (kJ kg K) and  $\Delta q_{st}$  - sorption differential enthalpy (kJ kg).

Replacing Equation 12 into Equation 14, it has:

$$\ln(a_w) = \frac{q_{st}}{RT} - \frac{S}{T} \quad (15)$$

The enthalpy-entropy compensation theory (or isokinetic theory) proposes a linear relationship between the sorption differential enthalpy ( $\Delta q_{st}$ ) and the sorption differential entropy ( $\Delta S$ ) for a given water content, according to Equation 16:

$$q_{st} = T_B \Delta S + \Delta G \quad (16)$$

On what:  $T_B$  - isokinetic temperature (K);  $\Delta G$  - Gibbs free energy at isokinetic temperature (kJ kg).

To confirm the validity of the compensation theory, the test proposed by Krug, Hunter and Grieger (1976a, 1976b) with respect to the mean harmonic temperature ( $T_{hm}$ ) was applied according to Equation 17. The theory is considered valid if  $T_B \neq T_{hm}$ .

$$T_{hm} = \frac{n}{\sum \left( \frac{1}{T} \right)} \quad (17)$$

On what:  $T_{hm}$  - mean harmonic temperature (K);  $n$  - number of temperatures used.

The experimental data of the adsorption isotherms were submitted to non-linear regression analysis and the thermodynamic properties were plotted using the computer program Statistica, version 7.0.

## RESULTS AND DISCUSSION

Tables 2, 3 and 4 show the adjustment parameters of the GAB, Halsey, Iglesias and Chirife, Kuhn, Oswin and Peleg models adjusted to the experimental data of equilibrium water content as a function of water activity at temperatures of 15, 25 and 35 °C of germinated seeds flours from pumpkins of the Coroa, Jacarezinho and Italiana varieties, respectively, with determination coefficients ( $R^2$ ) and mean percentage deviations (P).

**Table 2** - Parameters, determination coefficients ( $R^2$ ) and mean percentage deviations (P) of the models adjusted to the water adsorption isotherms of pumpkin seed flour of the Crown variety

Models	Temp. (°C)	Parameters					
		$X_m$	C	k	$R^2$	P (%)	
GAB	15	4.9601	2.1034	0.9437	0.9956	3.45	
	25	3.3880	6.7816	0.9833	0.9989	1.51	
	35	3.3847	2.5321	0.9799	0.9966	3.63	
Halsey	Temp. (°C)	a	b	$R^2$	P (%)		
	15	7.7509	1.2499	0.9889	5.55		
	25	5.3851	1.1686	0.9988	1.73		
Iglesias e Chirife	Temp. (°C)	a	b	$R^2$	P (%)		
	15	4.0793	3.1276	0.9737	8.41		
	25	3.0561	2.9659	0.9954	4.06		
Kuhn	Temp. (°C)	a	b	$R^2$	P (%)		
	15	3.1072	2.6929	0.9750	8.09		
	25	2.9417	1.7652	0.9961	3.62		
Oswin	Temp. (°C)	a	b	$R^2$	P (%)		
	15	6.4765	0.7095	0.9932	3.18		
	25	5.4336	0.7545	0.9970	3.94		
Peleg	Temp. (°C)	$k_1$	$n_1$	$k_2$	$n_2$	$R^2$	P (%)
	15	43.1060	7.5433	11.8787	0.9655	0.9978	2.08
	25	13.1999	1.1340	50.7055	10.4141	0.9986	1.83
	35	13.3984	1.4268	54.5642	11.4772	0.9963	4.83

**Table 3** - Parameters, determination coefficients ( $R^2$ ) and mean percentage deviations (P) of the models adjusted to the water adsorption isotherms of pumpkin seed flour of the Jacarezinho variety

Models	Temp. (°C)	Parameters						
		$X_m$	C	k	$R^2$	P (%)		
GAB	15	2.6962	2594785.00	0.9873	0.9944	4.38		
	25	2.3091	3.5177	1.0040	0.9955	4.72		
	35	2.1116	1.7156	1.0068	0.9933	4.47		
Halsey	Temp. (°C)	a	b	-	$R^2$	P (%)		
	15	5.3351	1.2385	-	0.9874	6.61		
	25	2.4654	1.0023	-	0.9962	4.38		
	35	1.7937	0.9268	-	0.9939	3.35		
Iglesias e Chirife	Temp. (°C)	a	b	-	$R^2$	P (%)		
	15	3.2743	2.3544	-	0.9963	3.07		
	25	1.1446	2.4570	-	0.9965	3.89		
	35	0.2996	2.3228	-	0.9933	4.72		
Kuhn	Temp. (°C)	a	b	-	$R^2$	P (%)		
	15	2.3320	2.2633	-	0.9958	3.40		
	25	2.4369	0.0700	-	0.9962	4.27		
	35	2.3083	-0.7343	-	0.9929	5.17		
Oswin	Temp. (°C)	a	b	-	$R^2$	P (%)		
	15	4.9225	0.7081	-	0.9747	9.34		
	25	3.2337	0.8911	-	0.9937	6.47		
	35	2.4473	0.9845	-	0.9927	5.97		
Peleg	Temp. (°C)	$k_1$	$n_1$	$k_2$	$n_2$	-	$R^2$	P (%)
	15	7.8112	0.4315	43.4465	9.1717	-	0.9995	0.99
	25	6.6209	0.8189	44.5265	9.3513	-	0.9991	1.23
	35	10.6007	1.8582	61.8949	14.7662	-	0.9937	5.32

**Table 4** - Parameters, determination coefficients ( $R^2$ ) and mean percentage deviations (P) of the models adjusted to the water adsorption isotherms of pumpkin seed flour of the Italian variety

Models	Temp. (°C)	Parameters				
		$X_m$	C	k	$R^2$	P (%)
GAB	15	4.0956	5.4607	0.9360	0.9990	V
	25	3.4795	4.4261	0.9602	0.9986	2.20
	35	3.1921	3.3765	0.9635	0.9988	2.07
Halsey	Temp. (°C)	a	b	-	$R^2$	P (%)
	15	10.7923	1.4311	-	0.9938	3.84
	25	6.5319	1.2853	-	0.9959	3.94
	35	4.9252	1.2203	-	0.9959	3.51
Iglesias e Chirife	Temp. (°C)	a	b	-	$R^2$	P (%)
	15	4.9947	2.3538	-	0.9660	8.89
	25	3.6892	2.4036	-	0.9799	8.86
	35	2.8419	2.3718	-	0.9835	7.09

Continuation Table 4

	Temp. (°C)	a	b	-	R <sup>2</sup>	P (%)		
Kuhn	15	2.3401	3.9464	-	0.9677	8.60		
	25	2.3889	2.6251	-	0.9814	8.45		
	35	2.3535	1.8016	-	0.9851	6.60		
	Temp. (°C)	a	b	-	R <sup>2</sup>	P (%)		
Oswin	15	6.4705	0.6182	-	0.9973	2.48		
	25	5.3711	0.6935	-	0.9981	2.54		
	35	4.6593	0.7275	-	0.9980	2.65		
	Temp. (°C)	k <sub>1</sub>	n <sub>1</sub>	k <sub>2</sub>	n <sub>2</sub>	-	R <sup>2</sup>	P (%)
Peleg	15	32.5770	7.5422	11.3664	0.8554	-	0.9991	1.29
	25	39.7610	10.5148	13.5151	1.2907	-	0.9971	3.71
	35	35.3613	8.7413	9.8072	1.0310	-	0.9994	1.30

Based on the data presented, it is observed that the applied models were well adjusted to the experimental data, with mean percentage deviation values (P) below 10% and determination coefficients (R<sup>2</sup>) above 0.970. The GAB and Peleg models, in general, represented with greater precision the isotherms of the three studied flours, with the highest determination coefficients (R<sup>2</sup> > 0.990) and smaller mean percentage deviations (P < 5.5%) at the three analyzed temperatures.

Considering the determination coefficients and the mean percentage deviations, Sharma *et al.* (2018) reported that the GAB model was considered adequate to represent the data of the water adsorption isotherms of germinated and non-germinated Foxtail millet (*Setaria italica* L.) seed flours at temperatures of 10, 25 and 40 °C; Santos *et al.* (2020) found that the Peleg model was the most adequate to represent the isotherms of *Coffea arabica* grains at temperatures of 30, 40, 50 and 60 °C.

The parameters of the GAB model (X<sub>m</sub>, C and K), which characterize the interactions of water with the macroconstituents of solids, maintained a similar behavior in most studies found in the literature. The monolayer water content (X<sub>m</sub>) is the amount of water that is strongly adsorbed on the product surface, being considered important for long periods storage. As shown in Tables 2, 3 and 4, the parameter X<sub>m</sub> had greater values in the Coroa variety flour (maximum of 4.9601% db) e lower values in the Jacarezinho flour (minimum of 2.1116% db), with intermediate values in the Italiana flour. Furthermore, the three varieties showing reduction of X<sub>m</sub> with increasing temperature.

According to Bettioli *et al.* (2020), this behavior is due to the reduction in the number of active sites as a result of physicochemical changes induced by increasing

temperature. According to Samapundo *et al.* (2007), the value of X<sub>m</sub> decreases with increasing temperature due to the disruption of water molecules from their sorption sites at high energy levels.

The constant C is associated with the potential chemical differences between the monolayers. The parameter K provides a measure of the interactions between the molecules in the multilayer with the adsorbent and the energy value of the molecules in the monolayer, taking into account the energy value of liquid water (ALPIZAR-REYES *et al.*, 2017). The values of K for the Coroa and Italiana varieties were less than 1, ranging from 0.93 to 0.98. However, the Coroa variety did not show a defined behavior in relation to the studied temperatures, whereas the Jacarezinho and Italiana varieties had an increase in K with the temperature increase. Regarding the parameter C, the varieties Coroa and Jacarezinho did not show a standard behavior in relation to the studied temperatures.

According to Santos *et al.* (2014), variations in the value of the constant C may be related to irreversible changes associated with increased temperature, such as enzymatic reactions and protein denaturation. When K = 1, the multilayer has the property of liquid water (FARAHNAKY *et al.*, 2016); and for K < 1, the GAB model becomes well represented for high water activity values (a<sub>w</sub> ≈ 0.9), being typical of food products.

The constants C and K of GAB model provide informations on the type of isotherms specific to each material. According to the classification of Blahovec (2004), the isotherms of the three flours are identified as Type II at the three studied temperatures, with a sigmoidal shape, because they presented values of 0 < K ≤ 1 and C > 2.

The Type II isotherms are characterized by three regions: the first region ( $a_w < 0.3$ ) is related to the water content in the monolayer, which is strongly linked to the product matrix; the second region ( $0.3 \leq a_w < 0.7$ ) indicates that the water from several layers present an almost linear behavior; the third region ( $a_w \geq 0.7$ ) is composed of water molecules that are weakly linked to the product matrix and that are available for chemical and microbiological reactions (POLACHINI *et al.*, 2016).

In Figure 1, there is a graphical representation of the water adsorption isotherms at temperatures of 15, 25 and 35 °C of pumpkin seed flours of the Coroa, Jacarezinho and Italiana varieties with adjustments by the GAB model.

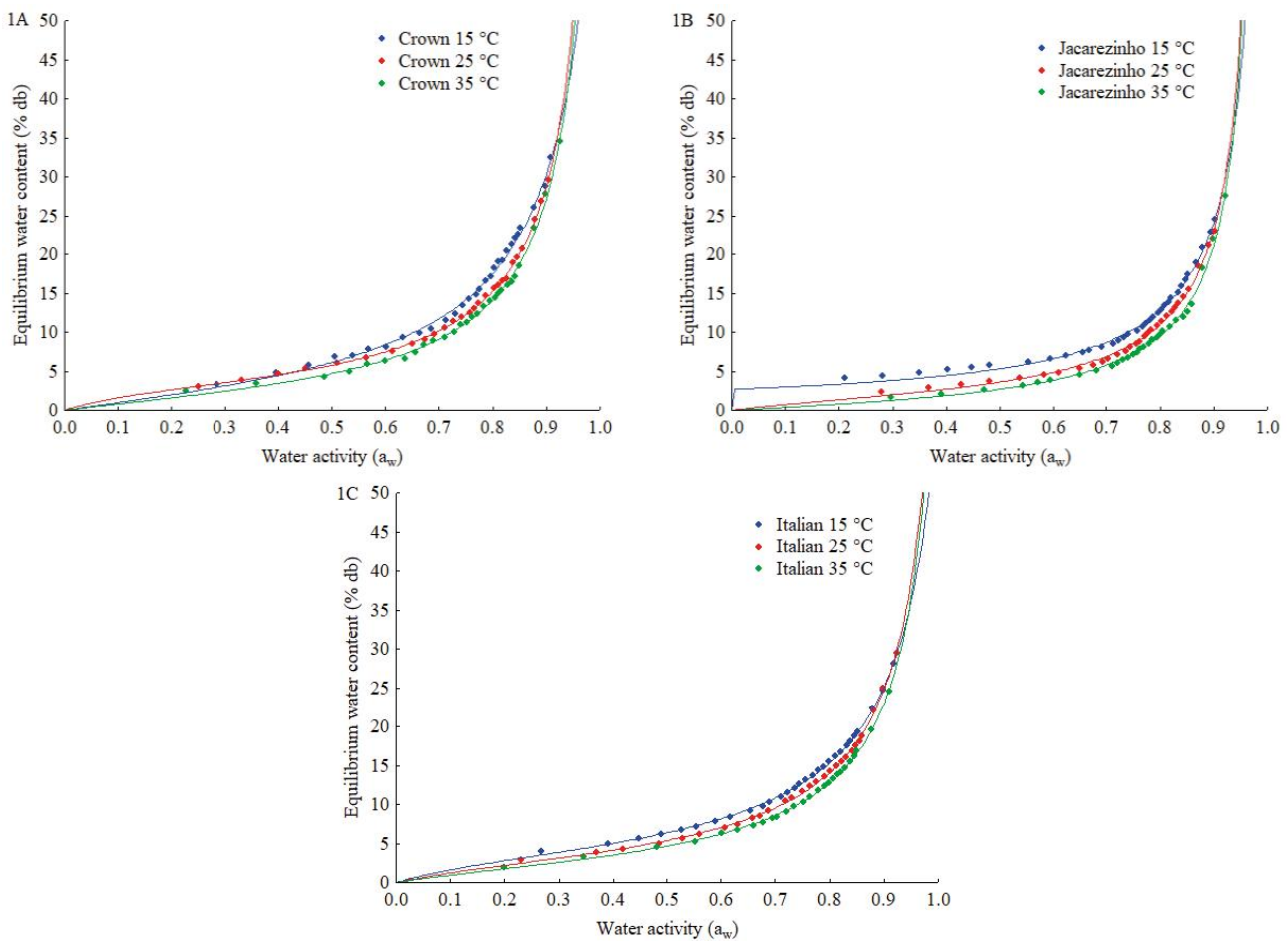
Figure 1A shows inflection points on the curves, typical of type II isotherms, with a sigmoidal shape. For water activity values above 0.6, the equilibrium water content increases rapidly for the three temperatures,

showing similar behavior across the entire range of water activity. For water activity values close to 0.9, the three curves converge and intersect.

In Figure 1B, the isotherm curves of the Jacarezinho variety flours at 25 and 35 °C are close to each other for lower water activity values, while that the curve at 15 °C remains distant, with equilibrium water content above the others. For water activity values above 0.7, the equilibrium water content increases rapidly at the three temperatures, showing similar behavior throughout the range, until in water activity values above 0.9, the three curves converge to close values.

It is observed in Figure 1C similarity in the behavior of the isotherms for the Italian variety flours at the three temperatures, demonstrating the effect of the increase in temperature throughout the range of water activity. The three curves converging, as in the other varieties, in ranges of  $a_w$  close to 0.9.

**Figure 1** - Water adsorption isotherms at temperatures of 15, 25 and 35 °C for pumpkin seed flour of the varieties with adjustments by the GAB model: A. Crown; B. Jacarezinho; and C. Italian



In all flours of the three varieties, there is a tendency to reduce the equilibrium water content with increasing temperature, to a constant  $a_w$ . This behavior was also observed by Bensebia and Allia (2016), that reported that the decrease in temperature causes an increase in the amount of sorbed water and, with this information, the level of water content and temperature are essential factors to avoid the deterioration of the quality of products during storage.

Figure 2 shows the data of the neperian logarithm of water activity ( $\ln a_w$ ) as a function of absolute temperature inverse ( $1/T$ ). It was considered the equilibrium water content values between 3 and 40% db for the pumpkin seed flours of the three varieties (Crown, Jacarezinho and Italian).

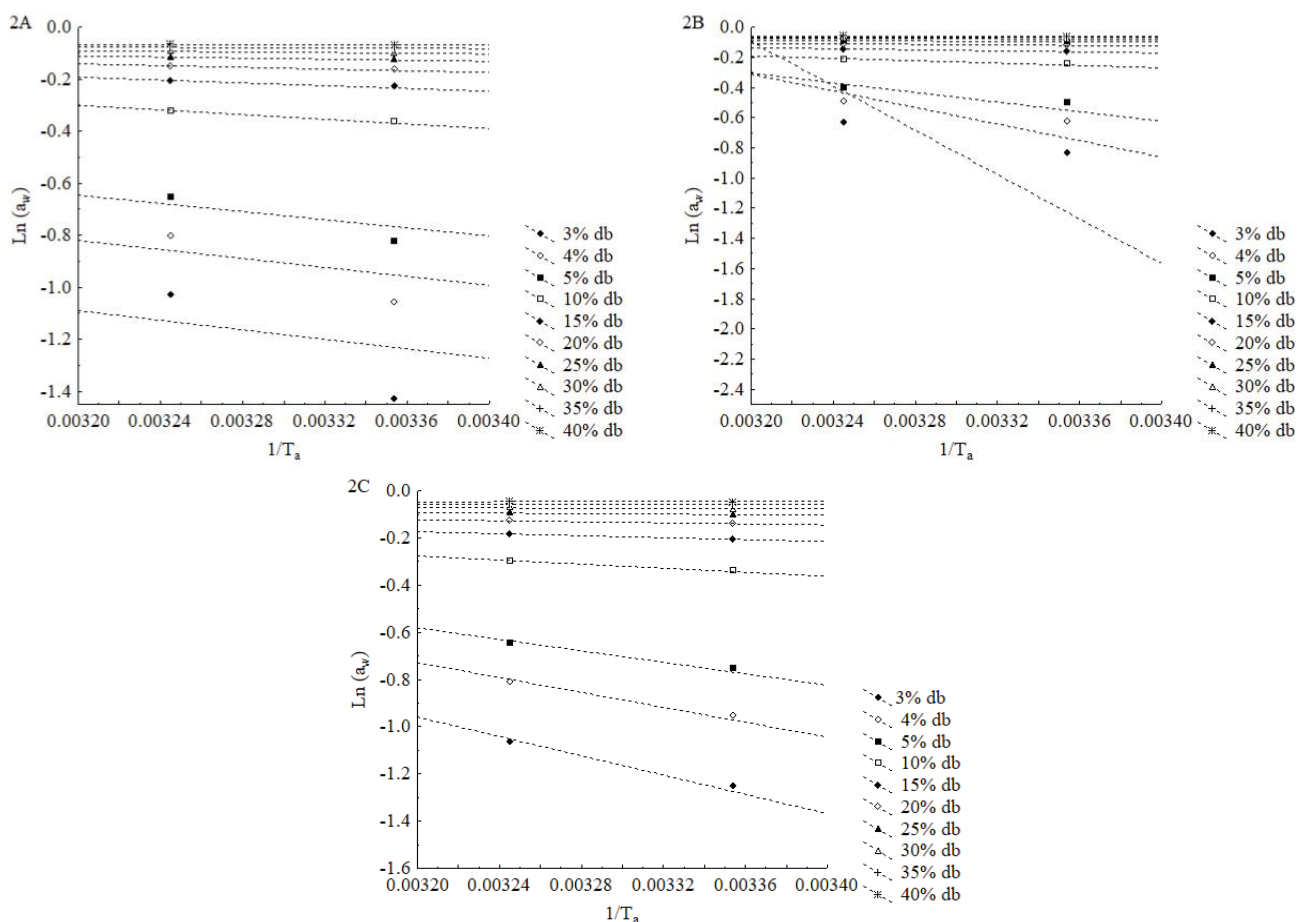
Water activity values were estimated by the GAB model. In this figure, the slopes of the straight lines correspond to the values of the sorption net isosteric heat or sorption differential enthalpy ( $\Delta q_{st}$ ). The  $\Delta q_{st}$  values for the three flours ranged from 2.08 to 3395.15 kJ kg, decreasing

with the increase of the equilibrium water content and presenting the highest values for the Jacarezinho variety flour, followed by the Italian one and with the lowest for the Crown. Similar behavior of  $\Delta q_{st}$  reduction with increasing of equilibrium water content was also verified by Oliveira *et al.* (2013) for corn grains.

From the data obtained from the sorption net isosteric heat or sorption differential enthalpy ( $\Delta q_{st}$ ), the sorption integral isosteric heat ( $Q_{st}$ ) was calculated. Figure 3 shows the values of the sorption integral isosteric heat ( $Q_{st}$ ) as a function of the equilibrium water content ( $X_e$ ) for pumpkin seed flours of the Crown, Jacarezinho and Italian varieties.

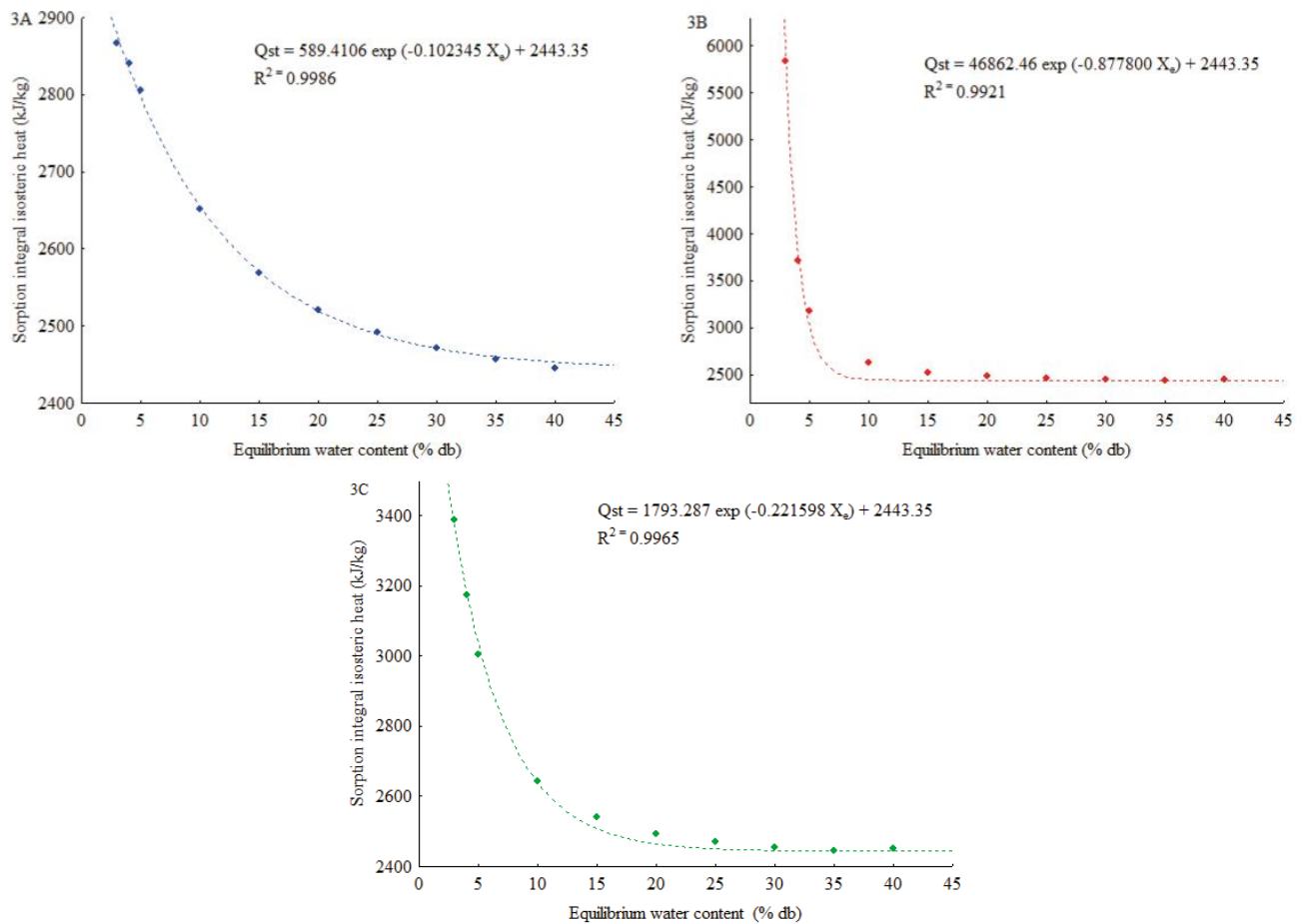
The values of sorption integral isosteric heat for pumpkin seed flours of the Crown, Jacarezinho and Italian varieties ranged from 2866.29 to 2445.43 kJ kg; 5838.50 to 2448.36 kJ kg and from 3388.63 to 2452.46 kJ kg, respectively.

**Figure 2** - Neperian logarithm of water activity as a function of absolute temperature inverse for pumpkin seed flours of the following varieties: A. Crown; B. Jacarezinho; and C. Italian





**Figure 3** - Experimental and estimated values of sorption integral isosteric heat as a function of equilibrium water content for pumpkin seed flours of the following varieties: A. Crown; B. Jacarezinho; and C. Italian



In the three flours, there is a reduction of the sorption integral isosteric heat with the increase of the equilibrium water content, with the equations satisfactorily adjusted, presenting determination coefficients ( $R^2$ ) varying from 0.9921 to 0.9986. These reductions were verified over the entire range of the equilibrium water content for the Coroa and Italiana flours samples. For the Jacarezinho variety, the reduction was more pronounced in the first 15% of equilibrium water content.

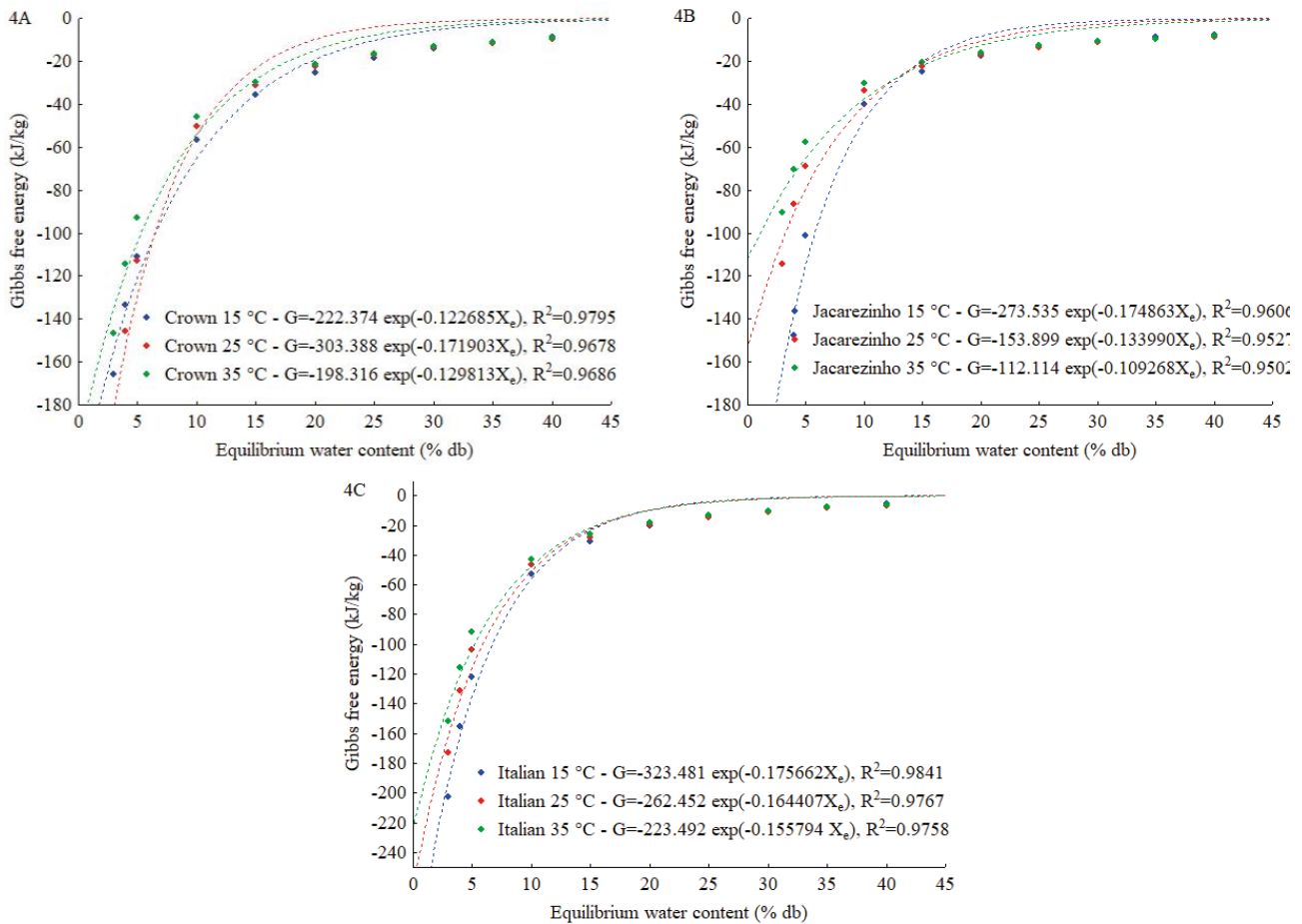
In the phase of  $Q_{st}$  reduction with increasing equilibrium water content, there is a transition from strongly linked water to capillary water, in which the water molecules bonds to the flour components with less strength than in the monolayer (LABUZA; ALTUNAKAR, 2008). Thus, for high water activity values, fewer sites are available for the bonds between the molecules, implying the need for movement of water molecules and, consequently, a reduction in isosteric heat, causing dissolution in the flour due the increase of molecules of water in free form (RESENDE *et al.*, 2017).

The integral isosteric heat variation can be explained by the difference between the binding strengths of the water molecules with the flours components.

In Figure 4 are presented the Gibbs free energies ( $\Delta G$ ) as a function of the equilibrium water content ( $X_e$ ) of pumpkin seed flours of the Crown, Jacarezinho and Italian varieties.

It is observed that the three flours at all temperatures presented negative Gibbs free energies, confirming the strong attraction between the water molecules and the samples, a consequence of the hygroscopic nature of the samples. The Gibbs free energy increased with increasing equilibrium water content, therefore, the increasing equilibrium water content of pumpkin seed flours decreased the energy requirement for the adsorption process to occur, indicating a spontaneous reaction and a exothermic process. The Gibbs free energy is a thermodynamic variable related to the work needed to make the sorption sites available (CORRÉA *et al.*, 2015).

**Figure 4** - Gibbs free energy as a function of equilibrium water content for pumpkin seed flours of the varieties: A. Crown; B. Jacarezinho; and C. Italian



Negative values for Gibbs free energy suggest strong intermolecular or connection interactions (related to enthalpy), which leads to a greater reduction in freedom in the configuration of water molecules and, consequently, to a higher order in the system (related to entropy) (RIZVI, 2014).

Negative values of Gibbs free energy and increase in equilibrium water content were seen by Cahyanti and Pattiserlihun (2018) when studying the thermodynamic properties of water adsorption in Gapelek flour (dry and sliced cassava root).

It is observed that, as the equilibrium water content increased, the discrepancies between the Gibbs free energy values are reduced in the different temperatures, since the binding force of water with the other components of the product is smaller. In this case, the temperature exerts lower influence and the three curves converging with each other.

The Gibbs free energy prediction equations showed good fits to the experimental data, with better results for the Italian variety flours at the three studied temperatures, since they presented highest  $R^2$ . Intermediate results were found for the Coroa variety.

Good fits for Gibbs free energy data were also verified by Rodrigues *et al.* (2020) in the determination of water adsorption isotherms and thermodynamic properties of ‘Cumari-do-Pará’ pepper seeds (*Capsicum chinense*), obtaining  $R^2$  of 0.9984.

Figure 5 shows the sorption differential entropy values ( $\Delta S$ ) as a function of the equilibrium water content ( $X_e$ ) for pumpkin seed flours of the Crown, Jacarezinho and Italian varieties.

It is observed that the sorption differential entropy is inversely proportional to water content of the flours, that is, similar to the behavior exhibited for

the sorption integral isosteric heat (Figure 5). This behavior was reported by Cheng, Zhang and Adhikari (2020) on aquatic caltrop powders or water chestnut (*Trapa bispinosa* Roxb). The result is consistent with the fact that the greater the water molecular coverage in agrifood materials, the lower the water molecules mobility present during the adsorption process (ISQUIERDO *et al.*, 2020).

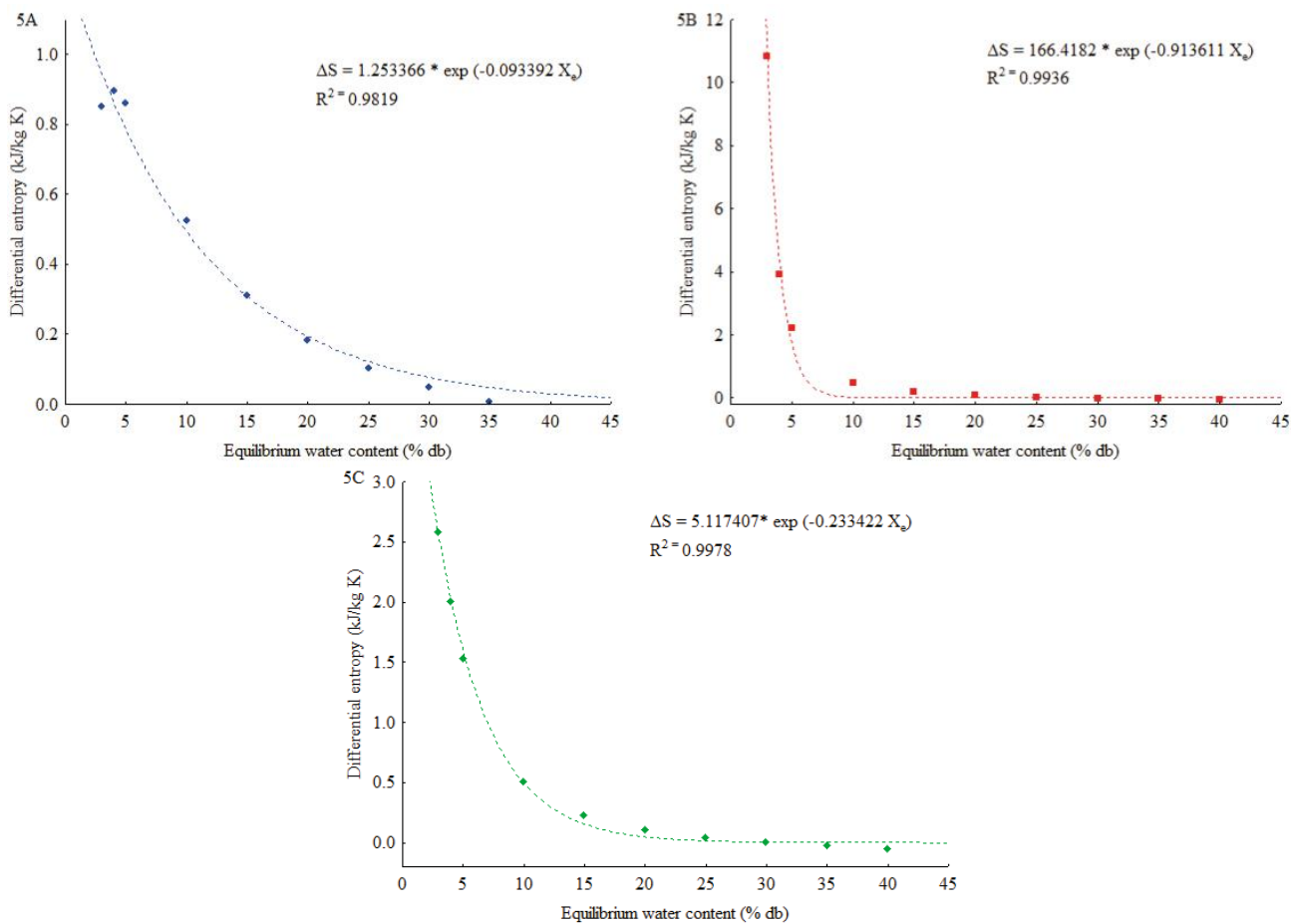
Crown variety flour (Figure 5A) had the lowest entropy values, while the highest values were observed for Jacarezinho variety flour. Such results are due to the amount of water present in the samples.

The equations adjusted (exponential type) to the data of the differential entropy of flours as a function of the equilibrium water content presented satisfactory adjustments, since  $R^2$  ranged from 0.9819 to 0.9978, indicating that these equations can be used to predict the entropy in flours of pumpkin seeds.

Negative entropy values were observed from 40% of equilibrium water content in Coroa variety flour (Figure 5A), 30% in Jacarezinho variety flour (Figure 5B) and 35% in Italian variety flour (Figure 5C), indicating a loss of water molecules mobility during the sorption process, as observed by Baptestini *et al.* (2020) in soursop powder.

Sorption differential entropy is dependent on the sorption sites number available at a specific energy level and the corresponding values can be calculated at different water content (SILVA *et al.*, 2015). With the increase in the water content of the seeds, there is a decrease in the available sites for the bonds between the water molecules and the product surface, implying a lower demand for the water molecules mobility and, consequently, lower values of sorption differential entropy (GONELI *et al.*, 2010).

**Figure 5** - Experimental and estimated values of sorption differential entropy as a function of equilibrium water content for pumpkin seed flours of the varieties: A. Crown; B. Jacarezinho; and C. Italian



**Figure 6** - Experimental and estimated values of differential enthalpy as a function of differential entropy for pumpkin seed flours of the varieties: A. Crown; B. Jacarezinho; and C. Italian

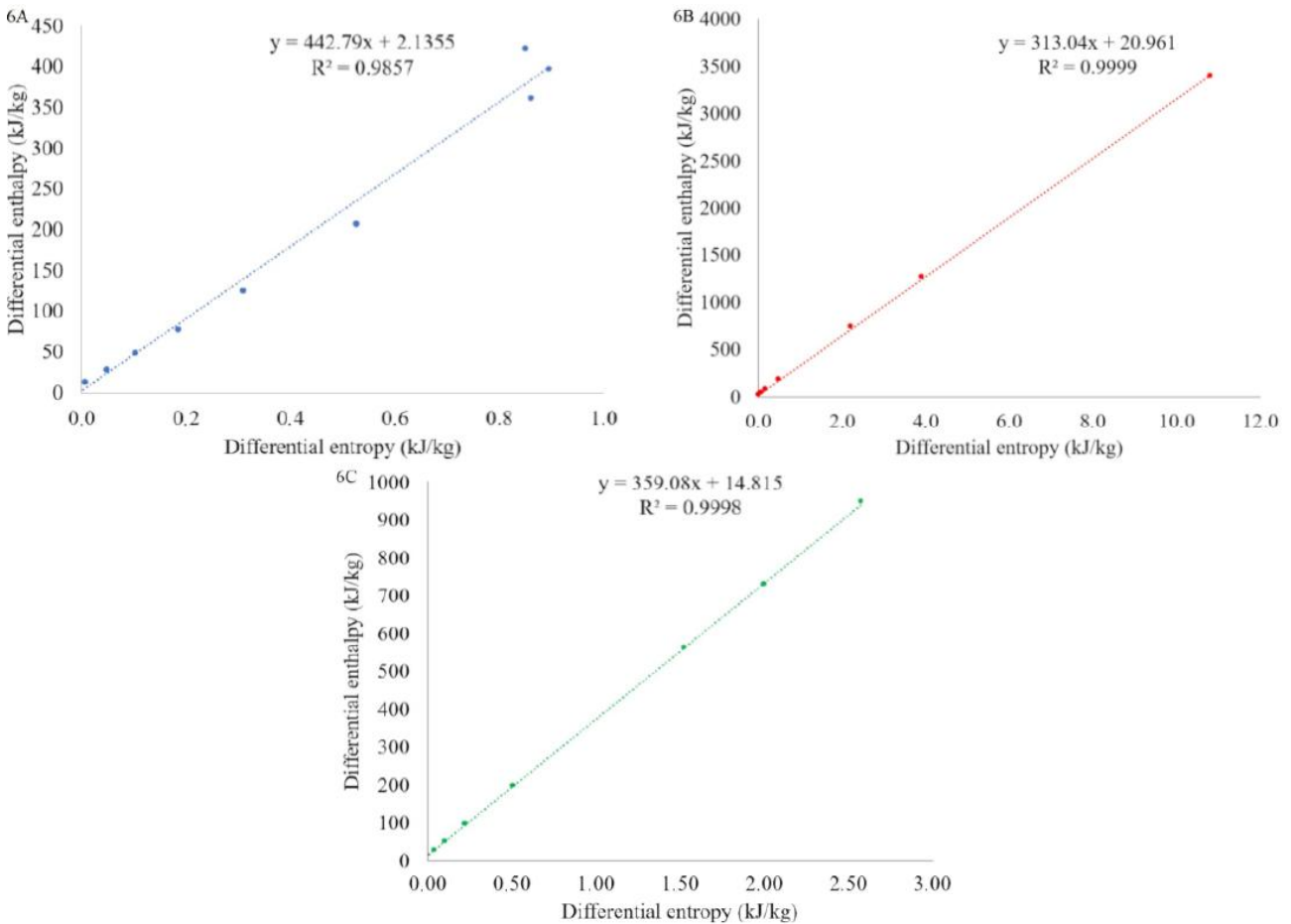


Figure 6 shows the values of sorption differential enthalpy ( $\Delta q_{st}$ ) as a function of sorption differential entropy ( $\Delta S$ ) for pumpkin seed flours of the Crown, Jacarezinho and Italian varieties.

A requirement to confirm the enthalpy-entropy compensation theory is the need to correlate the differential enthalpy with the differential entropy by a linear representation. Figure 6 shows a linear relationship between differential enthalpy and differential entropy, represented by equations with determination coefficients ( $R^2$ ) ranging from 0.9857 to 0.9999, which indicates a satisfactory description of the adsorption process, following the compensation theory enthalpy-entropy or isokinetic theory.

Therefore, it is observed that a change in enthalpy is accompanied by changes in both entropy and Gibbs free energy. As verified in pumpkin seed flours, a satisfactory

linear relationship of enthalpy-entropy was also reported by Bensebia and Allia (2016) working with rosemary leaves.

The isokinetic temperatures ( $T_B$ ) of the pumpkin flours were 442.79, 313.04 and 359.08 K for the Coroa, Jacarezinho and Italiana flours, respectively. These temperatures were different from the mean harmonic temperature ( $T_{hm} = 297.93$  K), which is the condition for the validation of the isokinetic theory. The isokinetic temperature represents the temperature at which all reactions during adsorption occur at the same rate (ČERVENKA; CACKOVÁ, 2016).

## CONCLUSIONS

1. The prediction models of water sorption isotherms were well adjusted to the experimental data. In general, the GAB and Peleg models represented with greater

precision the isotherms of the three studied flours at the temperatures of 15, 25 and 35 °C. The isotherms were classified as Type II, with sigmoidal shape, for the three flour varieties at the three temperatures;

2. It was observed that with increasing the water content, there was a reduction in the sorption integral isosteric heat and in the sorption differential entropy for the three studied flours;
3. The Gibbs free energy was negative for all temperatures and increased with increasing equilibrium water content, demonstrating that it is a spontaneous process and an exothermic reaction.

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