



Water desorption isotherms and thermodynamic properties of Ora-pro-nóbis (*Pereskia aculeata* Miller)

André Luiz Borges-Machado^{a,b,*}, Marcio Augusto Ribeiro-Sanches^a, Maria Júlia Neves-Martins^a, Priscila Alonso dos Santos^b, Guadalupe Luna-Solano^c, Javier Telis-Romero^a

^a Food Engineering and Technology Department, State University of São Paulo, São José do Rio Preto, São Paulo, 15054-000, Brazil

^b Department of Food Engineering, Instituto Federal Goiano - Campus Rio Verde, Rio Verde, Goiás, 75901-970, Brazil

^c División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Orizaba, Orizaba, Veracruz, 94300, Mexico

ARTICLE INFO

Keywords:

GAB model
Non-conventional edible plant
Barbados gooseberry
Storage
Drying

ABSTRACT

Desorption isotherms of ora-pro-nóbis leaves were determined at storage (5 °C, 10 °C, 20 °C, 30 °C, and 40 °C) and drying (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C) temperatures by the gravimetric static method using saturated saline solutions to obtain relative humidities ranging from 5.20% to 98.48%. The net isosteric heat of desorption and thermodynamic properties such as differential enthalpy, differential entropy, and Gibbs free energy were also estimated. The GAB model presented the best parameters of fitting and the lowest Akaike and Bayesian information criteria values. The desorption isotherm patterns presented a sigmoid shape and were categorized as BET Type II sigmoid shape. The monolayer moisture content was estimated in 0.06 kg of water/kg of dry matter using the GAB model, and it remained constant at all temperatures. The leaves presented an optimal water activity equal to 0.35 at storage temperatures. The net isosteric heat of desorption decreased with increasing X_{eq} , and differential entropy increased with rising equilibrium moisture content ($X_{eq} > 0.07$). The enthalpy-entropy compensation was evaluated, and the desorption process is revealed to be entropy-driven and non-spontaneous.

1. Introduction

Many people believe that a typical cactus is a green succulent plant with no leaves and many spines, but, *Pereskia* Miller is a genus consisting of broad-leaved trees and shrubs found throughout Central and South America. (Butterworth & Wallace, 2005). The leaves of ora-pro-nóbis (*Pereskia aculeata*), also known as Barbados gooseberry, present high mucilage content, a carbohydrate complex with a high water absorption capacity that has significant potential for usage as a hydrocolloid in processed foods (Martin et al., 2017) and pharmaceutical industries due to its emollient properties (Duarte & Hayashi, 2005). The high amount of protein in the leaves led to the plant being called "poor's meat" (Hoff et al., 2022). Some studies reported some chemical compounds associated with wound healing, antiulcer (Pinto et al., 2016), and analgesic properties (Pinto et al., 2015).

The production and consumption of ora-pro-nóbis leaves are extremely important due to their potential as a sustainable source of nutraceuticals and ingredients, favoring foods to enhance nutritional quality (Garcia et al., 2019), and being a good ally in guaranteeing food

security once the prevalence of malnutrition remained constant for five years and increased with the COVID-19 pandemic, indicating that the problem of food insecurity was not going towards a solution until 2030 (FAO et al., 2021). In this way, providing data concerning the water desorption isotherms and thermodynamic properties of ora-pro-nóbis leaves is of great importance due to its applicability in shelf-life estimation, storage conditions, and drying process design.

Moisture sorption isotherms are a handy tool for food scientists since they permit predicting which chemical reactions would reduce stability at a particular moisture level, enable ingredient selection to adjust the water activity, improve stability, and estimate moisture gain or loss in a package with known water vapor permeability (Labuza & Altunakar, 2020). Further investigations into the sorption phenomenon can be conducted using thermodynamic properties such as differential enthalpy and entropy, which are variables that provide information about the material microstructure as well as theoretical interpretations for matrix-water interactions (Rizvi, 2014). The enthalpy-entropy compensation theory states that compensation happens when the behavior of the solvent-solute interaction changes and that there is a

* Corresponding author. Food Engineering and Technology Department, State University of São Paulo, São José do Rio Preto, São Paulo, 15054-000, Brazil.
E-mail address: albmrv@gmail.com (A.L. Borges-Machado).

linear relationship between reaction enthalpy and entropy, with the associated slope representing the isokinetic temperature, which is the temperature at which all subsequent reactions proceed at the same rate (Moreira et al., 2008; Polachini et al., 2016). The evaluation of this theory also allows the estimation of Gibb's free energy at isokinetic temperature. According to Rizvi (2014), Gibb's free energy is indicative of the water-absorbent affinity, providing knowledge on the spontaneity of the sorption phenomenon.

Thus, this study aimed to (i) determine the water desorption isotherms of *Pereskia aculeata* Miller at storage and drying temperatures, (ii) estimate the thermodynamic parameters (net isosteric heat of desorption, differential enthalpy, differential entropy, and Gibbs free energy), and (iii) evaluate the enthalpy-entropy compensation theory.

2. Material and methods

2.1. Raw material

Ora-pró-nobis leaves were cultivated and harvested at UNESP (Campus São José do Rio Preto) and conducted to the Laboratory of Physical Measurements of the Department of Engineering and Food Technology. After 20 min of sanitizing with a chlorinated solution (100 ppm), they were dried with absorbent paper and stored under refrigeration (4 ± 2 °C). The saturated saline solutions utilized to simulate environments with relative humidity ($RH = 100 \cdot a_w$) ranging from 7.43% to 98.48% were prepared with distilled water and salts from Sigma-Aldrich (St. Louis, MO, USA). Lithium iodide (LiI), ammonium sulfate ($(NH_4)_2SO_4$), sodium bromide (NaBr), lithium bromide (LiBr), sodium iodide (NaI), magnesium chloride ($MgCl_2$), lithium chloride (LiCl), potassium iodide (KI), potassium carbonate (K_2CO_3), potassium chloride (KCl), magnesium nitrate ($Mg(NO_3)_2$), potassium sulfate (K_2SO_4), sodium chloride (NaCl), and potassium nitrate (KNO_3) were used in this work.

2.2. Proximate composition

Lipid content was determined according to the Ai 3–75 procedure by the Soxhlet method using petroleum ether (AOCS, 2009). Moisture, ash, protein, and total fiber contents were determined following the Association of Official Analytical Chemistry's procedures (Horwitz & Latimer, 2007). The moisture content was measured in an oven at 105 °C for 24 h (method 950.46), and the ash content was measured in a muffle at 550 °C until white or slightly grey ashes were obtained (method 923.03). Micro-Kjeldahl was used to determine total nitrogen, and the protein amount was converted using 6.25 as the conversion factor (method 981.10). The total fiber content was determined using the enzymatic gravimetric approach, which used thermostable α -amylase, glucoamylase, and protease to break down proteins and starches. The insoluble and soluble fractions of the fibers were subsequently separated using a centrifuge (method 991.43). Carbohydrates were calculated by difference. The water activity (a_w) was measured using a digital hygrometer (Aqualab Model Series 3, Decagon Devices Inc., Pullman, USA).

2.3. Determination of the desorption isotherms

Desorption isotherms were assessed at nine temperatures: storage (5 °C, 10 °C, 20 °C, 30 °C, and 40 °C) and drying (40 °C, 50 °C, 60 °C, 70 °C, and 80 °C). The studies were carried out in a chamber-typeBOD (MA415, Marconi, Piracicaba, Brazil) to obtain storage temperatures, and the drying temperatures experiments were carried out in an oven (MA030, Marconi, Piracicaba, Brazil). The static gravimetric method proposed by Spiess and Wolf (1983) was used to determine the desorption isotherms of ora-pró-nobis leaves, which consists of putting saturated saline solutions into desiccators to keep constant water activity (a_w) at each sample value while the equilibrium between the

atmosphere and food sample was reached. The leaves were cut into a square shape with sides equal to 1 cm and allocated in small containers inside the desiccators. At the beginning of the experiment, which was conducted in triplicate, the moisture content and mass of the samples were determined using an analytical balance (AUW220D, Shimadzu, Japan), and the samples were weighted until they attained constant mass. Aiming to avoid microbial spoilage, a beaker containing toluene was put inside the desiccators where relative humidity was higher than 60% ($a_w > 0.6$). The experiments lasted six weeks and were based on a weight difference expressed on a dry basis that did not exceed 0.001 g/g dry solids. The salt solutions used to create atmospheres with different relative humidities (Table S1) were made according to Labuza (1963) and Martins et al. (2023).

2.4. Modelling of desorption isotherms

The theoretical (GAB), empirical (Peleg and Oswin), and semi-empirical (Halsey and Henderson) sorption isotherm models typically used to describe the water sorption process in foodstuffs are shown in Table 1. The values of X_{eq} were plotted against a_w using the Origin 2023 program (OriginLab Corporation, Northampton, MA), and nonlinear regression was performed.

The adjusted coefficient of determination (R^2_{adj}) and residual analysis of reduced chi-square (χ^2) and root mean square error (RMSE) were used to assess the quality of the nonlinear fit of the water desorption models to the experimental data. Furthermore, using Equations (6) and (7), Akaike (AIC) and Bayesian (BIC) information criteria were calculated to identify the optimum model for ora-pró-nobis leaves water desorption by comparing the fitting results of the five models shown in Table 1 (Akaike, 1974; Stone, 1979). AIC and BIC are composed of a goodness-of-fit term and a penalty to prevent overfitting and they provide a standardized method for balancing sensitivity and specificity. The better the model, the lower the AIC and BIC (Wolfinger, 1993).

$$AIC = -2 \log \mathcal{L}(\hat{\theta}) + 2p \quad (6)$$

$$BIC = -2 \log \mathcal{L}(\hat{\theta}) + p \ln(n) \quad (7)$$

where n is the total number of observations, p is the total number of estimated parameters, and $\mathcal{L}(\hat{\theta})$ is the value of the likelihood function regarding the parameters of the model.

2.5. Optimal water activity

The experimental desorption points at storage temperatures were plotted on the same graph. A polynomial equation of the third degree was used to model the sorption isotherm. This calculating procedure entails doing a polynomial decomposition of the X_{eq} based on the a_w , allowing us to compute the “inflection point” of the second derivative of

Table 1
- Mathematical models for adjusting the isotherms of ora-pró-nobis leaves.

Model	Equation	
GAB	$X_{eq} = \frac{X_m C k a_w}{(1 - k a_w)(1 + (C - 1) k a_w)}$	(1)
Peleg	$X_{eq} = k_1 a_w^{n_1} + k_2 a_w^{n_2}$	(2)
Oswin	$X_{eq} = M \left(\frac{a_w}{1 - a_w} \right)^N$	(3)
Halsey	$X_{eq} = (-h_1 \ln(a_w))^{-\frac{1}{h_2}}$	(4)
Henderson	$X_{eq} = \left(-\frac{1}{H_1} \ln(1 - a_w) \right)^{\frac{1}{H_2}}$	(5)

C , k , k_1 , n_1 , k_2 , n_2 , M , N , h_1 , h_2 , H_1 , and H_2 are constants of the models, X_m represents the monolayer moisture content (kg of water/kg dry matter), X_{eq} is the equilibrium moisture content, and a_w is the water activity.

X_{eq} (Lahnine et al., 2016).

2.6. Thermodynamic properties

The isosteric heat of sorption informs about the energy required for drying and the design of drying equipment. It is defined as the smallest quantity of energy needed for eliminating water in the desorption or adding water in the adsorption of a hygroscopic material (Jhider & Bagané, 2019). The net isosteric heat of desorption (q_{st}) was calculated using the Clausius-Clapeyron equation (Equation (8)) at different X_{eq} (Rizvi, 2014).

$$\left. \frac{\partial(\ln a_w)}{\partial(1/T)} \right|_{X_{eq}} = -\frac{Q_{st} - \lambda}{R} = -\frac{q_{st}}{R} \quad (8)$$

in which Q_{st} is the integral heat of sorption, λ is the latent heat of pure water vaporization and R is universal gas constant ($8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$). Assuming q_{st} constant over the temperature range investigated, linear regression was used to obtain the slope of each isostere of $\ln a_w$ versus $1/T$, and hence, the net isosteric heat of desorption.

Differential enthalpy (ΔH) and differential entropy (ΔS) were calculated using the same approach as q_{st} but with Equation (9), derived from the Gibbs-Helmholtz equation (Rizvi, 2014).

$$\ln a_w = \left(\frac{\Delta H}{R} \right) \frac{1}{T} - \frac{\Delta S}{R} \quad (9)$$

The enthalpy-entropy mechanism could be verified by plotting q_{st} , which is equal to the negative of enthalpy, against entropy in the expectation of a linear correlation. Using Equation (10), the figure was also used to compute Gibbs' free energy (G_B) and the isokinetic temperature (T_B).

$$q_{st} = T_B(\Delta S) + \Delta G_B \quad (10)$$

Krug's statistical method was used to validate the enthalpy-entropy compensation theory (Krug et al., 1976a; Krug et al., 1976b). The procedure involved comparing the harmonic mean temperature (Equation (11)) to the isokinetic temperature.

$$T_{hm} = \frac{n}{\sum_{i=1}^n \left(\frac{1}{T} \right)} \quad (11)$$

in which n is the number of sorption patterns. An interval of confidence for T_B close to $(1-\alpha)$ 100% was estimated by Equation (12).

$$T_B = T_B \pm t_{m-2, \alpha/2} \sqrt{\text{Var}(T_B)} \quad (12)$$

where,

$$T_B = \frac{\sum (\Delta H - \overline{\Delta H})(\Delta S - \overline{\Delta S})}{\sum (\Delta S - \overline{\Delta S})^2} \quad (13)$$

$$\text{Var}(T_B) = \frac{(\Delta H - \overline{\Delta H} - T_B \Delta S)^2}{(m-2) \sum (\Delta S - \overline{\Delta S})^2} \quad (14)$$

in which, $\overline{\Delta H}$ is the average enthalpy (kJ mol^{-1}), m is the number of data pairs (ΔH , ΔS), $\overline{\Delta S}$ is the average entropy ($\text{kJ/kg} \cdot \text{K}^{-1}$).

3. Results and discussion

3.1. Proximate composition

The proximate composition findings are shown as the media $\pm$ standard deviation of three repetitions. The ora-pro-nóbis leaves presented, in wet basis: $88.20 \pm 0.36 \text{ g}$ of water/100 g; $4.99 \pm 0.02 \text{ g}$ of total fibers/100 g; $3.10 \pm 0.10 \text{ g}$ of proteins/100 g; $1.78 \pm 0.50 \text{ g}$ of carbohydrates/100 g; $1.64 \pm 0.01 \text{ g}$ of ashes/100 g; $0.30 \pm 0.01 \text{ g}$ of

lipids/100 g. Analogous results were found by Takeiti et al. (2009) and Botrel et al. (2020). The leaves presented $a_w = 0.991 \pm 0.02$, suggesting that ora-pro-nóbis leaves are a highly perishable vegetable.

3.2. Desorption isotherms

The desorption isotherms were obtained for a relative humidity range of 5.80%–98.48% at storage temperatures and 5.20%–96.41% under drying temperatures (Fig. 1, Table S2). At storage and drying temperatures, the a_w increased with increasing temperature for a constant X_{eq} . In contrast, the X_{eq} diminished with rising temperature at constant a_w , showing that the leaves became less hygroscopic. This behavior could be attributed to a decrease in the number of active sites for water binding caused by physical and chemical modifications in the leaves due to temperature (Hidar et al., 2018). Furthermore, as the temperature rises, the sorbed water molecules gain a high degree of freedom and kinetic energy allowing them to escape from the surface of the sorbent, and the volume of sorbed water reduces (Ojike et al., 2022), and consequently, the moisture content.

At storage temperatures, when $0.15 < a_w < 0.60$ (Fig. 1a), the X_{eq} increases linearly with increasing a_w . During storage, oxidative and biological reactions are favored when a_w is greater than 0.6, reducing the shelf life of food products and influencing the incidence of microorganisms (Pitt & Hocking, 2009). Therefore, leaves must be dried until 0.1058, 0.1032, 0.1003, 0.0960 kg of water/kg of dry matter to achieve $a_w = 0.6$ and prevent microbial spoilage when stored at 5°C , 10°C , 20°C , 30°C and 40°C , respectively. As stated by Brunauer-Emmett-Teller classification (Brunauer et al., 1938), the desorption isotherm patterns presented a typical sigmoidal shape and hence classified as BET type II, which is typical of a lot of foodstuffs (Hassini et al., 2015) such as black and green tea (Ocieczek et al., 2023), leaves and stems of lemon balm (Argyropoulos et al., 2012), papaya seeds (Rosa et al., 2021), *Cucumis melo* L. seeds (Mallek-Ayadi et al., 2020), and tiger nuts (Zhang et al., 2022).

Table 2 presents the estimated constants and fitting parameters of the evaluated models. Halsey's model showed the lowest values of coefficients of determination (R_{adj}^2) and the highest values of reduced chi-square (χ^2) and square root mean error (RMSE), followed by Oswin and Henderson models, respectively. In contrast, the GAB and Peleg models showed R_{adj}^2 close to one and low calculated values of χ^2 and RMSE at all studied temperatures. Comparing AIC and BIC values (Table 2) for the GAB and Peleg models, the first presented the lowest values; thus, the GAB model was selected to describe the desorption patterns of ora-pro-nóbis leaves at all temperatures. Moreover, the three constants of the GAB model pursue physical meaning (Labuza & Altunakar, 2020).

The monolayer moisture content (X_m) provides information regarding the volume of water strongly attached to the polar sites of the food matrix, and it is a relevant value in ensuring food stability during storage (Kurozawa et al., 2015). The X_m values were around 0.06 kg of water/kg dry matter at all the temperatures studied (Table 2). However, it was observed that there was a discreet increase in the X_m values as the temperature rose, which can be associated with the fitting of the GAB model to the data. During desorption, the water binding sites at the monolayer are initially fully satisfied, so an increase in temperature is expected to have a reduced impact on the sorption surface area (Yogendrarajah et al., 2015). Above the monolayer, chemical reactions which require a water phase start, while above and below the region, the rate of oxidation of lipids increases compromising shelf-life (Labuza & Altunakar, 2020). In this way, after reducing the moisture content until X_m , the leaves maintain their stability when stored under 13%–15% relative humidity ($\text{RH} = 100 \cdot a_w$) in a temperature range of 5°C – 30°C .

The constant 'C' determines the force of water molecule interaction with the main binding sites on the product surface (Muzaffar & Kumar, 2016) while the constant K is an estimation of the interactions between the food matrix and molecules in multilayers (Velázquez-Gutiérrez et al.,

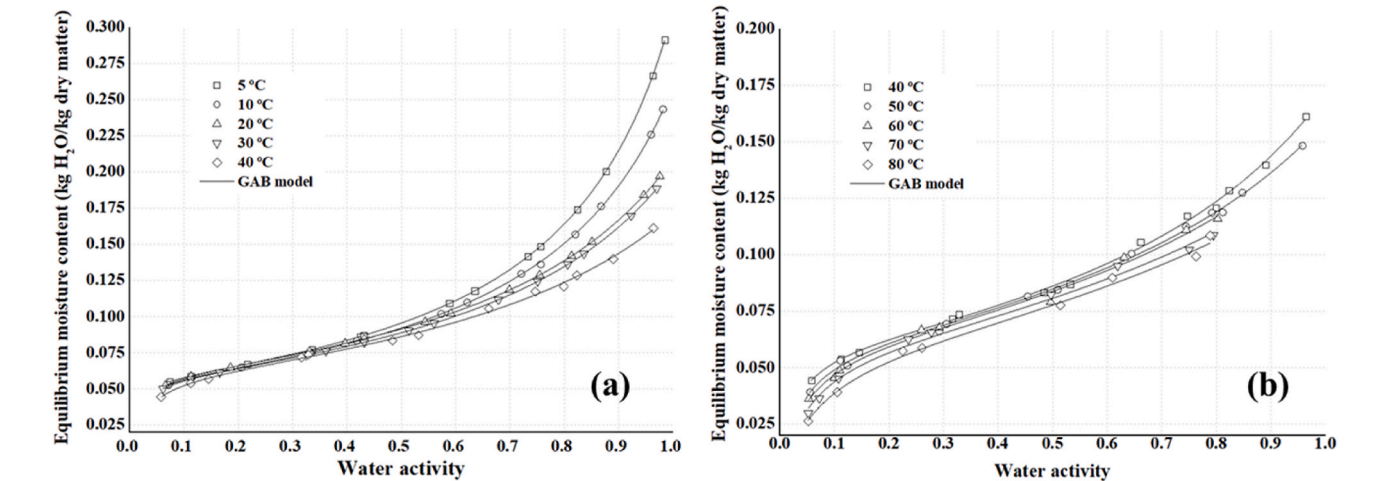


Fig. 1. Desorption isotherms of ora-pro-nóbis leaves at storage (a) and drying (b) temperatures.

Table 2
Constants and fitting parameters of the sorption equations for ora-pro-nóbis leaves.

Model		Temperature (°C)								
		5	10	20	30	40	50	60	70	80
GAB	X _m	0.057	0.057	0.056	0.061	0.060	0.061	0.062	0.062	0.062
	C	147.143	118.313	100.299	100.583	62.535	44.872	37.770	32.389	24.062
	k	0.817	0.781	0.715	0.715	0.653	0.619	0.604	0.573	0.558
	R ² _{adj}	0.999	0.999	0.998	0.996	0.998	0.998	0.993	0.991	0.992
	χ ² • 10 ⁵	0.001	0.099	0.001	0.001	0.309	0.248	0.634	0.729	0.692
	RSME	0.001	0.001	0.001	0.001	0.002	0.002	0.003	0.001	0.003
	AIC	−293.008	−184.536	−280.860	−279.649	−155.337	−158.204	−93.370	−105.033	−78.079
Peleg	BIC	−294.897	−186.425	−282.748	−281.537	−158.078	−160.944	−102.581	−114.244	−91.095
	k ₁	0.107	0.103	0.097	0.094	0.096	0.097	0.101	0.115	0.110
	n ₁	0.278	0.272	0.235	0.234	0.271	0.301	0.342	0.439	0.467
	k ₂	0.196	0.151	0.109	0.105	0.074	0.060	0.052	15.204	770.415
	n ₂	5.025	4.629	3.767	3.742	3.597	3.259	3.670	35.525	47.6563
	R ² _{adj}	0.999	0.999	0.999	0.999	0.997	0.997	0.990	0.996	0.993
	χ ² • 10 ⁵	0.828	0.441	0.084	0.071	0.371	0.307	0.836	0.365	0.599
Oswin	RSME	0.003	0.002	0.001	0.001	0.002	0.002	0.003	0.002	0.003
	AIC	−151.039	−159.868	−183.137	−185.383	−148.774	−151.229	−80.515	−87.986	−61.743
	BIC	−155.344	−164.173	−187.441	−189.688	−154.520	−156.98	−99.529	−106.999	−91.346
	M	0.106	0.099	0.096	0.092	0.087	0.084	0.083	0.079	0.075
	N	0.262	0.243	0.215	0.224	0.207	0.207	0.259	0.261	0.280
	R ² _{adj}	0.966	0.970	0.970	0.974	0.972	0.961	0.989	0.971	0.975
	χ ² • 10 ⁵	19.311	11.186	6.329	4.712	3.725	4.438	0.939	2.448	2.113
Halsey	RSME	0.014	0.011	0.008	0.007	0.006	0.007	0.003	0.005	0.005
	AIC	−113.489	−121.133	−129.108	−133.237	−126.076	−123.8	−95.647	−87.021	−76.419
	BIC	−113.972	−121.616	−129.591	−133.720	−127.048	−124.772	−99.855	−91.229	−82.181
	H ₁ • 10 ⁵	32.206	15.747	5.651	8.343	3.866	3.755	94.678	91.980	114.000
	H ₂	3.392	3.602	3.966	3.746	3.966	3.918	2.593	2.553	2.43
	R ² _{adj}	0.939	0.939	0.932	0.939	0.920	0.895	0.959	0.915	0.928
	χ ² • 10 ⁵	34.689	22.340	14.168	11.229	10.524	11.944	3.490	7.199	6.095
Henderson	RSME	0.019	0.015	0.012	0.011	0.010	0.011	0.006	0.009	0.008
	AIC	−105.289	−111.45	−117.825	−121.080	−112.576	−110.93	−83.8292	−77.3122	−67.9448
	BIC	−105.772	−111.933	−118.308	−121.563	−113.547	−111.902	−88.0375	−81.5205	−73.7065
	H ₁	36.048	67.394	203.312	220.339	600.772	799.359	892.730	952.788	610.703
	H ₂	1.744	1.9870	2.448	2.454	2.823	2.901	2.921	2.894	2.662
	R ² _{adj}	0.974	0.975	0.973	0.974	0.987	0.993	0.990	0.991	0.989
	χ ² • 10 ⁵	15.012	9.335	4.884	4.831	1.726	0.788	0.869	0.731	0.926
	RSME	0.012	0.010	0.007	0.007	0.004	0.003	0.003	0.003	0.003
	AIC	−117.015	−123.666	−132.736	−132.888	−136.077	−146.271	−96.342	−97.896	−83.018
	BIC	−117.498	−124.149	−133.219	−133.371	−137.049	−147.243	−100.550	−102.104	−88.780

2015). In this study, both constants C and k diminished with rising temperature, indicating a decrease in the binding energies associated with the dry matter and the monolayer water, related to the constant C, while a lower value of K implies that the sorbate is in a significantly less structured state in the layer succeeding the monolayer, which is the sorbate's pure liquid state (Ojike et al., 2022).

3.3. Optimal storage conditions

The second derivative of the third-degree polynomial equation indicated that the optimal water activity for preserving the ora-pro-nóbis leaves is 0.35, corresponding to 0.08 kg of water/kg dry matter (Fig. 2). Knowledge and determination of the optimal water activity are

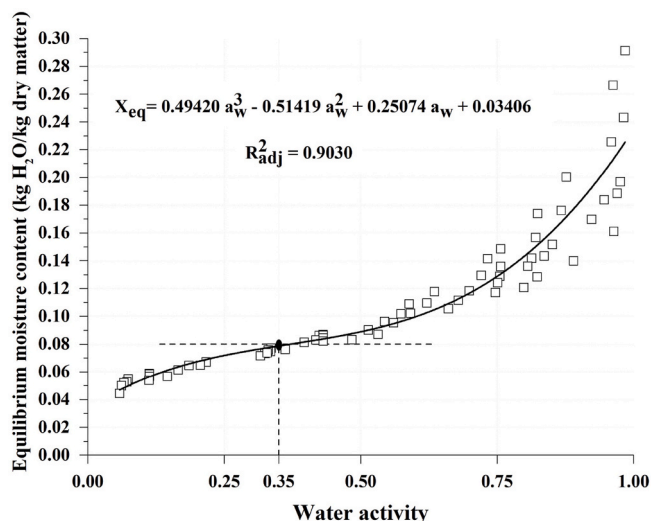


Fig. 2. - Determination of the optimal water activity for preservation of ora-pro-nóbis leaves.

necessary during the drying process because they ensure the best drying and processing conditions for hygroscopic materials (Manga Bengono et al., 2023). Peppermint (Machhour et al., 2012) and stevia leaf powder (Hidar et al., 2018) presented the same optimal a_w .

3.4. Thermodynamic properties

The isosteric heat of desorption is a measure of the energy necessary to break the intermolecular interactions between the bound water and the food matrix in the hygroscopic zone. The heat required to remove water molecules in the hygroscopic domain is the sum of the heat necessary for the liquid-vapor phase change and the desorption isosteric heat (Ouertani et al., 2014). The GAB model was used to calculate the values of a_w and hence, the q_{st} which were plotted against the X_{eq} . The q_{st} decreased abruptly from 7059.25 J/mol to 1342.13 J/mol at the lowest moisture contents (Fig. 3). The highest value of q_{st} is the highest binding energy for water removal, and it is also indicative of the strongest water-solid interaction once the water occupies the most active accessible sites (Khiari et al., 2020). Then, q_{st} slightly increased up to 1782.06 J/mol at 0.13 kg of water/kg of dry matter and thereafter remained approximately constant. The hydrophilic sites became scarcer as the moisture content increased, resulting in decreased coverage of

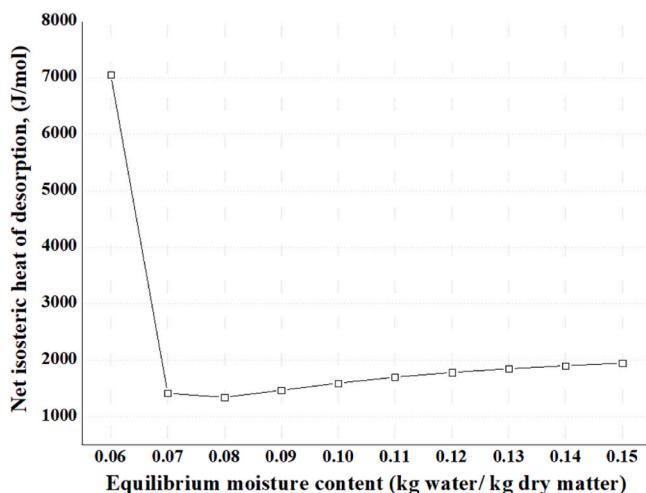


Fig. 3. - Calculated net isosteric heat of desorption of ora-pro-nóbis leaves as function of the equilibrium moisture content.

active sorption sites and the creation of a multilayer. This may need less binding energy for water removal and, as a result, less heat (Ojike et al., 2022). A similar trend was observed in another leaves (Argyropoulos et al., 2012; Dalgıç et al., 2012; Moussaoui et al., 2019).

Similar to q_{st} , the differential enthalpy (ΔH) of sorption measures the water binding strength, which is critical for designing efficient dehydration process equipment and understanding qualitatively the status of water on the food surface (Taghnamas et al., 2021). Generally, differential enthalpy is a positive quantity when heat is evolved during adsorption and negative when heat is absorbed during desorption (Al-Muhtaseb, McMinn, & Magee, 2002). Fig. 4 shows that the ΔH increased as the X_{eq} decreased, indicating the occupation of highly accessible sites (Velázquez-Gutiérrez et al., 2015); thus, more energy is required to remove water as the X_{eq} reduces from 0.15 to 0.06 kg of water/kg of dry matter once the water binding strength is higher. Differential entropy was calculated as the intercept of the line $\ln(a_w)$ vs. $1/T$ using Equation (9), and it showed a considerable dependence on moisture content. The change in differential entropy (ΔS) is proportional to the number of available sorption sites associated with a certain energy level and is related to the degree of disorder or randomness (spatial arrangement) in the water-sorbent system (Khiari et al., 2020). In Fig. 4, it is shown that the ΔS presented its biggest value, 8.36 J/(mol•K), at X_m . The highest water mobility is shown by the biggest entropy value, which may be explained by the strongest interactions between water molecules and the adsorbent surface that has the most active sorption sites (Mbarek & Mihoubi, 2019). As the moisture content increased, ΔS achieved its minimum value of -5.72 J/(mol•K), then increased until 5.18 J/(mol•K). This is indicative of some mobility and vibrational/rotational freedom at low moisture coverage, followed by a decrease in entropy due to localization as the first layer builds up. Finally, the entropy of sorbed water increases with the higher mobility associated with the buildup of layers further removed from the food surface (Rizvi, 2014). Other vegetables, such as apple (Moraes et al., 2008), sugar beet (de Oliveira et al., 2017) and tiger nut (Zhang et al., 2022) presented the same behavior.

The first condition to ensure enthalpy-entropy compensation is a strong linear correlation between enthalpy and entropy (Sanches et al., 2023), and the second is concerning the isokinetic temperature (T_B), in which T_B must be statistically different from the harmonic mean temperature (T_{hm}) (Krug et al., 1976a; Krug et al., 1976b). In Fig. 5, it is shown the linear relationship ($R^2_{adj} = 0.9924$) between q_{st} and entropy, confirming the existence of a compensation mechanism. In this study, $T_B = 75.72 \pm 6.11$ K was significantly ($p < 0.05$) different from the $T_{hm} = 311.72$ K, corroborating the enthalpy-entropy compensation theory. Moreover, the desorption process is entropy-driven because $T_B < T_{hm}$

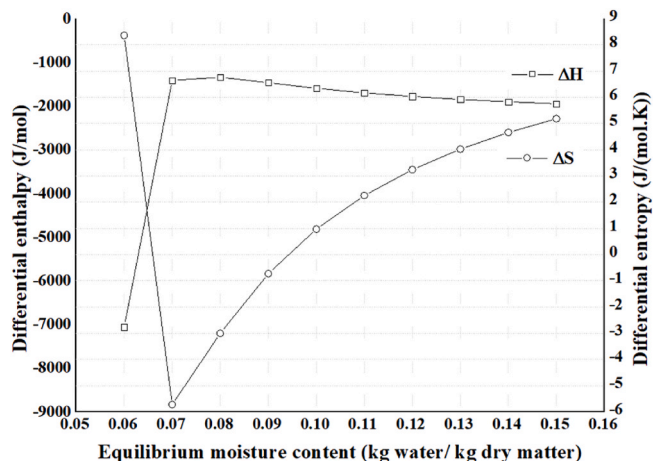


Fig. 4. - Calculated differential enthalpy and differential entropy of ora-pro-nóbis leaves as function of the equilibrium moisture content.

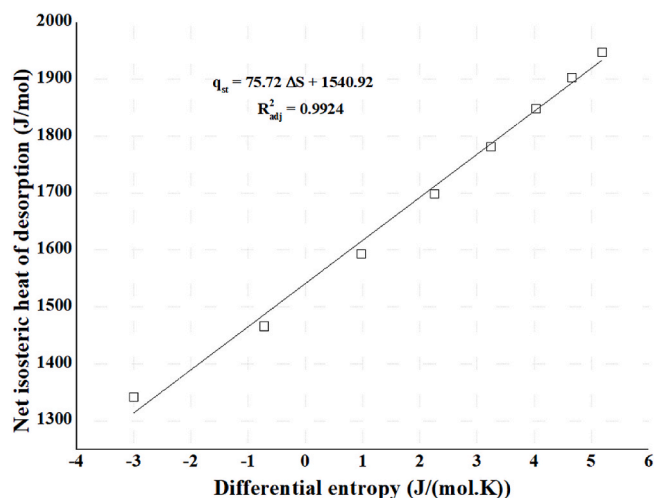


Fig. 5. - Linear relationship between net isosteric heat of desorption and entropy.

(Leffler, 1955). When the sorption process is entropy-driven, the barriers that confine the water molecules inside the microstructure of the food matrix are more relevant than energy interactions regarding the chemical composition of food (Spada et al., 2013). Gibb's free energy was equal to +1540.92 J/mol, thus, the desorption process is non-spontaneous. A positive value for Gibbs free energy is characteristic of an endothermic reaction, meaning that the reaction is not spontaneous and needs energy from the surroundings to proceed (de Oliveira et al., 2017).

4. Conclusion

The reduction in temperature and increase in relative humidity resulted in increase of equilibrium moisture content. The desorption isotherm patterns present a sigmoid shape, which were classified as BET Type II, best described by the GAB model due to its good fitting parameter and lowest AIC and BIC values. Ora-pro-nóbis leaves must contain about 0.1 kg of water/kg dry matter when stored at temperatures between 5 and 40 °C to guarantee microbiological safety ($a_w \leq 0.6$), in addition, the optimal water activity is 0.35 in the same range of

temperature. The X_m indicated that ora-pro-nóbis leaves maintain their stability when stored under 13%–15% relative humidity ($RH = 100 \cdot a_w$) in a temperature range of 5 °C–30 °C. The net isosteric heat of desorption decreased with rising X_{eq} , and differential entropy increased directly when $X_{eq} > 0.07$. The enthalpy-entropy compensation theory was confirmed, and desorption was entropy-driven ($T_B < T_{hm}$), endothermic, and non-spontaneous ($\Delta G_B > 0$).

CRediT authorship contribution statement

André Luiz Borges-Machado: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Marcio Augusto Ribeiro-Sanches:** Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Maria Júlia Neves-Martins:** Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Priscila Alonso dos Santos:** Investigation, Methodology, Resources, Supervision, Writing – original draft, Writing – review & editing. **Guadalupe Luna-Solano:** Methodology, Resources, Supervision, Writing – original draft, Writing – review & editing. **Javier Telis-Romero:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) - Award Number: 314459/2021-9.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lwt.2024.115749>.

Nomenclature

LiBr	Lithium bromide
LiCl	Lithium chloride
MgCl ₂	Magnesium chloride
NaI	Sodium iodide
K ₂ CO ₃	Potassium carbonate
Mg(NO ₃) ₂	Magnesium nitrate
NaBr	Sodium bromide
KI	Potassium iodide
NaCl	Sodium chloride
(NH ₄) ₂ SO ₄	Ammonium sulfate
KCl	Potassium chloride
KNO ₃	Potassium nitrate
K ₂ SO ₄	Potassium sulfate
a_w	Water activity
C	Constant of GAB model
GAB	uggenheim-Anderson-de Boer

h_1 and h_2	Constants of Halsey model
H_1 and H_2	Constants of Henderson model
k	Constant of GAB model
k_1 and k_2	Constants of Peleg model
m	Number of (ΔH , ΔS) data pairs
M and N	Constants of Oswin model
n	Number of isotherms
n_1 and n_2	Constants of Peleg model
C_r	Isosteric heat of sorption at the first water molecule
B_r	Constant of Riedel's model
Q_{st}	Integral heat of sorption
q_{st}	Net isosteric heat of sorption
R	Universal gas constant (8.314 J/mol•K)
R^2_{adj}	Adjusted coefficient of determination
RMSE	Root mean square error
RH	Relative humidity
T	Temperature
T_B	Isokinetic temperature
T_{hm}	Harmonic mean temperature
X_{eq}	Equilibrium moisture content
X_m	Monolayer moisture content
λ	Heat vaporization of pure water
ΔG_B	Free Gibbs energy at isokinetic temperature
$\overline{\Delta H}$	Average enthalpy
ΔH	Differential enthalpy of sorption
$\overline{\Delta S}$	Average entropy
ΔS	Differential entropy of sorption
χ^2	Reduced chi-square

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