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Physics

Mathematical modelling of the hygroscopicity of *Moringa oleifera* Lam cake and thermodynamic properties

Modelagem matemática da higroscopicidade da torta de *Moringa oleifera* Lam e propriedades termodinâmicas

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ABSTRACT

Moringa oleifera L. is a plant that was introduced and adapted to the environmental conditions of Brazil. Different parts of the plant are used for various purposes; specifically, the cake residue from the extracted oil from its grains are normally used to treat wastewater. The objective of this study was to examine the hygroscopicity using the adsorption isotherms and carry out mathematical modelling to subsequently calculate the thermodynamic properties of *Moringa oleifera* L. cake. For this purpose, saline solutions at a relative air humidity between 10.75 and 85.11% and temperatures ranging from 20 to 70 °C were used. The static gravimetric method was used to obtain the equilibrium water content, and nine mathematical models were tested with the experimental data. As a result, the Sigma Copace and modified Halsey models provided the optimal results. As the water content increased during the adsorption process, the energy released (Q_{st}) in the process decreased, fewer sites for sorption (ΔS) were present, and the process became less spontaneous (ΔG).

Keywords: Hygroscopic equilibrium; Mathematical models; Energy

RESUMO

Moringa oleifera L. é uma planta que foi introduzida e está adaptada às condições ambientais do Brasil. Diferentes partes da planta são usadas para vários propósitos; especificamente, o resíduo da torta do óleo extraído de seus grãos é normalmente usado para tratar águas residuárias. O objetivo deste estudo foi examinar a higroscopicidade usando as isotermas de adsorção e realizar modelagem matemática para posteriormente calcular as propriedades termodinâmicas da torta de *Moringa oleifera* L. Para este propósito, foram utilizadas soluções salinas com umidade relativa do ar entre 10,75 e 85,11% e temperaturas variando de 20 a 70 °C. O método estático gravimétrico foi utilizado para

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obtenção do teor de água de equilíbrio, e nove modelos matemáticos foram testados com os dados experimentais. Como resultados, os modelos de Sigma Copace e Halsey modificado forneceram os melhores resultados. A medida que o teor de água aumenta no processo de adsorção a energia liberada (Δst) no processo diminui, menos sítios para a adsorção (ΔS) estavam presentes, e o processo tornou-se menos espontâneo (ΔG).

Palavras-chave: Equilíbrio higroscópico; Modelos matemáticos; Energia

1 INTRODUCTION

Moringa oleifera is a plant originating from India that was introduced and adapted to the climate conditions in Brazil. This plant belongs to the Moringaceae family, which comprises one genus and fourteen species, and *Moringa oleifera* is the best known species (Anwar et al., 2007). Roots, tree cortexes, leaves, and grains of this species are used in industrial sectors, animal and human consumption and medicine. The cationic protein contained in the grains of this plant acts as a natural clarifier for wastewater; this is one of its main applications (Sánchez-Peña et al., 2013; Agustini et al., 2015).

Environmental conditions, soil fertility and mainly plant genetics are responsible for the variation in the chemical composition of the grain (Sánchez-Machado et al. 2010). For the processing of oilseeds, the physical extraction process uses a mechanical press; however, this process is less efficient because not all of the oil is removed and excess oil remains in the cake (Singh; Bargale, 2000). The constituents of agricultural products include starch, fat, proteins, etc. These products may or may not have an affinity for water. Products with a greater proportion of lipids have lower equilibrium water contents than that the starches under the same storage conditions (temperature and relative humidity) (Brooker et al., 1992).

Agricultural products are hygroscopic, that is, when they are in contact with the environment, they can lose or gain water in the form of vapour, these phenomena are known as desorption and adsorption, respectively. These products maintain a balance between the relative humidity and air temperature, resulting in an equilibrium water content or hygroscopic equilibrium, which can change depending on the characteristics of the constituents (Almeida et al., 2013; Granella et al., 2020; Isquierdo et al., 2020a).

In the drying and storage of agricultural products, this equilibrium water content is important for determining the water gain or loss under certain temperature and relative humidity conditions (Ghodake et al., 2007). According to Borém (2008), when

the product is in hygroscopic equilibrium with the environment, the water activity (a_w) and relative humidity are approximately equal, and this water activity (a_w) can be understood as the free water in the biological product.

Free water can compromise the quality of the agricultural products, as it is available for chemical, physical and biological reactions (Welti-Chanes; Vergara, 1997). According to Pumacahua-Ramos et al. (2017), a water activity above 0.7 enables the development of fungi, which causes the product to deteriorate. The hygroscopic behaviour of biological products can be studied via the analysis of sorption isotherms; these isotherms can determine the chemical, physical and microbial stability conditions required to maintain the quality of the stored product (Sogi et al., 2003; Corrêa et al., 2015). According to Goneli et al. (2007), through sorption isotherms, the water activity range (aw) of the product can be determined with respect to where the microorganisms form. Mathematical models can predict the equilibrium water content of a product under certain environmental conditions; the curves formed by these models are known as sorption isotherms. Empirical models are used more than theoretical models because the latter do not accurately predict the equilibrium water content for a wide range of water activities and temperatures (Resende et al., 2006; Corrêa et al., 2016).

Sorption isotherms constructed through mathematical models have been investigated for a wide variety of agricultural products; the models used with experimental data for different products include the following: the Copace and GAB models for Feijão Adzuki (Almeida et al., 2013); the models by Henderson, Modified Henderson, Cavalcanti Mata, Chung Pfost, Modified Chung Pfost, and Chen Clayton for the Cabacinha pepper (Silva et al., 2015); the Chung-Pfost model for Crotalaria seeds (Granella et al., 2020); and the Chung-Pfost model for Tunge seeds (Costa et al., 2021). To understand the relationships among the product, water and energy required for designing equipment for drying the agricultural products (Oliveira et al., 2013) and to understand sorption during storage, thermodynamic properties are needed. Thermodynamic properties such as enthalpy, entropy and Gibbs free energy (Corrêa et al., 2010) are the most commonly used and can be calculated through the sorption isotherms (Silva et al., 2015).

According to McMinn et al. (2005), in the sorption process, the variation in energy due to the interaction of the water molecules with the product constituents causes a change in enthalpy. Entropy is related to the degree of order or disorder in the system in the water-constituent relationship of the product. According to Oliveira et al. (2014), the Gibbs free energy provides information regarding the energy required for the water molecules of the product to transition to the vapour state and vice versa. Given the importance of the hygroscopicity of agricultural products and their relationships with their constituents, the objective of this work was to determine the adsorption isotherms of *Moringa oleifera* Lam grain cake, adjust the mathematical models to these experimental data and calculate its thermodynamic properties.

2 MATERIALS AND METHODS

After reaching physiological maturity, the grains were harvested when they reached a brown colour in the pods (Agustini et al., 2015). The grains were removed from the pods, placed in Styrofoam boxes and sent by Controle Consultoria Ambiental in the State of Pará to the Federal University of Lavras (UFLA), where the experiments were conducted.

The grains were dried in the agricultural products processing laboratory. Artificial drying was carried out in a laboratory convective dryer, the drying air temperature was 40 °C, the air speed was 0.33 m s^{-1}, and drying was carried out until the grains had a water content of 6%. The water content before and after drying was determined using the oven method at 105 ± 3 °C for 24 h (Brasil, 2009). Drying was carried out in triplicate, with ± 0.55 kg in each tray.

The extraction of oil from the grains and analysis of the hygroscopicity of the cake were carried out in the Oleaginous Plants, Oils, Fat and Biodiesel Laboratory of the Department of Agricultural Engineering of the same university. The extraction of oil from the dried grain was carried out using a Scott Tech expeller press, model ERT 50, at the same pressure. Samples were collected from the cakes after the extraction for subsequent hygroscopicity testing. The methodology used by Isquierdo et al. (2020b) was adopted for modelling the adsorption isotherms of moringa cake. The cake from drying at 40 °C was used, and the initial water content was determined. Then, the samples were placed in hermetic “Gerbox” containers with saturated saline

solution and subjected to biochemical oxygen demand (BOD) at controlled temperatures of 20, 30, 55 and 70 °C.

The static-gravimetric method was used to determine the hygroscopic equilibrium water content, and in each repetition, 2 ± 0.3 g of cake was placed inside the airtight containers. The moringa cake samples were weighed using a semi-analytical balance with a precision of 0.01 g every 24 h until there was no more variation in mass; at this time, hygroscopic equilibrium was reached between the cake and the environment. At this point, the equilibrium water content was determined by the difference in water mass from the starting point to the end.

Table 1 lists the saline solutions and their generated relative humidities upon exposure to certain temperatures. For this study, three repetitions were made for each combination of temperature and relative humidity.

Table 1 – Relative humidity of saline solutions when exposed to different temperatures

Temperature (°C)	**Salts**		**RH (%)**
20	Magnesium chloride	$MgCl_2$	33.07 ± 0.18
	Lithium chloride	LiCl	11.31 ± 0.31
	Potassium chloride	KCl	85.11 ± 0.29
	Magnesium nitrate	$Mg(NO_3)$	54.38 ± 0.23
	Potassium acetate	CH_3COOK	23.11 ± 0.25
30	Magnesium chloride	$MgCl_2$	32.44 ± 0.14
	Lithium chloride	LiCl	11.28 ± 0.24
	Potassium chloride	KCl	83.62 ± 0.25
	Magnesium nitrate	$Mg(NO_3)$	51.40 ± 0.24
	Potassium acetate	CH_3COOK	21.61 ± 0.53
55	Lithium chloride	LiCl	11.03 ±0.23
	Potassium chloride	KCl	80.70 ± 0.35
	Sodium bromide	NaBr	50.15 ± 0.65
	Magnesium chloride	$MgCl_2$	29.93 ± 0.16
70	Lithium chloride	LiCl	10.75 ± 0.33
	Potassium chloride	KCl	79.49 ± 0.57

Source: Greemspan (1977)

Mathematical simulations were carried out with the equations provided in Table 2; these equations describe the phenomenon of hygroscopicity in the different products. This was done with the aim of obtaining the adsorption isotherms of moringa cake for different water activities.

Table 2 – Mathematical models for obtaining the adsorption isotherms of *Moringa oleifera* L. cake

Model Name	Model	Equation
BET[1]	$Xe = \left\{ \frac{1}{[(1-a_w)(1/a \cdot b + ((a-1)/a \cdot b))]} \right\}$	(1)
Chung Pfost[2]	$Xe = a - b\ln[-(T+c)\ln(a_w)]$	(2)
Copace[3]	$Xe = \exp[a - (bT) + (ca_w)]$	(3)
Modified GAB[4]	$Xe = (a \cdot b \cdot a_w) \cdot \frac{(c/T)}{[1-b \cdot a_w + (c/T) \cdot b \cdot a_w] \cdot (1-b \cdot a_w)}$	(4)
Modified Henderson[5]	$Xe = \{\ln(1-a_w)/[-a(T+b)]\}^{1/c}$	(5)
Sabbah[6]	$Xe = a(a_w^b / T^c)$	(6)
Sigma Copace[7]	$Xe = \exp\{a - (bT) + [c\exp(a_w)]\}$	(7)
Modified Halsey[8]	$Xe = \left(\frac{\exp(a-(b \cdot T))}{-\log(a_w)}\right)^{1/c}$	(8)
Andrade[9]	$Xe = \exp\left\{(a \cdot a_w) + (T^b) + \left[\frac{(T-a_w)^b}{a_w}\right]\right\}^c$	(9)

Source: (Brunauer; Emmett; Teller, 1938)[1]; (Chung; Pfost, 1967)[2]; (Corrêa; Martins; Melo, 1995)[3]; (Van den Berg, 1984)[4]; (Thompson; Peart; Foster, 1968)[5]; (Mesquita *et al.*, 2001)[6]; (Corrêa; Martins; Melo, 1995)[7]; (Iglesias; Chirife, 1976)[8]; (Andrade *et al.*, 2017)[9]

where:

X_e: equilibrium moisture content, in db;

T: ambient air temperature, °C;

T_{abs}: absolute ambient air temperature, in K;

a_w: water activity, decimal;

a, b, c: parameters that depend on the nature of the product.

To adjust the mathematical models to the experimental data, the Quasi-Newton method was used. The best model that represented the moringa cake hygroscopicity data was selected based on the magnitude of the adjusted coefficient of determination (R_a^2), relative mean error (P) and estimated mean error (SE). According to equations 10, 11 and 12,

To compare models with different numbers of parameters, the adjusted coefficient of determination was used, which considers the number of parameters in the model. In the estimated model, the coefficient of determination R^2 does not weigh the parameters (Ratkowski, 1983; Draper; SMITH, 1998).

$$R_a^2 = 1 - \left[\frac{(n-i)(1-R^2)}{n-p}\right] \tag{10}$$

where:

R_a^2: adjusted coefficient of determination;

R^2: determination coefficient;

n: number of observations;

i: related to the adjustment of the curve intercept, being equal to 1 if there is an intercept and equal to 0 if there is no intercept in the model;

p: number of parameters.

The formula adjusts the number of variables between one model and another and enables a homogeneous comparison.

$$P = \frac{100}{n}\sum \frac{|Y_{\text{obs}} - \hat{Y}_{\text{est}}|}{Y_{\text{obs}}} \tag{11}$$

$$SE = \sqrt{\sum \frac{(Y_{\text{obs}} - \hat{Y}_{\text{est}})^2}{DF}} \tag{12}$$

where:

Y_{obs}: experimentally observed moisture content;

$\hat{Y}_{\text{est}}$: moisture content estimated by the model;

n: number of experimental observations;

DF: model degrees of freedom (number of experimental observations minus number of model coefficients).

The mathematical model that best fit the experimental adsorption data was determined, and this model was used to obtain the thermodynamic properties based on the predicted equilibrium water contents.

Equations 13 and 14 were used to determine the latent heat of condensation of the water vapour and the integral isosteric heat of adsorption or enthalpy, respectively (Chaves et al., 2015):

$$L = -2502.2 + 2.39 \cdot T_m \tag{13}$$

$$Q_{\text{st}} = q_{\text{st}} + L \tag{14}$$

where:
Q_{st}: integral isosteric heat of adsorption sorption, kJ kg^{-1};
L: latent heat of condensation of the water vapour, kJ kg^{-1};
T_m: average temperature range of the study, °C.

According to Corrêa, Oliveira and Santos (2012), the net isosteric heat of adsorption or differential enthalpy for each equilibrium water content can be obtained using equation 15:

$$\ln(a_w) = \pm \left(\frac{\Delta q_{\text{st}}}{R T_{\text{abs}}} - \frac{\Delta S}{R} \right) \tag{15}$$

where:
q_{st}: net isosteric heat of adsorption, kJ kg^{-1};
T_{abs}: absolute temperature, K;
R: universal gas constant for the water vapour, 0.4619 kJ kg^{-1} K^{-1};
ΔS: differential entropy of adsorption, kJ kg^{-1} K^{-1}.

According to Rizvi (1995), differential entropy can be calculated from the Gibbs–Helmholtz using equation 16:

$$\Delta S = \frac{\Delta q_{\text{st}} - \Delta G}{T_{\text{abs}}} \tag{16}$$

where:

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

ΔG: Gibbs free energy, kJ kg^{-1}.

According to Oliveira et al. (2013), the Gibbs free energy can be calculated from equation 17:

$$\Delta G = R \cdot T_{\text{abs}} \cdot \ln(a_w) \tag{17}$$

3 RESULTS AND DISCUSSION

Table 3 provides the adjustment of the mathematical models to the experimental data on the adsorption of *Moringa oleifera* L. cake. Thus, the Sigma Copace, modified Halsey and modified GAB models are the optimal models that best represented the adsorption phenomenon, with coefficients of determination close to 100%, average relative errors below 10% and an estimated error close to 0.

Table 3 – Mathematical models adjusted to experimental adsorption data from *Moringa oleifera* L. cake with parameters and adjustment evaluators; coefficient of determination (R^2), mean relative error (P), and mean estimated error (SE)

Model	**a**	**b**	**c**	**R^2 (%)**	**P (%)**	**SE (decimal)**
BET	0.100	36.903	–	87.401	20.062	0.041
Chung Pfost	0.362	0.048	405.353	90.149	15.304	0.036
Copace	-3.469	0.004	2.080	93.225	10.725	0.030
Modified GAB	0.041	0.885	1895.685	92.555	9.519	0.032
Modified Henderson	0.147	197.432	1.570	91.183	15.729	0.034
Sabbab	0.241	0.964	0.088	86.718	21.673	0.042
Sigma Copace	-4.426	0.003	1.170	93.739	8.595	0.029
Modified Halsey	-4.836	0.004	1.771	93.385	9.249	0.030
Andrade	-1.236	0.028	-1.590	92.251	11.202	0.032

Source: Organized by the authors (2023)

As provided in Table 3, the Sigma Copace and modified Halsey models obtained R^2 values of 93.739 and 93.385%, P values of 8.595 and 9.249 and SE values of 0.029 and 0.030, respectively. Using equation 10, R_a^2 was calculated to be 90.608 and 90.077%, respectively. To calculate the thermodynamic properties of *Moringa oleifera* L. cake, the modified Halsey model was used because it did not yield negative values in the calculation of the water activity (a_w) for the different combinations of equilibrium water content and temperature.

In the literature, several mathematical models have been adjusted to experimental data on the hygroscopicity of agricultural products; these models include the Andrade model for the Dedo-de-Moça pepper (Andrade et al., 2017), the Smith model for sunflower seeds (Campos et al., 2019), the Chung-Pfost model for Tunge seeds (Costa et al., 2021), and the Chung-Pfost model for safflower seeds (Bessa et al., 2021).

The salt solutions from Table 4 at the specific stated temperatures generate certain equilibrium relative humidity conditions. When the cake reaches the equilibrium water content under these temperature and relative humidity conditions, the relative humidity is approximately equal to the water activity of the cake (Sauer, 1995).

Table 4 lists the equilibrium water content estimated by the modified Halsey model, in addition to the absolute temperature used in the calculations. Based on the data in Table 4, for the same temperature, when the relative humidity of the environment increases, the equilibrium water content follows the same trend.

Table 4 – Equilibrium water content estimated with the modified Halsey model for *Moringa oleifera* L. cake

Salt	HR (decimal)	Temp (°C)	Calculated equilibrium water content (db)	Estimated equilibrium water content (db)	T_{abs}	$1/T_{abs}$
Potassium chloride	0.851	20	0.157	0.174	293	0.0034
Magnesium nitrate	0.544	20	0.081	0.082	293	0.0034
Potassium acetate	0.231	20	0.048	0.050	293	0.0034
Potassium chloride	0.836	30	0.176	0.160	303	0.0033
Magnesium nitrate	0.514	30	0.078	0.076	303	0.0033
Potassium acetate	0.216	30	0.046	0.048	303	0.0033
Lithium chloride	0.110	55	0.042	0.036	328	0.0030
Potassium chloride	0.807	55	0.162	0.136	328	0.0030
Lithium chloride	0.108	70	0.032	0.035	343	0.0029
Potassium chloride	0.795	70	0.103	0.126	343	0.0029

Source: Organized by the authors (2023)

Table 5 shows the water activities in decimal form for *Moringa oleifera* L. cake according to the equilibrium water content (db) and temperature (°C) estimated by the modified Halsey model.

Table 5 – Water activity (a_w) estimated by the modified Halsey model for *Moringa oleifera* L. cake according to the equilibrium water content (db) and temperature (°C)

Equilibrium water content (db)	**Temperature °C**			
	20	**30**	**55**	**70**
0.035	0.063	0.071	0.093	0.107
0.036	0.077	0.086	0.110	0.127
0.048	0.202	0.216	0.253	0.276
0.050	0.231	0.246	0.284	0.307
0.076	0.499	0.514	0.550	0.571
0.082	0.544	0.558	0.592	0.612
0.126	0.752	0.761	0.783	0.795
0.136	0.779	0.788	0.807	0.818
0.160	0.830	0.836	0.852	0.860
0.174	0.851	0.857	0.871	0.878

Source: Organized by the authors (2023)

As shown in Table 5, for the same temperature, the increase in the water activity occurred at the same time as the increase in the equilibrium water content; this resulted in greater water availability in the cake, and similar results were observed by Campos et al. (2019) in their study on sunflower seeds.

Water activities between 0.6 and 0.7 can prevent the growth of microorganisms in many foods (BELL; LABUZA, 1992). According to Christensen and Kaufmann (1974), the development of the main fungi in products of plant origin for a temperature range of 26 to 30 °C occurs with water activities of 0.70 to 0.85 for *Aspergillus* species and 0.85 for *Penicillium* (several species). Regarding this study, values equal to or below 0.082 (db) in the equilibrium water content are within the safe range for storage at temperatures of 20, 30, 55 and 70 °C since they have water activities approximate of 0.544, 0.558, 0.592, and 0.612, respectively.

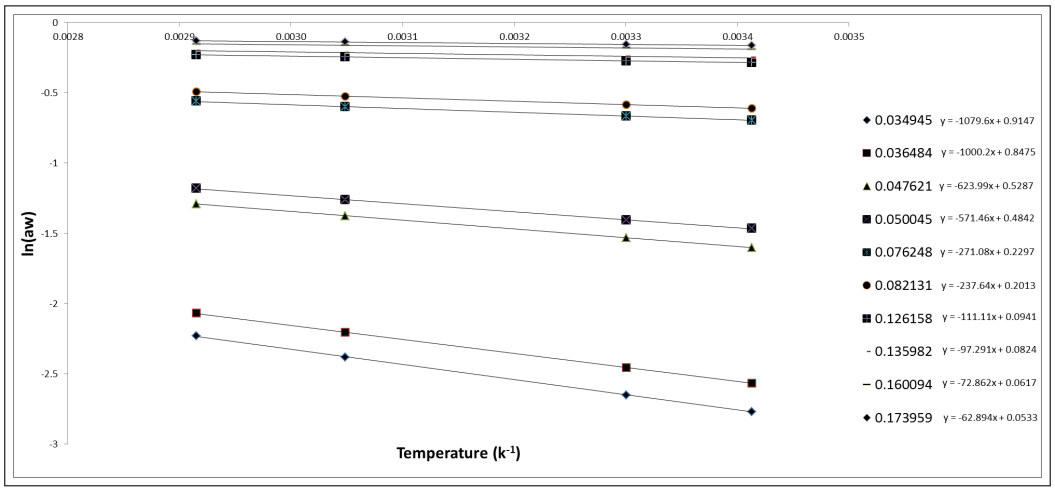
Figure 1 shows the slope angle coefficient of the equations for each equilibrium water content (db) obtained using the $\ln(a_w) \times (T_{abs}^{-1})$ graph. This angle of inclination of each equilibrium water content (db) was used to calculate the net isosteric heat of adsorption (or differential enthalpy) according to equation 15.

To calculate the net isosteric heat of adsorption (or differential enthalpy), the latent heat of condensation of water vapour was calculated using equation 13, with the average temperature used in the experiment (43.75 °C), and was determined to be -2397.638 kJ kg^{-1}. The results of the inclination angle coefficients, net isosteric heat of adsorption, and calculated and estimated integral isosteric heat (equation 18) for each equilibrium water content (db) are listed in Table 6.

Equation 18 was used to calculate the integral isosteric heat estimated for each equilibrium water content (db), and the coefficients were as follows: a of 1526.556 and b of -33.1903, with a coefficient of determination (R^2) of 98.327%.

$$Q_{st} = a \cdot \exp(b \cdot U_e) + 2397.638 \quad (18)$$

Figure 1 – Values of the inclination angle coefficients for each equilibrium water content (db) for *Moringa oleifera* L. cake



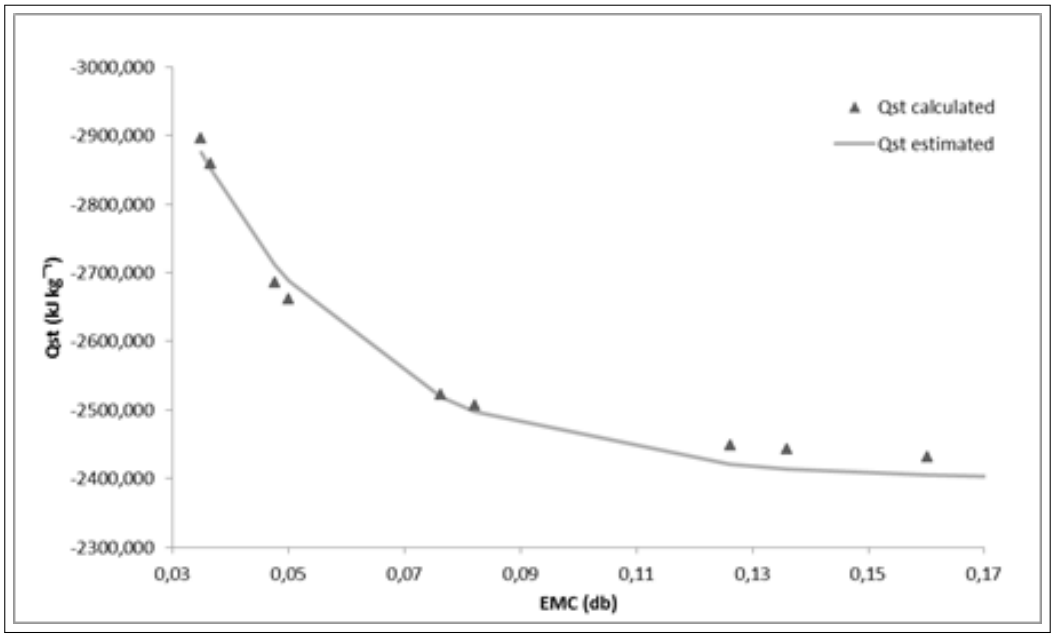
Source: Authors (2023)

Table 6 – Slope of the straight line, net isosteric heat, and integral isosteric heat calculated and estimated by the model for *Moringa oleifera* L. cake

Slope of the straight line	Net isosteric heat (kJ kg^{-1})	Integral isosteric heat Q_{st} calculated (kJ kg^{-1})	Integral isosteric heat Q_{st} estimated (kJ kg^{-1})
-1079.6	-498,667	-2896,305	-2876,271
-1000.2	-461,992	-2859,630	-2852,436
-623.99	-288,221	-2685,858	-2711,896
-571.46	-263,957	-2661,595	-2687,603
-271.08	-125,212	-2522,849	-2519,157
-237.64	-109,766	-2507,403	-2497,602
-111.11	-51,322	-2448,959	-2420,824
-97.291	-44,939	-2442,576	-2414,372
-72.862	-33,655	-2431,292	-2405,155
-62.894	-29,051	-2426,688	-2402,382

Source: Organized by the authors (2023)

Figure 2 – Integral isosteric heat calculated and estimated as a function of the equilibrium water content (db) for *Moringa oleifera* L. cake



Source: Authors (2023)

For equilibrium water content values between 0.035 and 0.174 (db), the calculated values for the integral isosteric heat are between -2896.305 and -2426.688 kJ kg^{-1}. Figure 2 shows that as the equilibrium water content (db) increases, less energy is released by the adsorption process; additionally, the negative signal indicates an exothermic process, as demonstrated by Isquierdo et al. (2020b) for passion fruit seeds and Teixeira et al. (2018) for pumpkin seeds.

According to Aviara & Ajibola (2002), the decrease in integral isosteric heat with increasing equilibrium water content (db) verifies the decrease in the bond strength between the water molecules and dry matter. According to Kaya & Kahyaoglu (2005), greater energy and heat of adsorption are released to adsorb water vapour in products with low water content.

To calculate the differential entropy and Gibbs free energy, equations 16 and 17, respectively, were used. Table 7 shows the Gibbs free energy and differential entropy values for each equilibrium water content (db) for *Moringa oleifera* L. cake.

Table 7 – Gibbs free energy and differential entropy for each equilibrium water content (db) for *Moringa oleifera* L. cake

Equilibrium Water Content (db)	**Net isosteric heat (kJ kg^{-1})**	**R**	**Gibbs free energy (kJ kg^{-1}) ΔG**	**Differential entropy (kJ kg^{-1} K^{-1}) ΔS**
0.035	-498,667	0.462	-353,750	-0,422
0.036	-461,992	0.462	-333,593	-0,391
0.048	-288,221	0.462	-214,226	-0,244
0.050	-263,957	0.462	-198,427	-0,224
0.076	-125,212	0.462	-93,064	-0,106
0.082	-109,766	0.462	-82,523	-0,093
0.126	-51,322	0.462	-36,413	-0,043
0.136	-44,939	0.462	-32,455	-0,038
0.160	-33,655	0.462	-25,020	-0,028
0.174	-29,051	0.462	-21,837	-0,025

Source: Organized by the authors (2023)

For equilibrium water contents (db) between 0.035 and 0.174, the Gibbs free energies were -353.750 to -21.837 kJ kg^{-1}, respectively, and the differential entropies were -0,422 to -0.025 kJ kg^{-1} K^{-1}, respectively.

As shown in Table 7, as the equilibrium water content (db) increases, the process becomes less spontaneous, as determined by the Gibbs free energy. As the equilibrium water content increases, the differential entropy decreases. This result shows less energy as a result of the reduction in sorption space due to saturation and the higher mobility of water molecules in the *Moringa oleifera* L. cake. Similar trends in Gibbs free energy and differential entropy were found in the work by Oliveira et al. (2022) for chia seeds.

According to McMinn et al. (2005), the thermodynamic property of Gibbs free energy indicates whether the sorption process is spontaneous ($\Delta G < 0$) or nonspontaneous ($\Delta G > 0$) and provides information regarding the affinity between the product and water. The variation in Gibbs free energy values during the product sorption process is the energy required to change the state of the water molecules from a solid surface to a gaseous state or in the opposite direction (Nayak & Pandey, 2000).

At a specific energy level, the number of available sorption sites is proportionally related to the differential entropy, which indicates the state of mobility of water molecules in the material (Al-Muhtaseb; McMinn & Magee, 2004). With an increase in the water content, the sorption sites begin to saturate, and multiple layers are formed, causing more rotational movement of water molecules and increasing the differential entropy (Benado & Rizvi, 1985).

Similar results were obtained by Arruda-Silva et al. (2022) for Baru flours for their differential enthalpy, differential entropy and Gibbs free energy upon calculation of the thermodynamic properties through the water adsorption isotherm data.

4 CONCLUSIONS

The Sigma Copace and modified Halsey models were the optimal models that best represented the hygroscopicity of *Moringa oleifera* L. cake.

At the same temperature, an increase in relative humidity (RH) caused an increase in the equilibrium water content of *Moringa oleifera* L. cake.

With the increase in the equilibrium water content of *Moringa oleifera* L. cake, less energy was released (q_{st}), and the water molecules were more disordered (ΔS).

The adsorption process of *Moringa oleifera* L. cake was spontaneous, as determined by the negative values of the Gibbs free energy.

Due to the sorption isotherms of *Moringa oleifera* L. cake, a safe range of water activity (a_w) for storage, where harmful microorganisms are not present, was able to be identified.

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