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Assessment of moisture adsorption and desorption isotherms, hysteresis phenomenon and thermodynamic analysis of habanero chili (*Capsicum chinense*) powder

Evaluación de las isotermas de adsorción y desorción de humedad, fenómeno de histéresis y análisis termodinámico del chile habanero (*Capsicum chinense*) en polvo

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Abstract

Moisture adsorption and desorption isotherms (MSIs) of habanero chili powder were determined at different temperatures (20-55 °C) and water activities (a_w; 0.10-0.90) using the Dynamic Vapor Sorption (DVS) method and applying the conditions typically used during the storage, packaging, and drying of habanero chili. The MSIs were sigmoidal (Type II); the best fit models were GAB and Peleg. The sorption capacity of habanero chili powder decreased with increasing temperature and constant a_w, becoming less hygroscopic. The hysteresis phenomenon was observed for all the temperatures evaluated. Thermodynamic properties were strongly dependent on the equilibrium moisture content (EMC). The net and total isosteric heat were higher for desorption than for adsorption, in both, they decreased as EMC increased. Sorption entropy and Gibbs free energy also decreased with rising EMC. Furthermore, the sorption surface area (SSA) decreased with increasing temperature. This information is essential to know the optimal storage and processing conditions to preserve the quality and prolong the shelf life of habanero chili powder.

Keywords: Habanero chili powder, Moisture sorption isotherms, Dynamic vapor sorption, Mathematical modeling, Thermodynamic analysis.

Resumen

Las isotermas de adsorción y desorción de humedad (MSIs) de chile habanero en polvo fueron determinadas a diferentes temperaturas (20-55 °C) en un rango de actividad de agua (a_w) de 0.10-0.90, aplicando el método sorción dinámica de vapor (DVS) a condiciones comúnmente utilizadas en los procesos de almacenamiento, envasado y secado del chile habanero. MSIs mostraron una forma sigmoidea (Tipo II) y los modelos que mejor se ajustaron fueron GAB y Peleg. El grado de sorción del polvo de chile habanero disminuyó al aumentar la temperatura a una a_w constante, volviéndose menos higroscópico. El fenómeno de histéresis se observó para todas las temperaturas estudiadas. Las propiedades termodinámicas dependieron en gran medida del contenido de humedad de equilibrio (EMC) del chile en polvo. El calor isostérico neto y total fueron mayor para la desorción que para la adsorción y en ambos disminuyeron a medida que aumentó la EMC. La entropía de sorción y la energía libre de Gibbs también disminuyeron con el aumento de EMC. Además, el área superficial de sorción (SSA) disminuyó con el aumento de la temperatura. Esta información es fundamental para conocer las condiciones óptimas de almacenamiento y procesamiento para preservar la calidad y prolongar la vida útil del chile habanero en polvo.

Palabras clave: Chile habanero en polvo, Isotermas de sorción de humedad, Sorción dinámica de vapor, Modelado matemático, Análisis termodinámico.

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1 Introduction

The growing use of habanero chili in the food industry has prompted studies on optimal processing conditions. Currently, habanero chili is an important ingredient in Mexican gastronomy due to its characteristic color, flavor, aroma, and pungency, as well as being a rich source of important phytochemical compounds and antioxidants (Medina-Torres *et al*., 2021). On the other hand, dehydrated foods offer more advantages over fresh ones since moisture is decreased by evaporation, and thus, their stability is increased. Water plays an important role in the conservation and preservation of food systems; therefore, it is important to generate information about the behavior of free or bound water that constitutes the a_w (Pavon-Garcia *et al*., 2015; Soleimanifard and Hamdami, 2018; Guillen-Velazquez *et al*., 2023).

In food engineering, the quality parameters of a powder, such as color, nutritional compounds, flowability, shelf life, and its surface structure depend on its sorption characteristics. Thus, it is considered important to acquire information on the behavior of water, especially for powdered food systems with strong hygroscopicity, such as habanero chili powder, because it represents a determining factor that leads to microbial growth, affecting some physical, chemical and enzymatic reactions. MSIs describe the relationship between a_w, or the equilibrium relative humidity, and the EMC of a food system at constant pressure and temperature (Muzaffar & Kumar, 2016; Arslan-Tontul, 2020). That is, the amount of water adsorbed or desorbed under equilibrium conditions. Adsorption isotherms describe the behavior of dehydrated foods, which tend to gradually adsorb water molecules from their surroundings until reaching equilibrium conditions. In contrast, desorption isotherms describe the behavior of hydrated foods, which tend to remove water molecules from their surroundings under equilibrium conditions of moisture content and relative humidity or a_w. These tendencies depend on the interaction between water content and the structure and composition of a product, such as specific surface area (Pavon-Garcia *et al*., 2015). MSIs are thermodynamically reversible processes frequently occurring in adsorption and desorption but without going through the same trajectory, presenting a phenomenon sorption hysteresis.

Obtaining sorption isotherms of powders from plant matrices has several benefits, thus, and are essential in food science and technology because they provide information for different applications. Arslan-Tontul (2020) and Viganó *et al*. (2012) mentioned some of them, such as designing and optimizing food processes, predicting moisture transfer during the drying process, estimating food stability to extend shelf life, estimating the critical level of moisture, select the most suitable packaging materials to maintain its quality, control unstable storage conditions and predict a_w of mixtures of ingredients in powders. To date, isotherm behavior is still a significant research problem because although various mathematical models have been proposed to describe the MSIs of food systems, not all equations provide accurate results in sorption analyses (Yogendrarajah *et al*., 2015). Of the proposed theoretical and empirical models, the GAB, BET, Henderson, Halsey, Oswin, Smith, Peleg and Curie models have been widely applied and adjusted (Guadarrama-Lezama *et al*., 2014). Additionally, previous studies have reported that these mathematical models are based on theories of sorption mechanisms; completely empirical or semi-empirical. The degree of fit and goodness to the experimental data and its physical meaning is an effective criterion in the selection of the most appropriate model to describe the MSIs of agri-food products. Getahum *et al*., (2020) evaluated sorption isotherms of different green, brown and red chile varieties, of which they reported that the OSWIN, GAB and BET models adequately explained the adsorption and desorption data. However, most of these studies have been conducted on dehydrated food products, which differ from powdered ones. Powdered food products can show a high degree of hygroscopicity, often related to their greater contact surface area with the air in the environment. Therefore, the previously reported isotherm models may provide different results due to the particle size, moisture, and water activity of the food product so that it is advisable to test them and study their fit.

Thermodynamic functions provide fundamental information for the analysis of sorption isotherms. These functions help understand the physicochemical binding of water under different temperatures and relative humidity conditions (Viganó *et al*., 2012). For example, we can estimate the energy required to dry fresh products using the net isosteric heat of sorption. Additionally, the net isosteric heat of sorption parameter provides relevant information on the state of the water (“bound-water") released by a specific food product until it reaches the latent heat of vaporization at a given moisture content (Yan *et al*., 2008). During the sorption process, enthalpy changes (ΔH) occur due to the energy variation from mixing water molecules with the sorbent. Moreover, it is important to mention that within a system, the arrangement of the water-sorbent interface that results from the sum of the binding and repulsive forces will create an entropy variation (ΔS). In addition, the linear relationship between ΔS and ΔH explains the physical and chemical water-food interactions. The Gibbs free energy (ΔG) variation is an indicator of spontaneity during the adsorption and desorption of the food-water vapor system, depending on the sign of the ΔG value (Al-Muhtaseb *et al*., 2004; Yogendrarajah *et al*., 2015).

In the literature, there is no study to determine the sorption isotherms of habanero chili powder. In this way, moisture sorption isotherms reflect a key opportunity in the commercialization conditions of powdered foods as spicy agents. Furthermore, unstable storage conditions can be crucial for their conservation and use. For this reason, the objective of this study was to evaluate the moisture adsorption and desorption isotherms of habanero chili powder by fitting mathematical models and also, a thermodynamic analysis to understand the binding interaction of the water-food sorption system.

2 Materials and methods

2.1 *Raw material conditioning*

Habanero chilies were obtained from a local market in Orizaba, Veracruz, Mexico. The study was carried out with orange habanero chili samples. The selected samples had similar size (4-7 cm long and 3-5 cm wide). Whole habanero chilies were washed, sliced (0.6 cm wide), and placed on the metal trays of a convective dryer (Polinox SEM-2). The convection drying process was carried out at 60 °C and an air velocity of 1 m s^{-1} for 360 min. Dried habanero chilies were milled in a 3000 W-blade grinder (GRT-20B) at 25000 rpm for 3 min. The average size of particles obtained was 180 μm. This particle size was homogeneous. Phenolic compounds, carotenoids and capsaicinoids are the main compounds of habanero chili powder. Figure 1 shows a schematic diagram of sample processing.

2.2 *Moisture sorption isotherms*

The adsorption and desorption isotherms of habanero chili powder were determined by DVS using a Vapor Sorption Analyzer (AquaLab VSA, Decagon, USA). This method has been previously used to obtain moisture sorption isotherms and reported to provide precise results (Villegas-Santiago *et al*., 2019; Araújo and Pena 2022). Before use, the DVS instrument was calibrated using five saturated salt slurries: LiCl, $MgCl_2$, NaBr, NaCl, and KCl, at each temperature. For this method, the weight of the sample is continuously recorded at a constant a_w and temperature. We recorded the EMC at different a_w values (0.113, 0.328, 0.577, 0.755 and 0.855). These values were programmed as a fixed step and the weight of the samples was recorded until the EMC was achieved. Approximately 1 g of the sample was weighed out and evenly distributed on a stainless-steel tray, which was placed inside the generator chamber. The isotherms were carried out at 20, 25, 35, 45, and 55 °C. For each temperature, sorption isotherms were carried out in triplicate.

2.3 *Modelling and fitting of sorption isotherms*

Means of EMC was plotted against a_w and the mathematical models of GAB, Oswin, Henderson, BET, Henderson, Halsey, Smith and Peleg were fitted to the experimental data. The equations shown in Table 1 were chosen to fit the sorption isotherms obtained for all temperatures. The OriginPro 8.0 software (OriginLab Corporation, Northampton, MA, USA) was used for non-linear regression analyses and curve fitting. The goodness of fit for each model was assessed based on the coefficient of determination (R^2) and the root mean squared error (RMSE).

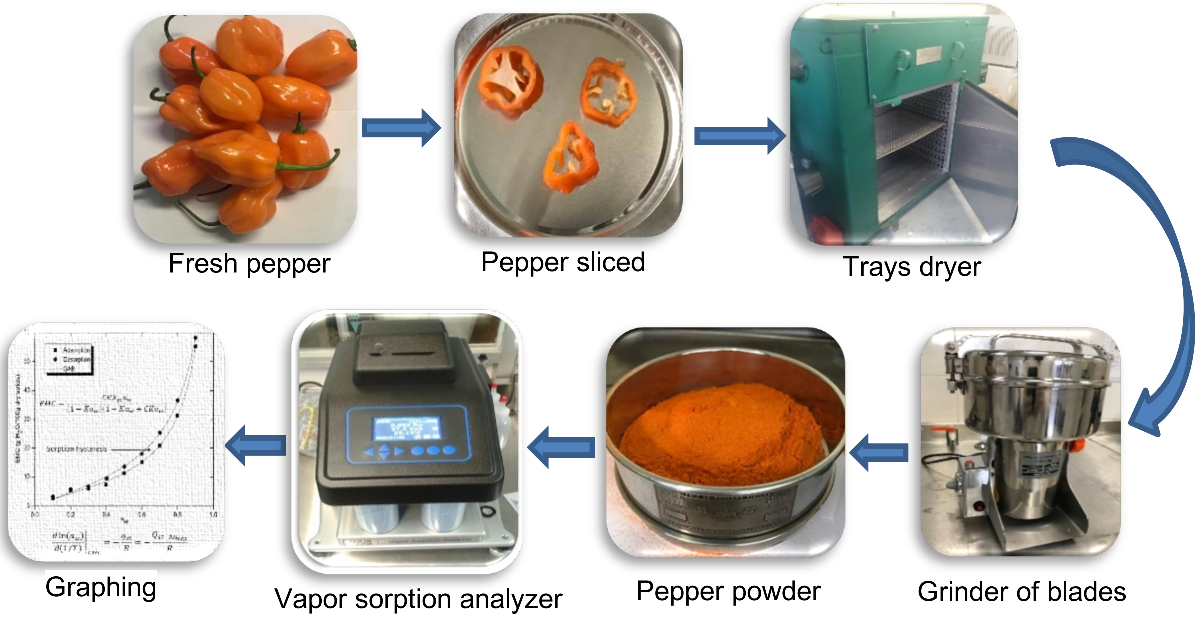

Figure 1. General scheme of the methodology followed for obtaining thermodynamic properties of habanero pepper powder.

Table 1. Models to fit sorption experimental data of habanero chili powder.

Model	Equation
GAB (Guggenheim-Anderson-de Boer)	$EMC = \frac{CKX_m a_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$
BET (Brunauer-Emmett-Teller)	$EMC = \frac{CX_m a_w}{(1-a_w)(1-a_w+Ca_w)}$
Oswin	$EMC = A\left[\frac{a_w}{(1-a_w)}\right]^B$
Henderson	$EMC = \left[-\frac{1}{H_1}\ln(1-a_w)\right]^{1/H_2}$
Halsey	$EMC = \left(-\frac{1}{h_1}\ln a_w\right)^{-1/h_2}$
Smith	$EMC = C_1 - C_2 \ln(1-a_w)$
Peleg	$EMC = K_1 a_w^{n_1} + K_2 a_w^{n_2}$

$A, B, C, C_1, C_2, H_1, H_2, h_1, h_2, K, K_1, K_2, n_1, n_2$ are constants of the models, a_w is the water activity, EMC is the equilibrium moisture content (g H_2O/100g dry solids) and X_m is the moisture content in the monolayer (g H_2O/100g of dry solids).

A good fit and fidelity in the experimental data is represented by an R^2 greater than 0.98 and an RMSE closer to zero. The mathematical kinetic model that resulted in the best fit to the experimental values, was chosen to calculate the thermodynamic properties.

2.4 Analysis of thermodynamic properties

The thermodynamic properties of a food system inform the energy required for drying food products and predict the storage and packaging conditions for proper food stability (Yogendrarajah *et al.*, 2015). Using the MSIs of the habanero chili powder-water system, we determined the following thermodynamic properties: isosteric heat, sorption entropy, and Gibbs free energy. This method requires obtaining sorption isotherms with at least three or more temperatures.

Isosteric heat of sorption can be calculated from the derivative of the Clausius-Clapeyron equation (eq.1).

$$\left.\frac{d\ln a_w}{d(1/T)}\right|_{EMC} = -\frac{q_{st}}{R} = -\frac{Q_{st}-\Delta H_{vap}}{R} \tag{1}$$

Where q_{st} represents the net isosteric heat of sorption (J mol^{-1}), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The isosteric heat of sorption was obtained from the slope of ln (a_w) against 1/T by linear regression analysis of specific moisture content. Furthermore, the total heat of sorption (Q_{st}) represents the interaction between water vapor and the sorbent material and is expressed in (J mol^{-1}). Q_{st} is defined as the addition of the net isosteric heat of sorption and the heat of vaporization of pure water.

$$Q_{st} = q_{st} + \Delta H_{vap} \tag{2}$$

In this equation, ΔH_{vap} represents the latent heat of vaporization of free water (J mol^{-1}). This parameter was calculated using the average temperature used to generate the isotherms (Al-Muhtaseb *et al.*, 2004). Equation 3 was obtained by linear regression of the reported values of the heat of vaporization of saturated water, using steam tables.

$$\Delta H_{vap} = 2502.2 - 2.39(T) \tag{3}$$

ΔS generate information to understand the interaction between the number of sorption sites available at a specific energy level (Rizvi, 2005). This thermodynamic property can also be determined from the Gibbs-Helmholtz relationship given by the equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

At the same time, Gibbs free energy (ΔG) was calculated from equation (5).

$$\Delta G = RT\ln a_w \tag{5}$$

Often, the enthalpy and entropy changes of sorption result from a water sorption change on the Gibbs free energy. Therefore, substituting equation (4) in equation (5), we obtain:

$$\ln a_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{6}$$

Sorption entropy was calculated from the intercept (ΔS/R) of the ln a_w versus $1/T$.

2.5 Calculation of the sorption surface area

The sorption surface area of habanero chili powder was determined from the monolayer moisture content obtained using the GAB model (equation 7).

$$SSA = X_m * \frac{N_A A_m}{M_w} \tag{7}$$

Where SSA is the solid surface area (m^2 g^{-1} dry solids), X_m is the monolayer moisture content (g water/ g d.s.), N_A is Avogadro's number (6.02×10^{23} molecules mol^{-1}), A_m is the area of a water molecule (1.06×10^{-19} m^2), and M_w is the molecular weight of water (18 g mol^{-1}).

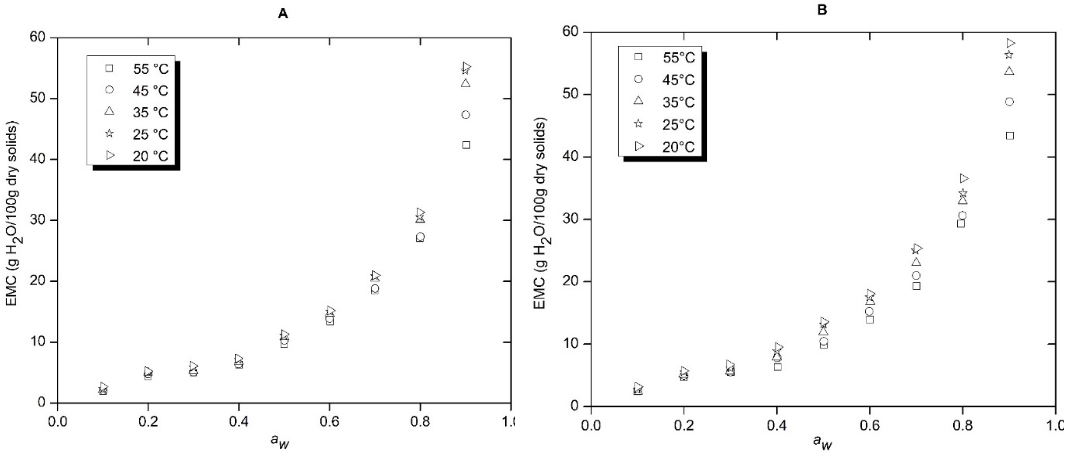

Figure 2. Adsorption (A) and desorption (B) of habanero pepper powder.

3 Results and discussions

3.1 *Moisture adsorption and desorption isotherms*

The initial moisture content of the habanero chili powder was 3.49 ± 0.45 g water 100 g^{-1} solids. All the sorption isotherm curves (Fig. 2) showed characteristics corresponding to type II isotherms, i.e., a non-linear trend and a sigmoidal shape, typical for porous biological materials and most agricultural foods (Hernández-Carrillo *et al.*, 2019), this behavior was probably observed due to the main components of the food such as fiber and carbohydrates coupled with the particle size and the morphology of the characteristic powder. Likewise, these types of isotherms take into account the existence of multilayers on the inner surface of the material. The sorption capacity of the material is highly related to the chemical composition and the structure, being affected by the temperature. Powdered foods with hydrophilic and porous structures have more water sorption capacity. Woldermariam *et al.* (2021) reported that powders with smaller particle size may have larger surface area and hydrophilic groups in the powder are exposed, generating interaction of the powdered food with water vapor from the surrounding air. On the other hand, a relatively slow increase in sorption capacity at low a_w, and a marked increase at higher a_w can be observed, as previously reported for chili foodstuff (De Sá Mendes *et al.*, 2019). As expected, the adsorption and desorption data were significantly different (P<0.05). The EMC values were lower for adsorption than for desorption at a given a_w, ranging from 1.98 to 55.26 (g H_2O/100g solid) and 2.44 to 58.26 (g H_2O/100g solid), respectively.

Moisture adsorption isotherms of habanero chili powder are plotted in Figure 2A. The experimental data for adsorption indicated that the EMC decreased with increasing temperature at a constant a_w. This behavior can be attributed to the fact that the activated water molecules that result from the change in water vapor pressure inside the habanero chili powder particles become less stable, caused by temperature-induced physical changes in the sample. In addition, the increase in temperature accelerates the transfer of moisture from the food system to the surrounding air. (Kaleemullah & Kailappan, 2004). Thus, the water adsorption capacity of habanero chili powder decreased with an increase in temperature given that water molecules are activated at higher energy levels. This energy triggers their detachment from the food matrix. On the other hand, the EMC of habanero chili powder increased with an increase in a_w at constant temperature. This result is probably due to the food particles becoming saturated with water molecules. Previous studies have reported similar trends for different food powders, such as concentrated whey protein (Sawhney *et al.*, 2013), tamarind pulp (Muzaffar & Kumar, 2016), and stevia (Hidar *et al.*, 2018).

On the other hand, the equilibrium moisture desorption isotherms of habanero chili powder are shown in Figure 2B and presented similar trends for all the studied temperatures (20, 25, 35, 45, and 55 °C). Based on the desorption isotherms, EMC decreases with increasing temperature at constant a_w, demonstrating a strong dependence of sorption with the temperature. During desorption, the temperature dependence may be due to the increase in the state of excitation of the water molecules where the kinetic energy of the water molecules increases and, therefore, the attractive forces are reduced. Furthermore, this decline depends on the nature and constitution of the food (Kurozawa *et al.*, 2015; Araújo and Pena 2022). High and intermediate a_w values resulted in a remarkable decrease in EMC due to the significant dissipation of water molecules from the food surfaces towards the surroundings. In addition, at low a_w values (0.1-0.3), the desorption curves are very close, indicating that the water molecules are tightly bound to the capillaries of the habanero chili powder. It was also observed that the EMC values turned out to be very high when the a_w is higher than 0.8, due to a greater solubility of the fiber and carbohydrates of the food in water (Getahun *et al*., 2020). Similar results have been reported for different food products, such as red chilies (Kaleemullah & Kailappan, 2004), grapes, apricots, apples, and potatoes (Kaymak-Ertekin & Gedik, 2004), and chili flour (De Sá Mendes *et al*., 2019).

3.2 Fitting sorption models to experimental data

The parameters of the non-linear regression analysis are shown in Table 2. The results include the estimated parameter values and the respective coefficient of determination (R^2) and root mean square error (RMSE). We found that the models with the best fit for the adsorption and desorption of habanero chili powder were GAB ($R^2 >$ 0.997 and RMSE<1.126) and Peleg ($R^2 >$ 0.994, RMSE < 1.153). However, the GAB model has an advantage over the empirical Peleg model; it presents theoretical bases in its parameters, such as the monolayer moisture content, compared to the Peleg model, which has no physical significance. The corresponding fits of the experimental data for the adsorption and desorption isotherms with the GAB model are shown in Figure 3, presenting a good agreement between the experimental and predicted data, with a relative error of less than 5%. Monolayer moisture content (X_m) is essential for physical and chemical stability, enzymatic activity, non-enzymatic browning, preservation of flavor components and structural characteristics, this parameter is generally affected by hydrophilic bonds and polar components (polysaccharides, fiber, carbohydrates, proteins, etc.) on the surface of the food (Hidar *et al*., 2018). Additionally, X_m represents the minimum moisture that covers the hydrophilic sites on the food surface, thus providing information about the amount of water strongly adsorbed or desorbed on the active sites on the food surface, which is also related to food stability, by reducing the rate of reaction of degradation and avoiding physical changes. Therefore, X_m varied from 7.962 to 7.119 (g of water/100 g of dry solids) for adsorption and 11.150 to 9.311 (g of water/100 g of dry solids) for desorption by increasing the temperature from 20 to 55 °C. Goneli *et al*. (2013) found a similar trend and reported that the monolayer moisture content decreased from 10.75 to 7.64, 9.99 to 4.34, and 7.92 to 5.67 (g of water/100 g dry solids) as the adsorption isotherm temperature increased from 10 to 50 °C for coffee fruits, coffee pulp, and green coffee, respectively. As observed, the X_m values were higher for desorption than adsorption and decreased with increasing temperature. This trend has been attributed to the reduction in the number of active sites (or hydrogen bonds) due to swelling of the fibers and, futher to the binding of water with other carbohydrates in the food, these physical and chemical changes are induced by the gradient of the temperature. In addition, it was observed that the X_m calculated by B*et al*so presented a similar trend, however the values were lower than the parameters of the GAB model. This result can be due to the fact that the BET model is generally only applied in the range of a_w from 0.1 to 0.5. Kaymak-Ertekin & Gedik (2004) also obtained higher X_m values in desorption than in adsorption for grapes, apricots, apples, and potatoes. The C and K values correspond to the Type II classification, according to Brunauer $0<K<1$ and $C \geq 2$, and these parameters are also within the limits previously reported for fruits and agricultural foods. Furthermore, the parameters C and k are linked to the interaction energy between the habanero chili powder and the water vapor molecules (Getahun *et al*., 2020). Firstly, the constant C corresponds to the heat of sorption of the first layer, higher values were found for the adsorption than desorption isotherms, which indicates a greater force of interaction between water-food molecules in the first layer. On the other hand, the k values of adsorption and desorption isotherms were close to 1.0 due to the high solubility of the soluble components (fiber and carbohydrates) of chili powder for $a_w >0.8$, representing the interaction energies between the properties of the multilayer associated with the sorption of water molecules. Pascual-Pineda *et al*., (2022) also found C and k values less than 2 and 1, respectively, for soluble coffee adsorption isotherms.

3.3 Sorption hysteresis

Hysteresis behavior can vary for each food; even identical products can present different isotherm patterns when a variable is altered. The sorption equilibrium moisture isotherms of the habanero chili powder were plotted using the GAB model (Figure 3A-E). For the temperatures studied, it was found that the desorption curves were greater than the adsorption curves, which indicates the presence of the hysteresis phenomenon. The hysteresis loop occurs at a_w values ranging from 0.1 to 0.90. However, we observed that the hysteresis zone was greater at a_w values between 0.4 to 0.9. Similar trends occurred in the sorption isotherms of red chilies (Kaleemullah & Kailappan, 2004), instant (soluble) green tea powder (Sinija & Mishra, 2008), chili flour (De Sá Mendes *et al*., 2019), and soluble coffee powder (Villegas-Santiago *et al*., 2019). Furthermore, sorption hysteresis decreased with increasing temperature (20 °C to 55 °C). De Souza *et al*. (2015) also observed the hysteresis loop in the entire a_w range studied, decreasing when the temperature increases. Moussaoui *et al*. (2019) observed a more pronounced hysteresis phenomenon for the pulp and negligible for the fruit. Sorption hysteresis is known to be affected by temperature, equilibration methods, and food nature and constitution, reflecting possible structural and conformational rearrangements (Yan *et al*., 2008). Desorption isotherms follow a different path than adsorption isotherms, probably because the habanero chili powder particles vary in size and present a wide range of compounds.

Table 2. Estimated parameters of the isotherm models for habanero chili powder at different temperatures.

Models and parameters	Adsorption					Desorption				
	20°C	25°C	35°C	45°C	55°C	20°C	25°C	35°C	45°C	55°C
GAB										
X_m (g H_2O/100 g d.s)	7.962	7.897	7.561	7.365	7.119	11.15	10.61	10.47	9.491	9.311
C	3.177	2.957	3.145	2.902	3.334	2.353	2.362	2.006	2.154	2.049
K	0.958	0.959	0.959	0.947	0.935	0.915	0.919	0.915	0.915	0.898
R^2	0.999	0.999	0.998	0.998	0.996	0.999	0.998	0.999	0.998	0.996
RMSE	0.688	0.658	0.727	0.699	0.89	0.67	0.824	0.718	0.744	1.126
BET										
X_m (g H_2O/100 g d.s)	5.777	5.761	5.547	5.005	4.554	6.282	6.132	5.802	5.279	4.726
C	11.92	9.828	10.21	12.92	19.27	20.53	16.76	14.63	18.67	25.11
R^2	0.988	0.989	0.986	0.982	0.958	0.965	0.968	0.969	0.966	0.942
RMSE	1.982	1.834	2.071	2.051	2.906	3.604	3.308	3.143	2.958	3.522
Oswin										
A	11.43	11.16	10.9	10.23	10.19	13.97	13.35	12.44	11.55	10.9
B	0.715	0.726	0.717	0.698	0.652	0.654	0.663	0.672	0.662	0.637
R^2	0.999	0.999	0.998	0.998	0.994	0.997	0.997	0.996	0.996	0.987
RMSE	0.653	0.601	0.675	0.675	1.133	1.11	1.071	1.112	1.687	1.687
Henderson										
H_1	0.067	0.05	0.486	0.117	0.486	0.055	0.315	0.434	0.064	0.112
H_2	0.717	0.961	0.122	0.43	0.122	0.779	0.142	0.109	0.799	0.504
R^2	0.952	0.949	0.979	0.954	0.979	0.979	0.977	0.974	0.975	0.979
RMSE	3.966	4.017	2.052	3.699	2.052	2.801	2.82	2.856	2.53	2.089
Halsey										
h_1	3.242	10.92	5.402	14.66	2.001	0.499	0.461	1.27	0.576	0.785
h_2	0.524	1.768	0.911	2.73	0.408	0.074	0.069	0.203	0.101	0.154
R^2	0.973	0.977	0.971	0.964	0.929	0.936	0.942	0.946	0.94	0.908
RMSE	2.966	2.719	2.901	3.765	3.765	4.868	4.469	4.151	3.959	4.418
Smith										
C_1	-2.933	-3.151	-3.019	-2.36	-1.692	-2.126	-2.261	-2.459	-1.952	-1.515
C_2	22.95	22.88	22.08	19.67	18.11	24.69	24.01	22.94	20.79	18.74
R^2	0.964	0.946	0.969	0.972	0.986	0.985	0.984	0.983	0.982	0.985
RMSE	3.405	3.375	3.052	2.609	1.683	2.383	2.348	2.293	2.139	1.806
Peleg										
K_1	77.68	78.58	71.89	64.03	49.84	69.16	66.72	63.59	59.43	52.85
K_2	20.08	22.22	21.5	20.97	14.17	22.76	28.11	23.31	16.3	9.688
n_1	7.137	7.744	7.382	7.719	5.163	5.894	7.165	6.359	5.417	4.181
n_2	0.931	1.056	1.071	1.091	0.833	0.919	1.148	1.066	0.814	0.593
R^2	0.998	0.998	0.997	0.997	0.994	0.999	0.997	0.998	0.999	0.994
RMSE	0.846	0.947	0.986	0.958	0.583	0.707	1.153	0.95	0.658	0.595

3.4 *Thermodynamic properties*

3.4.1 *Isosteric heat of sorption*

From a thermodynamic approach, the adsorption and desorption behavior of water can be evaluated according to the heat of sorption, differential entropy, and Gibbs free energy. Net isosteric heat of sorption or sorption enthalpy was calculated from equilibrium data at different temperatures using eq. (1) and plotted against different EMC. As shown in Figure 4A, the net isosteric heat of adsorption and desorption of habanero chili powder is highly dependent on the EMC.

We observed that the net isosteric heat of sorption (qst) decreases with increasing moisture content, ranging from 4.86-1.07 KJ mol^{-1} for adsorption and 7.59 KJ mol^{-1} to 1.43 KJ mol^{-1} for desorption, with an EMC ranging from 5-45 (g of water/100 g dry solids), therefore, the values are higher for desorption than adsorption. The isosteric heat of sorption quantifies the interaction forces between the water vapor molecules and the surface of habanero chili powder. Compared to other food products, habanero chili has a very complex phytochemical composition, including vitamins, capsaicinoids, carotenoids, flavonoids,

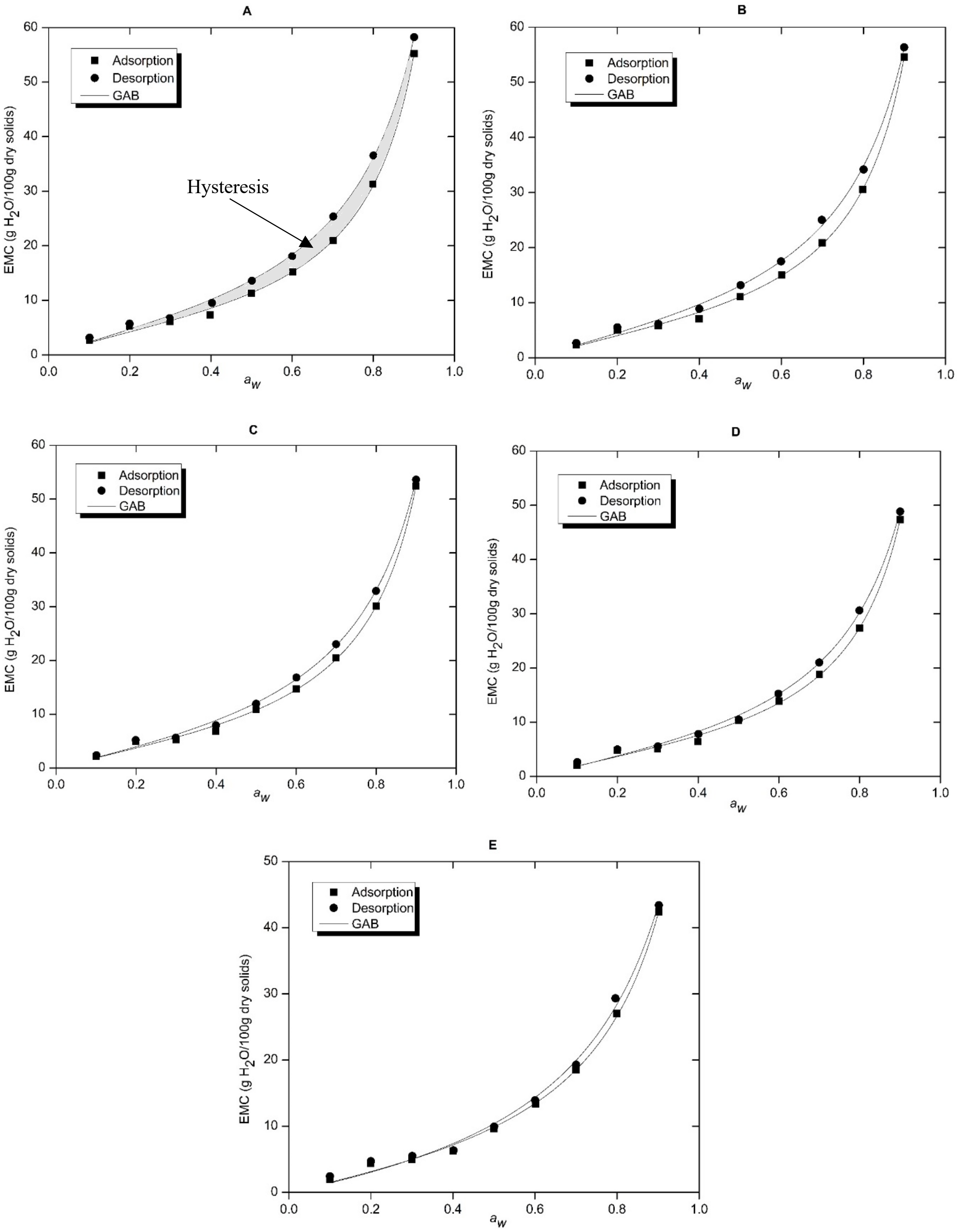

Figure 3. Sorption hysteresis of habanero pepper powder at (A) 20, (B) 25, (C) 35, (D) 45 y (E) 55 ºC fitted with the GAB model.

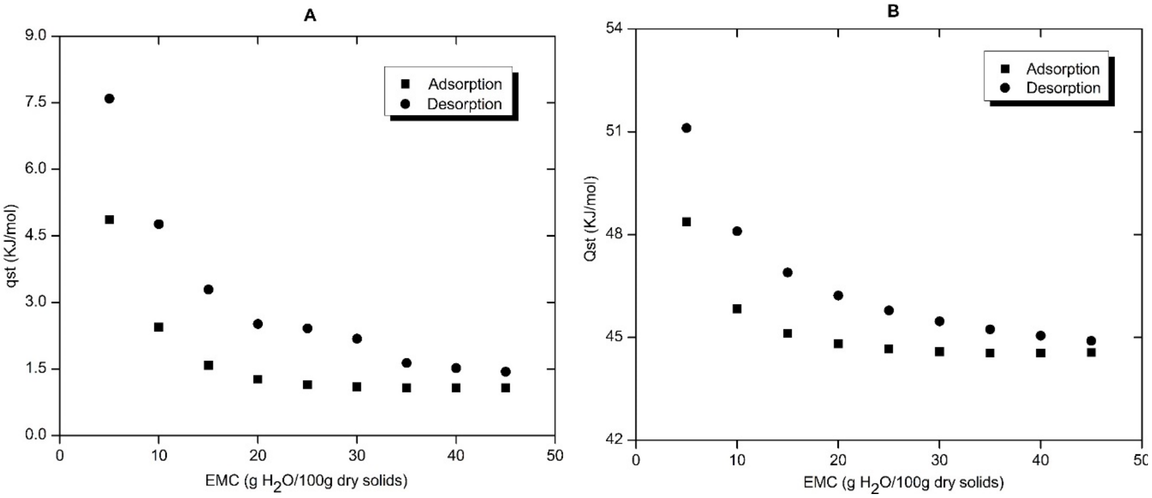

Figure 4. Effect of EMC on the net (A) and total (B) isosteric heat of sorption of habanero pepper powder.

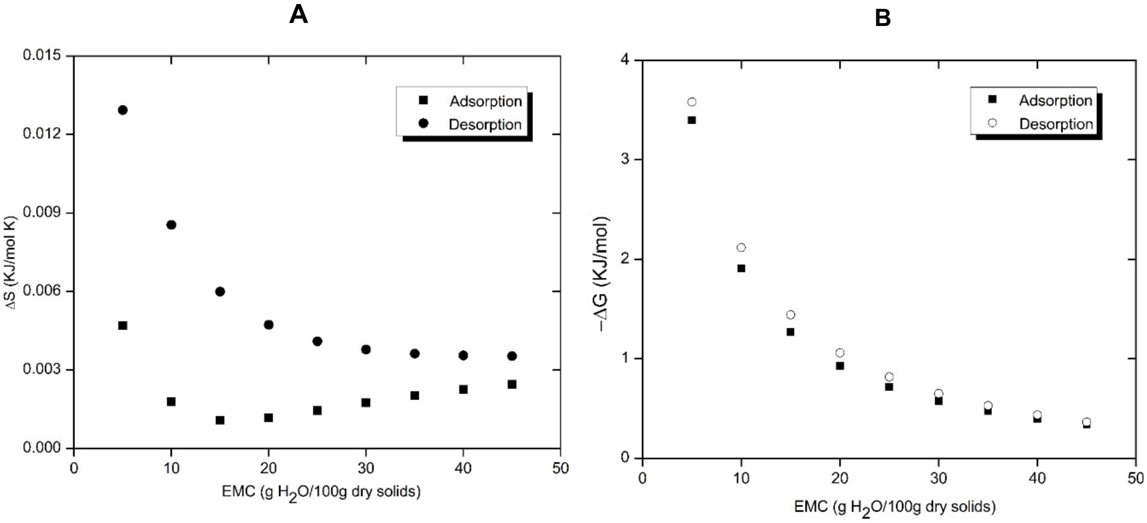

Figure 5. A) Behaviour of the sorption entropy and B) variation in Gibbs energy free of habanero pepper powder as a function of EMC.

and phenolic and aromatic compounds (Medina-Torres *et al*., 2021; Woldermariam *et al*., 2021), which can interact with water vapor molecules in the active sites on the multilayer surface, promoting the union by chemical bonds between the components of the adsorbent with the adsorbate, being driven by the chemisorption process. However, with the data available in this research, it is difficult to predict which components could exert greater interaction forces with water molecules. On the other hand, the adsorbate can interact with other components, such as fiber and carbohydrates, in the active sites of the adsorbent through van der Waals forces, due to good solubility. Therefore, this sorption process would be governed mainly by physisorption. According to Figure 4A, the highest values of qst were found at low moisture contents; this could be due to the water molecules strongly bound to the monolayer structure of the powder and the sorption sites with high interaction energies (De Souza *et al*., 2015). However, a rapid decrease in the net isosteric heat of sorption was observed when the moisture content began to increase due to the evaporation of the water molecules from the habanero chili powder multilayer, giving lower qst values in higher EMC. Similar trends were found by Kaymak-Ertekin and Gedik (2004), who calculated the net isosteric heat of adsorption and desorption of grapes, apricots, apples, and potatoes. Soleimanifard and Hamdami (2018) observed a similar trend in split pistachios, pistachio kernels, and shells.

The relationship between total isosteric heat of sorption (Q_{st}) and EMC is shown in Figure 4B. At fixed EMC, Q_{st} values were higher for desorption than adsorption.

Therefore, the amount of energy required for desorption is greater than for adsorption regarding the water molecules on the surface of food. Additionally, the Q_{st} decreased gradually with increasing EMC. It was also observed that at an EMC greater than 45g of water/100 g of dry solids, the isosteric heat of sorption was almost in line with the heat of vaporization of pure water. This observation is similar to that of Sinija and Mishra (2008), who reported isosteric heat of sorption values of 48.54 KJ mol^{-1} and 47.96 KJ mol^{-1} for instant green tea powder and green tea granules, respectively.

3.4.2 Entropy of sorption

As shown in Figure 5A, the evolution of the adsorption and desorption differential entropy decreased sharply from 0.0047-0.0024 KJ mol^{-1} K^{-1} and from 0.0129-0.0035 KJ mol^{-1} K^{-1}, respectively, with an increase in EMC from 5-45 (g of water/100 g dry solids) for habanero chili powder. At a given moisture content, lower entropy values occurred for adsorption. The entropy change is higher for desorption, being that the kinetic energy of the molecules that interact during the exchange of water vapor is directly proportional to the release of active sites, making the system more disordered. While the entropy change for the adsorption is lower, due to the restriction of the movement of the water vapor molecules in the adsorbent, which makes the habanero chili powder adsorption process thermodynamically more stable and structured compared to the desorption process. Rizvi (2005) established that differential entropy represents the change in order or disorder (after water molecules are adsorbed/desorbed by the system) between the water molecules and the food system because, at higher values for sorption isotherms, lower interactions are presented between sorbent and sorbate. In addition, the attraction-repulsion forces in the system (habanero chili powder-water steam) are lower, as well as the sorption capacity. These trends are in the same order as those reported for pineapple (Simal *et al.*, 2007), papaya (Kurozawa *et al.*, 2015), whole black chilicorns (Yogendrarajah *et al.*, 2015), and stevia powder (Hidar *et al.*, 2018).

At lower moisture content, adsorption values presented up to 15 g of water/100 g dry solids; 25 g of water/100 g dry solids for desorption. As available sites become saturated, the rotational movement of water molecules decreases. Therefore, an increase in moisture content decreases entropy and, thus, results in an ordered system. The minimum value of adsorption entropy was 0.00108 KJ mol^{-1} K^{-1} at a moisture content of 15 g of water/100 g dry solids. Yogendrarajah *et al.* (2015) reported that water molecules could occupy the active sites on the surface; hence, entropy is reduced at higher EMC.

3.4.3 Changes in Gibbs free energy

Gibbs free energy is closely related to the water affinity of the sorbent, in addition to providing a criterion on the spontaneity of the water molecules in the sorption process (Rizvi, 2005). The ΔG values for adsorption and desorption as a function of moisture content are presented in Figure 5B. The ΔG values decreased from -3.39 to -0.33 KJ mol^{-1} for adsorption and from -3.58 to -0.36 KJ mol^{-1} for desorption, with increasing EM (5 to 45 g of water/100 g dry solids), respectively. As the moisture content increased to 45 g water/100 g dry solids, ΔG got closer to zero. Thus, the system reached maximum sorption capacity. Furthermore, it is possible to assume that higher levels of water content result in the absence of available sorption sites (Yogendrarajah *et al.*, 2015).

In turn, ΔG values were higher for adsorption than desorption with increasing moisture content, indicating that the adsorption process is more spontaneous than the desorption process. This is probably due to the hydrophilic characteristics of the habanero chili powder multilayers, which allow the adsorption of water molecules. The difference in Gibbs free energy in the adsorption and desorption processes increased when the moisture content fell below 20 g of water/100 g dry solids. This trend, -ΔG, indicates that the adsorption and desorption of water are spontaneous processes. These behaviors were recently reported for pineapple pulp powder (Viganó *et al.*, 2012), whey protein concentrate of buffalo milk (Sawhney *et al.*, 2013), and mango skin (De Souza *et al.*, 2015).

Table 3. Sorption surface area values of habanero chili powder.

Temperature (°C)	Adsorption (m^2 g^{-1} dry solids)	Desorption (m^2 g^{-1} dry solids)
20	282.26	395.27
25	279.95	376.13
35	268.04	371.17
45	261.09	336.46
55	252.37	330.08

3.4.4 Sorption surface area

Sorption surface area is fundamental in determining the water-binding capacity of a food powder (Hidar *et al.*, 2018). Table 3 shows the SSA values, which were determined through the X_m values of the GAB model. SSA values decreased with increasing temperature and were higher for desorption than adsorption at a given temperature. In the same way, it can be observed that, as X_m decreases, SSA decreases with increasing temperature. This behavior describes a decrease in the binding capacity of the active sites with hydrogen bonds due to the dilation of the fibers and carbohydrate solubility induced by increasing temperature. The water sorption capacity of the habanero chili powder was affected by the surface interaction, the structure, and the chemical composition. Arslan-Tontul (2020) used the GAB model to determine the SSA of chia seeds and Pavón-García *et al.* (2015) used the Caurie model to determine the SSA of microcapsules of a nutraceutical system, both reported the same behavior and found lower values of SSA, which could be due to the reduction of pores on the surface coupled with a lower capacity for food sorption.

Conclusions

Moisture adsorption and desorption isotherms of powdered habanero chili showed a sigmoidal shape (type II). A clear dependence on temperature was observed for values of a_w ≥0.8, where a higher hygroscopicity occurred. In contrast to the Peleg model, both fit, the GAB model helped to estimate with adequate precision the water content of the monolayer and perfectly fit the adsorption and desorption isotherms of habanero chili powder up to water activities of 0.95. The desorption curves were found above the adsorption curves, presenting the hysteresis phenomenon, which as the temperature increased the magnitude decreased. Net and total isosteric heats indicated stronger bonds between solids-water molecules for desorption than adsorption. The entropy change showed that adsorption tends to present a more structured and stable system than desorption. According to the Gibbs free energy, it was found that both sorption processes are spontaneous (-ΔG), being the adsorption easier to reach its stable state. The SSA values were affected by the increase in temperature due to a decrease in the binding capacity of the active sites. Finally, the moisture content of the habanero pepper powder will be affected if it is exposed in places with intermediate and high relative humidity (RH≥60%), causing the a_w to increase rapidly to values that damage the microbial safety conditions required for a food. These results explained that the sorption isotherms and thermodynamic analysis provide suitable conditions to effectively preserve the microbial quality of habanero chili powder and its thermodynamic interaction between the multilayers and the water vapor molecules.

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References

Al-Muhtaseb, A. H., McMinn, W. A. M. and Magee, T. R. A. (2004). Water sorption isotherms of starch powders. Part 1: mathematical description of experimental data. *Journal of Food Engineering 61*, 297-307. https://doi.org/10.1016/S0260-8774(03)00133-X

Araújo, A. L. de, and Pena, R. da S. (2022). Moisture desorption behavior and thermodynamic properties of pulp and seed of jambolan (*Syzygium cumini*). *Heliyon 8(5)*, e09443. https://doi.org/10.1016/j.heliyon.2022.e09443

Arslan-Tontul, S. (2020). Moisture sorption isotherm, isosteric heat and adsorption surface area of whole chia seeds. *LWT - Food Science and Technology 119*, 108859. https://doi.org/10.1016/j.lwt.2019.108859

De Sá Mendes, N., Santos, M. C. P., Santos, M. C. B., Cameron, L. C., Ferreira, M. S. L. and Gonçalves, É. C. B. A. (2019). Characterization of pepper (*Capsicum baccatum*) - A potential functional ingredient. *LWT - Food Science and Technology 112*, 108209. https://doi.org/10.1016/j.lwt.2019.05.107

De Souza, S. J. F., Alves, A. I., Vieira, É. N. R., Vieira, J. A. G., Ramos, A. M. and Telis-Romero, J. (2015). Study of thermodynamic water properties and moisture sorption hysteresis of mango skin. *Food Science and Technology 35(1)*, 157-166. https://doi.org/10.1590/1678-457X.6557

Getahun, E., Gabbiye, N., Delele, M. A., Fanta, S. W., Gebrehiwot, M. G., and Vanierschot, M. (2020). Effect of maturity on the moisture sorption isotherm of chili pepper (Mareko Fana variety). *Heliyon 6(8)*, e04608). https://doi.org/10.1016/j.heliyon.2020.e04608

Goneli, A. L. D., Corrêa, P. C., Oliveira, G. H. H. and Afonso Júnior, P. C. (2013). Water sorption properties of coffee fruits, pulped and green coffee. *LWT - Food Science and Technology 50(2)*, 386-391. https://doi.org/10.1016/j.lwt.2012.09.006

Guadarrama-Lezama, A.Y., Carrillo-Navas, H., Cruz-Olivares, J., Martínez-Vargas, S.L., Román-Guerrero and A., Pérez-Alonso, C. (2014). Determination of the minimum integral entropy, water sorption and glass transition temperature to establishing critical storage conditions of beetroot juice microcapsules by spray drying. *Revista Mexicana de Ingeniería Química 13*, 405-416.

Guillén-Velázquez, P., Cantú-Lozano, D., Rascón-Díaz, M., Jimenez-Fernández, M., & Luna Solano, G. (2022). Swelling, erosion and physicochemical characteristics of plum powder tablets obtained by spray drying. *Revista Mexicana de Ingeniería Química 21(3)*, Alim2867. https://doi.org/10.24275/rmiq/Alim2867

Hernández-Carrillo, J. G., Mújica-Paz, H., Welti-Chanes, J., Spatafora-Salazar, A. S., and Valdez-Fragoso, A. (2019). Sorption behavior of citric pectin films with glycerol and olive oil. *Revista Mexicana de Ingeniera Quimica 18(2)*, 487-500. https://doi.org/10.24275/uam/izt/dcbi/revmexingquim/2019v18n2/Hernandez

Hidar, N., Ouhammou, M., Idlimam, A., Jaouad, A., Bouchdoug, M., Lamharrar, A. and Mahrouz, M. (2018). Investigation of water adsorption and thermodynamic properties of stevia powder. *Journal of Food Measurement and Characterization 12(4)*, 2615-2625. https://doi.org/10.1007/s11694-018-9879-0

Kaleemullah, S. and Kailapan, R. (2004). Moisture sorption isotherms of red chillies. *Biosystems Engineering 88 (1)*, 95-104. https://doi.org/10.1016/j.biosystemseng.2004.01.003

Kaymak-Ertekin, F. and Gedik, A. (2004). Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. *LWT - Food Science and Technology 37(4)*, 429-438. https://doi.org/10.1016/j.lwt.2003.10.012

Kurozawa, L. E., de Oliveira, R. A., Hubinger, M. D. and Park, K. J. (2015). Thermodynamic properties of water desorption of papaya. *Journal of Food Processing and Preservation 39(6)*, 2412-2420. https://doi.org/10.1111/jfpp.12491

Medina-Torres, N., Cuevas-Bernardino, J. C., Ayora-Talavera, T., Patrón-Vázquez, J. A., Rodríguez-Buenfil, I., and Pacheco, N. (2021). Changes in the physicochemical, rheological, biological, and sensorial properties of habanero Chili pastes affected by ripening stage, natural preservative and thermal processing. *Revista Mexicana de Ingeniera Química 20(1)*, 195-212. https://doi.org/10.24275/rmiq/Alim1768

Moussaoui, H., Bahammou, Y., Idlimam, A., Lamharrar, A. and Abdenouri, N. (2019). Investigation of hygroscopic equilibrium and modeling sorption isotherms of the argan products: A comparative study of leaves, pulps, and fruits. *Food and Bioproducts Processing 114*, 12-22. https://doi.org/10.1016/j.fbp.2018.11.002

Muzaffar, K. and Kumar, P. (2016) Moisture sorption isotherms and storage study of spray dried tamarind pulp powder. *Powder Technology 291*, 322-327. https://doi.org/10.1016/j.powtec.2015.12.046

Pascual-Pineda, L., Guerrero-Hernández, A., Castillo-Morales, M., Salazar, R., Jiménez-Fernández, M., and Flores-Andrade, E. (2022). Determination of the spreading pressure and shelf-life of spray-dried coffee powder: quality assurance of a water-soluble food. *Revista Mexicana de Ingeniería Química 21(3)*, Alim2921. https://doi.org/10.24275/rmiq/Alim2921

Pavón-García, L.M.A., Gallardo-Rivera, R., Román-Guerrero, A., Carrillo-Navas, H., Rodríguez-Huezo, M.E., Guadarrama-Lezama, A.Y., and Pérez-Alonso, C. (2015). Moisture sorption properties and storage stability conditions of a nutraceutical system microencapsulated by spray drying. *Revista Mexicana de Ingeniería Química 14(3)*, 601-613. http://www.rmiq.org/ojs311/index.php/rmiq/article/view/1275

Rizvi, S. S. H. (2005). Thermodynamic properties of foods in dehydration: In Rao M.A., Rizvi S.S.H and Datta A.K, *Engineering Properties of Foods*. Pp. 78-84. Third edition. Taylor & Francis CRC. New York.

Sawhney, I. K., Sarkar, B. C., Patil, G. R. and Sharma, H. (2013). Moisture sorption isotherms and thermodynamic properties of whey protein concentrate powder from Buffalo skim milk. *Journal of Food Processing and Preservation 38(4)*, 1787-1798. https://doi.org/10.1111/jfpp.12148

Simal, S., Femenia, A., Castell-Palou, Á. and Rosselló, C. (2007). Water desorption thermodynamic properties of pineapple. *Journal of Food Engineering 80(4)*, 1293-1301. https://doi.org/10.1016/j.jfoodeng.2006.10.001

Sinija, V. R. and Mishra, H. N. (2008). Moisture sorption isotherms and heat of sorption of instant (soluble) green tea powder and green tea granules. *Journal of Food Engineering 86(4)*, 494-500. https://doi.org/10.1016/j.jfoodeng.2007.10.026

Soleimanifard, S. and Hamdami, N. (2018). Modelling of the sorption isotherms and determination of the isosteric heat of split pistachios, pistachio kernels and shells. *Czech Journal of Food Science 36*, 268-275. https://doi.org/10.17221/460/2016-CJFS

Viganó, J., Azuara, E., Telis, V. R. N., Beristain, C. I., Jiménez, M. and Telis- Romero, J., (2012). Role of enthalpy and entropy in moisture sorption behavior of pineapple pulp powder produced by different drying methods. *Thermochimica Acta 528*, 63-71. https://doi.org/10.1016/j.tca.2011.11.011

Villegas-Santiago, J., Gómez-Navarro, F., Dominguez-Niño, A., García-Alvarado, M., Salgado-Cervantes, M. and Luna-Solano, G. (2019). Effect of spray-drying conditions on moisture content and particle size of coffee extract in a prototype dryer. *Revista Mexicana de Ingeniería Química 19(2)*, 767-781. https://doi.org/10.24275/rmiq/Proc767

Yan, Z., Sousa-Gallagher, M. J. and Oliveira, F. A. R. (2008). Sorption isotherms and moisture sorption hysteresis of intermediate moisture content banana. *Journal of Food Engineering 86(3)*, 342-348. https://doi.org/10.1016/j.jfoodeng.2007.10.009

Yogendrarajah, P., Samapundo, S., Devlieghere, F., De Saeger, S. and De Meulenaer, B. (2015). Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (*Piper nigrum* L.). *LWT - Food Science and Technology 64(1)*, 177-188. https://doi.org/10.1016/j.lwt.2015.05.045

Woldemariam, H. W., Admassu Emire, S., Getachew Teshome, P., Toepfl, S., and Aganovic, K. (2021). Physicochemical, functional, oxidative stability and rheological properties of red pepper (*Capsicum annuum* L.) powder and paste. *International Journal of Food Properties 24(1)*, 1416-1437. https://doi.org/10.1080/10942912.2021.1969945