



Adsorption isotherms of hog plum (*Spondias mombin* L.) pulp powder obtained by spray dryer

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ABSTRACT. Food sorption isotherms are highly important to predict drying time and storage conditions of a product. Current assay evaluates the behavior of adsorption isotherms of hog plum powder obtained by spray-dryer, through mathematical models. GAB, BET, Henderson and Oswin models were adjusted to the experimental data at 25, 30, 35 and 40°C. The BET model best adjusted to the atomized hog plum for all temperatures tested, with an error ranging between 8.45 and 11.17%. The coefficient of determination (R^2) had rates higher than 0.9900 for all the adjusted models. The behavior of hog plum powder adsorption isotherms was classified as Type III.

Keywords: hygroscopicity, drying, fruit powder.

Isotermas de adsorção de polpa de cajá (*Spondia mombin* L.) em pó obtido em *spray-dryer*

RESUMO. As isotermas de sorção dos alimentos possuem uma grande importância na previsão do tempo de secagem e condições de armazenamento de um produto. Este trabalho teve como objetivo avaliar o comportamento das isotermas de adsorção para pós de cajá obtido em secador do tipo *spray-dryer* por meio de modelos matemáticos. Os modelos de GAB, BET, Henderson e Oswin foram ajustados aos dados experimentais nas temperaturas de 25, 30, 35 e 40°C. O modelo BET, em todas as temperaturas avaliadas, é a que melhor se ajustou para o pó de cajá atomizado com erro que variou entre 8,45 à 11,17%. Já o coeficiente de determinação (R^2) apresentou valores acima de 0,9900 para todos os modelos ajustados. O comportamento das isotermas do pó de cajá atomizado foi classificado como Tipo III.

Palavras-chave: higroscopicidade, secagem, pó de frutas.

Introduction

Brazil stands out as a great producer of native and cultivated tropical fruits, due to its extensive territory and climatic conditions favorable to fruit culture. Its economic activities comprise a robust agroindustry in exotic fruits which is one of Brazil's most relevant important segments responding to more than 35% of the country's agricultural production (MOREIRA et al., 2013).

Hog plum (*Spondias mombin* L.) is native to tropical America and is widely distributed throughout Brazil. In the Amazon region, it is commonly known as taperabá; in the states of São Paulo and Minas Gerais, it is known as cajazeira-miúda and cajá-pequeno; in the southern states of Brazil it is best known as cajazeira or cajá-mirim; and in most of the Brazilian northeastern region, it is simply called cajá. In Northeastern Brazil, *Spondias mombin* grows spontaneously and in the

wild, competing with other plants, in backyards, farms and even under cocoa trees (PINTO, 2003).

Aiming at conserving the fruit and its components, the development and application of drying techniques for *Spondias mombin* have been given special attention. Besides adding commercial value to the fruit, these techniques provide shelf life to the fruit, reduce its dependence on seasonal conditions and eliminate wastes and postharvest losses (MARQUES et al., 2009).

Aspersation dryers, also known as spray-dryers, are used for drying solutions, suspensions, emulsions and pastes. When well conducted, dehydration by aspersation generates a highly nutritive, stable and versatile product. Permanence time of particles inside the spray-dryer is usually less than 30 s (PEDRO et al., 2010).

The powder obtained from the pulp of the fruit is a physically stable product, easy to dose and, has several uses, such as coloring and flavoring to

foodstuffs (BHANDARI et al., 1993). Products from fruit powder have high hygroscopicity, which is the ability of absorbing moisture from the air (JAYA; DAS, 2004).

Storage exposes food to several temperature and relative humidity conditions, causing the food to reach a balance with the environment and, consequently, to alter its own moisture contents (TONELI et al., 2008).

Knowledge and understanding of sorption isotherms are very important for food science and technology since, conditions of drying, storage and packaging may be established and food may be conserved at its maximum limits (JAMALI et al., 2006).

Current analysis investigates the hygroscopic behavior of hog plum powder obtained by spray-drying, through sorption isotherms gathered by adjusting the following mathematical models: GAB (Guggenheim, Anderson and DeBoer), BET (Brunauer, Emmett and Teller), Henderson and Oswin.

Material and methods

The pulp of the hog plum was obtained from an industry in Fortaleza, Ceará State, Brazil. The pulps were placed in asbestos boxes and sent to the Laboratory of Food Quality and Drying of the Department of Food Technology of Federal University of Ceará. Were kept frozen at -18°C . Prior to the start of experiments, the pulps were thawed in a refrigerator (8°C) for 18h. After defrosting, 25% (p p^{-1}) of maltodextrin, DE 20 were added.

The samples were dehydrated in a spray-dryer (LM MSD 1.0 brand Labmaq do Brasil) with the following operational conditions: drying temperature - 160°C ; asperser beak diameter - 1.2 mm; drying air output - 3.0 L min^{-1} ; aspersion pressure - 689.5 kPa; feeding output - 0.55 L h^{-1} ; compressed air output - 3.0 L min^{-1} . After drying, the powders was weighed, vaccuum stored in polyamide (PA) and polyethylene (PE) bags and kept in the dark, at room temperature.

The static gravimetric method was employed to determine the isotherms. Powder samples (0.2 g) were weighed in triplicates in aluminum crucibles. The crucibles were placed in closed glass cells containing saturated saline solutions (CH_3COOK 21%, K_2CO_3 44%, NaBr 58%, SnCl_2 76%, KCl 84%, BaCl_2 90%), following Greenspan (1977). The process was monitored by sample weighing on an analytical balance every 24h until equilibrium moisture was reached. Further, the samples water

activity (a_w) was then determined at 25, 30, 35 and 40°C using a_w meter (AQUALab 4TEV). Moisture contents were determined in a vacuum drying hothouse at 60°C , at constant weight. Balance moisture (X_0) was calculated by the difference between the balance and dry mass with Equation 1 for that.

$$X_0 = \frac{m_{\text{eq}} - m_s}{m_s} \quad (1)$$

where:

X_0 = balance moisture (g g^{-1});

m_{eq} = sample balance mass (g);

m_s = dry sample mass (g).

The mathematical models displayed on Table 1 were adjusted to the experimental data to obtain the adsorption isotherms.

Table 1. Mathematical models used to adjust the experimental data of the adsorption isotherms.

Model	Equation
GAB	$X_0 = \frac{X_m \cdot C \cdot K \cdot a_w}{(1 - K) \cdot a_w + (1 - K \cdot a_w + C \cdot K \cdot a_w)}$
BET	$X_0 = \frac{X_m \cdot C \cdot a_w}{1 - a_w} \left[\frac{1 - (n + 1) \cdot (a_w)^2 + n \cdot (a_w)^{n+1}}{1 - (1 - C) \cdot a_w - C \cdot (a_w)^{n+1}} \right]$
Henderson	$X_0 = \left[\frac{-\ln(1 - a_w)}{b} \right]^{\frac{1}{n}}$
Oswin	$X_0 = a \cdot \left[\frac{a_w}{1 - a_w} \right]^b$

X_0 = balance moisture ($\text{g H}_2\text{O g}^{-1}$); X_m = water content in the molecular monolayer ($\text{g H}_2\text{O g}^{-1}$); a_w = water activity; n = number of molecular layers; C, K = sorption constants; a, b = adjustment parameters

The quality of the model adjustments was evaluated by the coefficient of determination (R^2) and by the relative average deviation (E), as defined by Equation 2:

$$E = \frac{100}{n} \sum_{i=1}^n \frac{|(M_i - M_{p_i})|}{M_i} \quad (2)$$

where:

E = relative average error (%);

M_i = experimental value;

M_{p_i} = value predicted by the model;

n = number of experimental data.

The models were adjusted with Statistica 7.0 (STATSOFT, 2007).

Results and discussion

Table 2 shows the parameters of the mathematical models (GAB, BET, Henderson and Oswin) adjusted to the experimental data with regard to hog plum pulp powder at 25, 30, 35 and 40°C . These temperatures were chosen according to the shelf conditions of the product.

Table 2. Mathematical model parameters representing the sorption isotherms of hog plum pulp powder.

Models	Temperature (°C)	Parameters			R ²	E (%)
		X _m	C	K		
GAB	25	0.0959	0.7122	0.9547	0.9964	18.54
	30	0.1074	0.6851	0.9489	0.9963	17.32
	35	0.1394	0.5722	0.9313	0.9958	17.57
	40	0.1322	0.6770	0.9166	0.9973	13.75
BET		X _m	C	N		
	25	0.2837	0.1154	9.6061	0.9950	10.81
	30	0.3129	0.1154	9.1330	0.9947	11.17
	35	0.3146	0.1154	8.2422	0.9953	10.89
Henderson		A	b			
	25	0.5741	3.2693		0.9974	12.85
	30	0.5839	3.1795		0.9969	11.54
	35	0.6109	3.2112		0.9965	13.14
Oswin		A	b			
	25	0.0761	0.9248		0.9946	22.76
	30	0.0838	0.8541		0.9865	24.44
	35	0.0885	0.8963		0.9931	24.32
	40	0.0941	0.9151		0.9938	21.34

R² = coefficient of determination; E = relative average error (%); X_m = water content in the molecular monolayer (g H₂O g⁻¹); a_w = water activity; n = number of molecular layers; C, K = sorption constants; a, b = adjustment parameters.

During the determination of the isotherm for the obtained powder, a certain level of agglomeration (caking) was observed in all samples, though it was more evident in samples within the cells with saturated solution of KCl (a_w = 0.7) and BaCl₂ (a_w = 0.9). In general, it has been observed that in cells with low water activity solutions, the hog plum pulp powder adsorbed small amounts of water.

It has also been reported that only the BET model at 40°C had an error lower than 10% (Table 2). The coefficients of determination (R²) varied between 0.9947 and 0.9976. Even though most errors were higher than 10%, the average errors were slightly higher in the adjustment of BET and Henderson model.

Among all the adjusted models, BET was the one that best represented the adsorption isotherm for hog plum pulp powder, since it had the lowest relative average errors (E%) and high coefficients of determination (R²). According to Andrade et al. (2011), the BET model is applicable to water activity rates between 0.05 and 0.45; in current assay, however, the model failed to adjust well to the highest water activity rates.

As predicted by BET and GAB models, water content levels in the monolayer X_m are particularly interesting since they point out the amount of water that is strongly adsorbed to the specific sites on food surface; they are considered high rates to ensure their stability (FENEMMA et al., 2010). In given temperatures, the amount of water in the monolayer provides greater stability and minimal quality loss to the food (GOULA et al., 2008). It has been observed that there was an increase in moisture in the

monolayer (X_m) in both mathematical models when temperature rose from 25 to 40°C. A similar behavior was observed by Moreira et al. (2013) where GAB and BET models had an increase in X_m between 25 and 35°C. Ferreira and Pena (2003) also observed this behavior while studying the hygroscopic behavior of peach palm flour and forwarded two justifications: changes in the product's physical structure by providing a greater number of active sites receptive of water molecules and an increase in the solubility of solutes intrinsic to the product, causing a greater number of water molecules stuck in the monolayer.

The Henderson model was the second best model since it presented relative errors between 11.17 and 12.85%. Tonon et al. (2008) obtained a maximum error of 14.73% with Henderson model, while adjusting isotherms of spray-dried açai powder at 25°C, with R² = 0.9950. Alexandre et al. (2007) detected errors lower than 7% with Henderson model while adjusting adsorption isotherms of pitanga in powder at 10 and 40°C.

The K rate in the GAB model decreased as temperature rose from 25 to 40°C. The sorption constant (K) increased as the interaction adsorbate-adsorbent became stronger and values higher than 1 were physically inadequate, since they indicated infinite sorption (TIMMERMANN, 2003). In current assay, all K rates were lower than 1 (Table 2).

Constants 'a' and 'b' of Henderson and Oswin models are within expectations. According to Blahovec (2004), in the case of Oswin model, constant 'a' should be higher than zero and 'b' should be higher than 1.0. According to the same author, 'a' should be higher than zero and 'b' should be between zero and 1.0 in the Henderson model. Under these conditions, the isotherm would not have an inflexion point and there would not be changes in concavity for the curves. Consequently, these constants would mathematically and physically consistent (ALCÂNTARA et al., 2009).

Adsorption isotherms were built for hog plum pulp powder at 25, 30, 35 and 40°C by adjustment to the BET model (Figure 1).

As may be observed in Figure 1, the isotherms for hog plum pulp powder showed a behavior characteristic to isotherms Type III, according to IUPAC classification Herbrard et al. (2003). Further, Moreira et al. (2013) with mango pulp powder, Oliveira et al. (2012) with grugru palm powder and Tonon et al. (2008) with açai in powder had isotherms according to the same classification. This behavior in which isotherms have a plainer area

than their first part is typical to foods that are rich in soluble compounds, such as sugars (AL-MUHTASED et al., 2004).

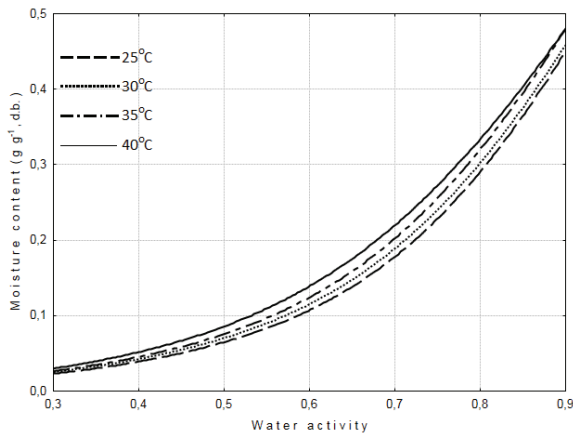


Figure 1. Adsorption isotherms according to the BET model for hog plum pulp powder at 25, 30, 35 and 40°C.

The behavior of food adsorption isotherms at temperature changes is important, because, during food storage the changes in temperature will cause variations in water activity. Temperature alterations affect water mobility and balance between their vapor and adsorbed phases and, in general, changes in temperature reduce food balance moisture. This behavior is caused by a reduction in the number of active sites available for linking with water molecules, due to physical and/or chemical changes (GOULA et al., 2008). Costa et al. (2013) observed this behavior with *crambe* fruit, as well as Goula et al. (2008) with the isotherms of tomato pulp powder.

Nevertheless, several researchers have observed a different behavior in isotherms of food rich in crystalline sugars, such as glucose (GOULA et al., 2008). Such behavior has been observed in current assay (Figure 1). Temperature increase in a given water activity caused greater moisture in the powder, especially between rates 0.5 and 0.8 of water activity. Fiorentin et al. (2010) in their studies on isotherms of orange bagasse and Anselmo et al. (2008) in their studies on the hygroscopic behavior of the dry extract of achiote, also perceived that a gain in temperature resulted in balance moisture increase. This behavior may be explained by increase in the solubility of sugars in water due to temperature (PEDRO et al., 2010).

Figure 1 shows that the powder increased balance moisture when water activity rates were above 0.6 and, therefore, exposing hog plum pulp powder to conditions where relative humidity is higher than 60% and represents a rapid increase in moisture content.

Conclusion

The sorption isotherms of hog plum pulp powder were better represented the BET model and revealed a type III behavior.

Gains in temperature of hog plum powder in the same balance relative humidity resulted in an increase in the powder moisture content.

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