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Physicochemical characterization and modeling of water sorption isotherms for sugarcane samples (*Saccharum officinarum* L.)

Caracterização físico-química e modelagem das isotermas de sorção de água em amostras de cana-de-açúcar (*Saccharum officinarum* L.)

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Sugarcane juice is a refreshing, energetic and highly nutritious beverage. Due to its composition, fresh sugarcane juice is prone to microbial deterioration. Therefore, the application of methods that extend its shelf life can be useful to obtain a product with desirable properties. The aim of this study was to perform physicochemical characterization of freeze-dried sugarcane samples and evaluate the capability of six different mathematical models to describe their water sorption isotherms at three temperatures. Higher mineral content and phenolic compounds were found in the freeze-dried sugarcane sample compared to *in natura* sugarcane sample. Several statistical indices were adopted to assess the mathematical models performances used for the isotherm studies. The Henderson model provided the best goodness-of-fit for the observed type-III experimental isotherms. The net sorption isosteric heat was negative, indicating the occurrence of exothermic reactions during the water absorption in sugarcane samples. An empirical equation for calculating the energy required for drying sugarcane samples by freeze-drying between two given moisture contents was obtained. The results described in this work could be used for designing and optimizing drying processes of sugarcane samples in real-world applications.
Keywords: freeze-drying, sugarcane, water sorption.

O caldo de cana é uma bebida refrescante, energética e altamente nutritiva. Devido à sua composição, o caldo de cana fresco está sujeito à deterioração microbiana. Portanto, a aplicação de métodos que ampliem sua vida útil pode ser útil para a obtenção de um produto com propriedades desejáveis. O objetivo deste estudo foi realizar a caracterização físico-química de amostras de cana-de-açúcar liofilizadas e avaliar a capacidade de seis diferentes modelos matemáticos para descrever isotermas de sorção de água em três temperaturas. Maior teor de minerais e compostos fenólicos foram encontrados na amostra de cana-de-açúcar liofilizada em comparação com a amostra de cana *in natura*. Vários índices estatísticos foram adotados para avaliar o desempenho dos modelos matemáticos usados para os estudos de isotermas. O modelo de Henderson forneceu o melhor ajuste para as isotermas experimentais tipo III observadas. O calor isostérico líquido de sorção foi negativo, indicando a ocorrência de reações exotérmicas durante a absorção de água nas amostras de cana-de-açúcar. Foi obtida uma equação empírica para o cálculo da energia necessária para a secagem de amostras de cana-de-açúcar por liofilização entre dois teores de umidade dados. Os resultados descritos neste trabalho podem ser usados para projetar e otimizar processos de secagem de amostras de cana-de-açúcar em aplicações do mundo real.
Palavras-chave: liofilização, cana-de-açúcar, sorção de água.

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1. INTRODUCTION

Fresh sugarcane (*Saccharum officinarum* L.) juice is a very popular pleasant, cheap drink produced in some countries of South America. Sugarcane crops have high economic values due mainly to the products obtained from sugarcane juice including crystal refined sugar, brown sugar and molasses. In the year of 2016, sugarcane was the most produced food in Brazil with 769 million ton being used mainly to produce alcohol combustible and sugar [1]. Sugarcane and its derivatives are widely known for their nutritional and healthy properties [2]. Moreover, several studies have reported the presence of different phytochemical compounds in sugarcane, such as phenols, sterols, terpenoids, and lignins [3-6].

One of the major problems of using sugarcane juice as food is its perishability due to its high sugar content. Thus, this feedstock is exposed to action of microorganisms aiming to fermentation and decrease of the sugar content [7]. Raw liquid sugarcane juice rapidly deteriorates even after storage at low temperatures [8]. An alternative to overcome this difficulty is to prepare this type of food by freeze-drying. This technique is the best sample drying method because it keeps the bioactive compounds in the different foods produced from sugarcane [9]. Freeze-dried sugarcane juice is a bioactive compound-rich food with extended shelf-life compared to the raw liquid sugarcane juice.

Water sorption isotherm models are useful tools for determining the stability of food products and describing the relationship between the equilibrium humidity content and relative humidity at constant temperature [10]. The water sorption capacities of freeze-dried foods are related with the structural changes occurring during the freeze-drying process. They provide important information on the shelf-life and chemical stability of the food product upon different storage forms [11]. According to the classification of Brunauer [12], there are five different types of sorption isotherms. These types depend on the shapes of the obtained experimental curves and processes that generated these shapes. Then, the possible behaviors exhibited by the experimental data are represented by several mathematical models as described in other study [11].

Thus, the purpose of the current study was to perform the physicochemical characterization properties of freeze-dried sugarcane juice and *in natura* sugarcane samples, and modeling water sorption isotherms for these samples. The sorption isotherm fits of six different mathematical models to the experimental data were studied at three different storage temperatures. Images of scanning electron microscopy were used for describing the water sorption behavior and morphology of the final food. The energy necessary for drying the freeze-dried sugarcane juice samples between two given moisture contents was evaluated. Such results provided useful information for the optimization of freeze-drying process of sugarcane juice.

2. MATERIALS AND METHODS

Sugarcane of the RB 765418 variety was collected from a plantation located in Nova Erechim, Santa Catarina, Brazil. After harvesting, all samples were immediately taken to the laboratory.

The sugarcane samples were cleaned and sugarcane juice was extracted with an electric milling machine (Maqtron, Brazil). The produced sugarcane juice was placed in polyethylene flasks and stored at 10 °C. Subsequently, this juice was filtered and sieved (0.315 mm). Next, the juice sample was frozen at -86 °C in an ultra-freezer (Indrel Ultra Freezer IULT 335D, Brazil) for about 3 h and freeze-dried (TFD5503, Ilshin Lab, Korea) for 28 h.

The following physicochemical measurements were conducted in both freeze-dried and non-freeze-dried samples: ash, moisture, water activity, color, and total phenolic compounds. The evaluation of titratable acidity (TA), soluble solid concentration (SSC), and pH were conducted in the reconstituted freeze-dried samples. It was also determined the mineral content of both samples (calcium, iron, potassium, magnesium, copper) and the solubility water index of the freeze-dried powder. Images of scanning electron microscopy were recorded for characterizing the freeze-dried sugarcane structure. All analyses were performed in triplicate.

Aliquots of 10 mL of liquid sugarcane juice and reconstituted sugarcane freeze-dried powder were titrated with 0.1 mol/L NaOH solution (Sigma Aldrich, St Louis, USA) up to achieve pH 8.1 with the aim of determining the TA values, expressing the results as % of citric acid. The SSC and pH values were determined by diluting 1.0 g of the powder freeze-dried sample in 10 mL of deionized water. The SSC values were measured using a digital refractometer (RFM 732, Bellingham and Stanley, Kent, UK), whereas pH values were measured using a digital pH meter (mPA 210, MS Tecnopon, Piracicaba, Brazil).

Ash and moisture were determined according to the Association of Official Analytical Chemists, official methods 969.36 and 966.20, respectively [13]. The water activity was measured using a Pre Water Activity Analyzer Aqualab (Decagon Devices Inc, USA) at 20 °C. The solubility water index was evaluated according to Cano-Chauca et al. (2005) [14].

Instrumental color was monitored using a Minolta colorimeter (Konica Minolta CR 400, Tokyo, Japan). Color space coordinates of the Commission International de L'Eclairage (CIE): L^* (lightness), a^* (redness/greenness), and b^* (yellowness/blueness) were determined for both freeze-dried and non-freeze-dried samples.

The total phenolic compound concentrations were determined by the Folin-Ciocalteu method, measuring the sample absorbencies by spectrophotometry UV-VIS (Shimadzu Mini 240 UV-Vis Spectrophotometer, Shimadzu Corporation, Kyoto, Japan) [15]. Gallic acid was used as external standard for the analytical calibration curve.

The mineral content was determined by flame (air-acetylene flame) atomic absorption spectroscopy (Analytik Jenna contra 700, Analytik Jenna, Germany). Calcium, copper, iron, magnesium, and potassium were determined at 422.6728, 248.3270, 324.7540, 248.3270, 285.2125, 766.4908 nm, respectively [13].

Images of scanning electron microscopy were recorded using a JSM 6701F-JEOL microscope (JEOL Ltd., Tokyo, Japan) operating at 10 kV voltage after depositing a gold thin film on the sample surfaces as previously described in other study [16].

The water sorption isotherms of the freeze-dried samples were studied using a static gravimetric method [17]. Samples of 1.0 g were placed in specific flasks (hygrostats) containing six saturated salts (CH_3COOK, K_2CO_3, NaBr, $SnCl_2$, KCl, and $BaCl_2$). These flasks were placed in an oven with temperature controlled at 20, 25, and 30 °C. The sample masses were measured every twenty four hours, until obtaining a constant value. These temperatures were adopted because sugarcane juice is commonly produced and exposed in Brazil at room temperature. Thus, the freeze-dried powder would be consumed at the same temperature.

The water sorption data were fitted by using the Brunauer-Emmett-Teller (BET) (Equation 1), Guggenheim-Anderson-de Boer (GAB) (Equation 2), Halsey (Equation 3), Henderson (Equation 4), Oswin (Equation 5), and Smith (Equation 6) [12] mathematical models.

$$X = \frac{X_\mathrm{m}\ \mathrm{C}\ a_\mathrm{w}}{(1-\ a_\mathrm{w})}\left[\frac{1-(\mathrm{n}+1)(a_\mathrm{w})^\mathrm{n}+\mathrm{n}(a_\mathrm{w})^{\mathrm{n}+1}}{1-(1-\mathrm{C})a_\mathrm{w}-\mathrm{C}(a_\mathrm{w})^{\mathrm{n}+1}}\right] \tag{1}$$

$$X = \frac{X_\mathrm{m}\ \mathrm{C}\ \mathrm{K}\ a_\mathrm{w}}{(1-\mathrm{K}\ a_\mathrm{w})\ (1-\mathrm{K}\,a_\mathrm{w}+\mathrm{C}\ \mathrm{K}\ a_\mathrm{w})} \tag{2}$$

$$X = \left[\frac{-\mathrm{a}}{\log(a_\mathrm{w})}\right]^\mathrm{b} \tag{3}$$

$$X = \left[\frac{-\ln(1-\ a_\mathrm{w})}{\mathrm{a}}\right]^{\frac{1}{\mathrm{b}}} \tag{4}$$

$$X = \mathrm{a}\left[\frac{a_\mathrm{w}}{1-\ a_\mathrm{w}}\right]^\mathrm{b} \tag{5}$$

$$X = \mathrm{a}+\mathrm{b}\log(1-a_\mathrm{w}) \tag{6}$$

in which, X is the equilibrium moisture content (dried basis), a_w is the water activity, a and b are empirical parameters, X_m is the monolayer moisture content, n is the number of molecular layers, C and K are the BET and GAB equation constants, respectively.

As there are various water sorption models available in the literature, it is necessary to use different criteria for comparing the goodness-of-fit of each model [18]. The fitting capability of the different models used for describing the experimental of this study was based on the coefficient of determination (R^2), mean relative percentage error (MRPE), root mean square error

(RMSE), mean absolute error (MAE), Akaike information criterion (AIC), and Bayesian information criterion (BIC). The respective mathematical equations used for expressing these statistical indices are given by Equations 7 to 12. Two additional performance indices (ϕ and γ) used in the current work are given by Equations 13 and 14, respectively [18]:

$$R^2 = \sum_i \frac{(\hat{y}_i - \bar{y})^2}{(y_i - \bar{y})^2} \tag{7}$$

$$\mathrm{MRPE} = \frac{100}{n} \sum_i \left| \frac{\hat{y}_i - y_i}{y_i} \right| \tag{8}$$

$$\mathrm{RMSE} = \sqrt{\frac{\sum_i (y_i - \hat{y}_i)^2}{n - p}} \tag{9}$$

$$\mathrm{MAE} = \frac{1}{n} \sum_i |\hat{y}_i - y_i| \tag{10}$$

$$\mathrm{AIC} = -2\log(\mathrm{Lp}) + 2[(p+1)+1] \tag{11}$$

$$\mathrm{BIC} = -2\log(\mathrm{Lp}) + [\,(p+1)+1]\ \log(n) \tag{12}$$

$$\phi = \frac{100\ R^2}{(\mathrm{RMSE})\ (\mathrm{MRPE})} \tag{13}$$

$$\gamma = \det\left(J^T J\right) \tag{14}$$

In Equations (7 to 14), the symbol $\hat{y}_i$ corresponds to the ith prediction, $\bar{y}_i$ corresponds to the mean of the observations, y_i represents the ith observation, Lp stands for the likelihood function, p is the number of parameters of the model, n is the number of experimental observations, and J represents the jacobian matrix of partial derivatives with respect to the estimated parameters.

The Shapiro-Wilk test was applied to verify if the residues obtained after fitting each model to the experimental data satisfy the assumption of normality [19]. All statistical analyses and model fits were conducted with the software R v. 3.6.1 [20].

The net sorption isosteric heat can be determined from the Clausius-Clapeyron equation [20]. The resulting mathematical expression is given by:

$$\ln\left(\frac{a_{w_2}}{a_{w_1}}\right) = \frac{\Delta H_S}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{15}$$

in which, a_{w_2} and a_{w_1} correspond to water activities at temperatures T_2 and T_1, respectively, R is the universal gas constant (8.314 J/molK), and ΔH_S represents the net sorption isosteric heat.

The ΔH_S value is estimated by plotting $\ln(a_w)$ as a function of $\frac{1}{T}$ for a specific moisture content. The slope of the curve is $\frac{-\Delta H_S}{R}$. The values of the water activity used in Equation 15 were calculated by using the mathematical model that provided the most accurate predictions of the sorption isotherms experimental data. This procedure was repeated for different moisture contents. The following empirical equation was used for modeling ΔH_S as a function of the equilibrium moisture content [21]:

$$\Delta H_{\mathrm{S}} = \Delta H_0 \exp\left(-\frac{X}{X_{\mathrm{C}}}\right) \tag{16}$$

in which, ΔH_0 (J/molK) is net sorption isosteric heat when $X = 0$ and X_{C} (%) is the moisture constant at which ΔH_{S} has changed by approximately 63%.

The net sorption isosteric heat of water from dryness to moisture content M is given by:

$$\Delta H = \int_0^X \Delta H_S \, \mathrm{d}X \tag{17}$$

After integration of Equation 17, the following expression holds for ΔH:

$$\Delta H = \Delta H_0 X_{\mathrm{C}} \left[1 - \exp\left(-\frac{X}{X_{\mathrm{C}}}\right)\right] \tag{18}$$

From Equation 18, it can be obtained the following expression to estimate the energy required for drying the sugarcane samples from moisture content X_1 to X_2:

$$Q_{12} = \Delta H_0 X_C \left[\exp\left(-\frac{X_1}{X_{\mathrm{C}}}\right) - \exp\left(-\frac{X_2}{X_{\mathrm{C}}}\right)\right] \tag{19}$$

3. RESULTS AND DISCUSSION

Table 1 presents the water activities of each salt at the considered temperatures. As can be visualized, there was a slight variation between the water activities at different temperatures, obtained for each saturated salt solution.

Table 1: Water activity of the six saturated salt solutions at 20, 25, and 30 °C.

Salt	**20 °C**	**25 °C**	**30 °C**
CH_3COOK	0.190	0.195	0.195
K_2CO_3	0.413	0.402	0.410
NaBr	0.578	0.541	0.540
$SnCl_2$	0.767	0.781	0.761
KCl	0.830	0.800	0.800
$BaCl_2$	0.920	0.873	0.870

Table 2 displays the physicochemical properties of the *in natura* and freeze-dried sugarcane samples. It can be seen that the moisture content decreased from 84.20 to 6.06% and the water activity decreased from 0.980 to 0.352. High water activity values favor the microbial growth and biochemical degradation reactions. Thus, foods containing higher water activity have lower shelf-life compared to dried products. Hence, dried foods are generally stored for a longer period of time without losing their physicochemical properties [22]. The moisture content of the freeze-dried sugarcane samples is in accordance with the Brazilian legislation for dehydrated vegetal origin foods, which establishes that the maximum moisture content must be 12% [23]. It was not observed statistically significant differences between the pH values of the sugarcane samples. Powder sugarcane samples have high water solubility (100%). This property is important for decreasing the preparation times of beverages [24].

Table 2: Physicochemical properties (mean ± standard deviation) of the in natura, freeze-dried sugarcane juice, and freeze-dried reconstituted samples.

Properties	***In natura***	**Freeze-dried**	**Freeze-dried reconstituted**
Moisture (%)	84.23 ± 0.08^{a}	6.06 ± 0.26^{b}	-
Ash (%)	0.46 ± 0.26^{b}	2.78 ± 0.01^{a}	-
Titratable Acidity (% of citric acid)	0.29 ± 0.06^{b}	-	0.96 ± 0.05^{a}
Soluble Solids Concentrations (ºBrix)	19.50 ± 0.05^{a}	-	9.90 ± 0.00^{b}
pH	5.26 ± 0.01^{a}	-	5.28 ± 0.02^{a}
Water Activity	0.98 ± 0.00^{a}	0.35 ± 0.00^{b}	-
Phenolic Compounds (mg GAE/g)	2.69 ± 0.19^{b}	27.91 ± 0.88^{a}	-
Lightness (L*)	12.10 ± 0.02^{b}	59.46 ± 0.18^{a}	-
Redness (a*)	-2.56 ± 0.08^{b}	-1.44 ± 0.04^{a}	-
Yellowness (b*)	8.05 ± 0.05^{b}	25.22 ± 0.10^{a}	-

*GAE: Gallic Acid Equivalent. *Different letters in the same row indicate significant differences ($p<0.05$).*

Another parameter related with the food quality is the titratable acidity. This parameter was significantly higher for the freeze-dried reconstituted sugarcane samples comparing with the *in natura* samples. The soluble solid concentration in the *in natura* sugarcane samples was similar to the results described in a previous study [25]. The ash content was significantly higher for the freeze-dried samples due to the increase of concentration during the freeze-drying process. Regarding the color of the sugarcane samples, it was observed that the freeze-dried samples exhibited higher values of the parameters lightness (L*) and yellowness (b*). Both samples showed a green color (negative a* value). It has been shown that sugarcane juice samples have phenolic compounds [26], corroborating with the results obtained for the *in natura* and freeze-dried samples. The phenolic compound concentrations determined in the *in natura* and freeze-dried sugarcane samples were 2.69 and 27.90 mg GAE/g, respectively. These results are in agreement with other studies [27]. Overall, the freeze-drying process preserved the phenolic compound concentrations in the final product. The phenolic compound concentrations in the freeze-dried samples were approximately 10 times higher than those determined in the *in natura* samples. On the other hand, soluble solids concentration values were higher for the *in natura* samples. This is probably a result of the rehydration step [28].

The results obtained for the minerals content of both samples are shown in Table 3. As can be observed, the concentration of all the analyzed minerals increased significantly after freeze-drying. Minerals like magnesium, potassium, and iron, which promote beneficial effects on health, are found in large concentrations in sugarcane [29].

Table 3: Mineral contents (mean ± standard deviation) in the in natura and freeze-dried sugarcane juice samples.

Mineral	***In natura***	**Freeze-dried**
Calcium	116.20 ± 1.40^{b}	652.40 ± 26.90^{a}
Copper	0.30 ± 0.01^{b}	2.76 ± 0.62^{a}
Iron	24.63 ±0.17^{b}	68.61 ± 28.17^{a}
Magnesium	91.39 ± 0.89^{b}	470.49 ± 26.10^{a}
Potassium	118.27 ± 5.80^{b}	552.30 ± 45.33^{a}

** Different letters in the same row indicate significant differences ($p<0.05$).*

Figure 1 shows images of scanning electron microscopy for the freeze-dried sugarcane and *in natura* samples oven-dried at 105 °C for 17 h. A porous rough surface with heterogeneous amorphous structure was noticed for the freeze-dried sugarcane sample. The freeze-drying process is used for removing water of samples by dehydration. In this process, non-crystallized solutes are converted to amorphous regions in the solid material when the temperature is lower than the glass transition temperature of the concentrated solute [30]. Otherwise, the *in natura* sugarcane samples had a solid, plain and compact surface. In general, the freeze-drying process increased the amorphous regions in the sugarcane samples, increasing their porosity.

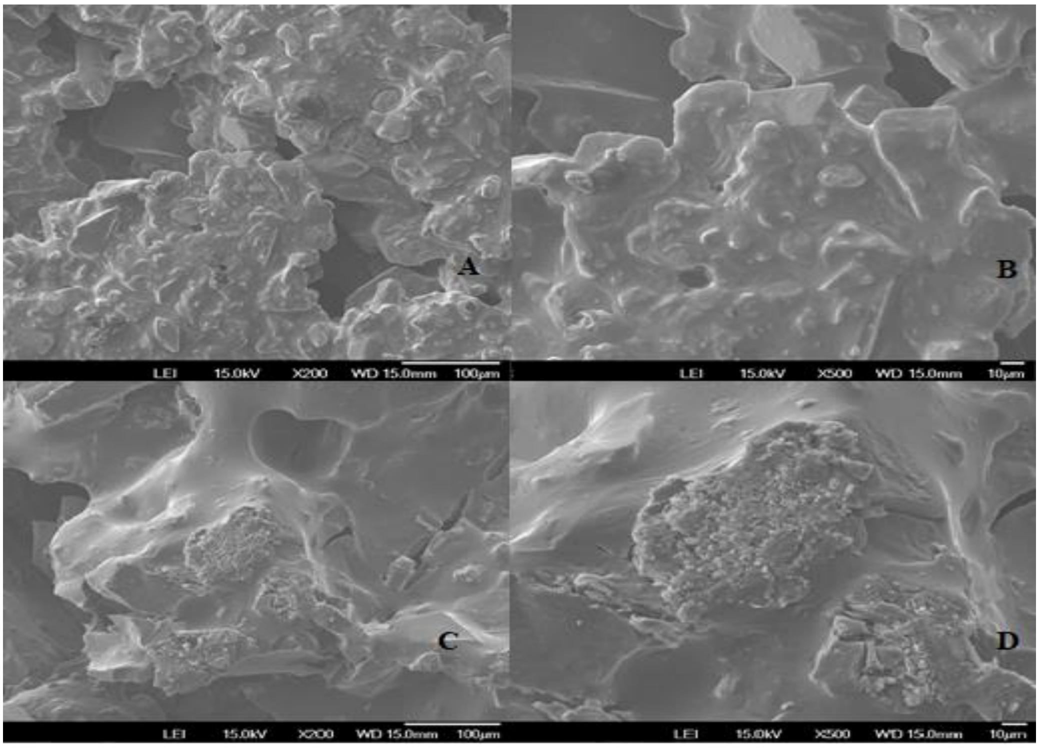

Figure 1: Images of scanning electron microscopy for the freeze-dried sugarcane juice samples with magnifications of a) 200 and b) 500 times and oven-dried in natura sugarcane samples with magnifications of c) 200 and d) 500 times.

The isotherm experiments were performed from 11 and 14 days up to constant sample masses. Figure 2 exhibits the results obtained after fitting the water sorption isotherm models at (a) 20, (b) 25, and (c) 30 °C for the freeze-dried sugarcane juice samples.

Table 4 displays the results of the water sorption isotherm models at 20 °C. Table 5 presents the statistical indices obtained after fit of the water sorption isotherm models. The experimental water sorption isotherms show a slight increase in the equilibrium moisture contents at lower water activity values, followed by a sharp increase at higher water activities. According to the classification of Brunauer [12], the water sorption isotherms at all study temperatures were classified as type III [31]. This kind of isotherm is characteristic of food products with high sugar content such as sugarcane [32]. In general, the equilibrium moisture content decreased with the temperature due to a decrease of the intermolecular attraction forces in the sugarcane sample. It increases the molecular mobility, resulting in weaker chemical bonds between water molecules and chemical groups contained in the sugarcane sample [33].

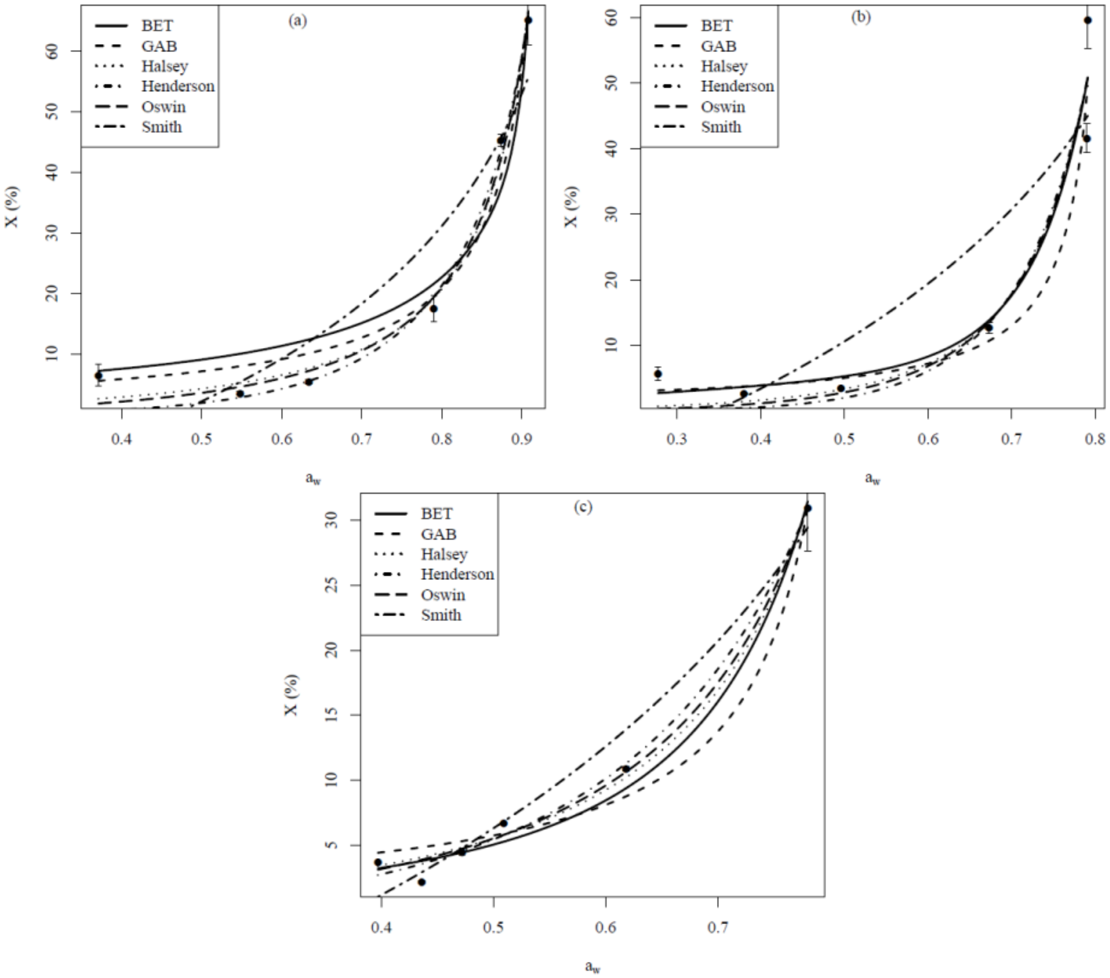

Figure 2: Results of the fits of the water sorption models at (a) 20, (b) 25, and (c) 30 °C for the freeze-dried sugarcane juice sample. The error bars correspond to the standard deviation of the mean.

Table 4: Results of the water sorption isotherm models at 20 °C.

Model	Parameter	Estimate	Standard Error	p-value	Shapiro-Wilk
Brunauer-Emmett-Teller (BET)	X_m	4.535	1.585	0.065	0.873 (0.239)*
	C	-5.018×10^{7}	1.290×10^{15}	1.000	
	n	6.048	1.819	0.045	
Guggenheim-Anderson-de Boer (GAB)	X_m	3.410	9.742	0.395	0.888 (0.310)*
	C	-5.990×10^{7}	8.793×10^{14}	1.000	
	K	1.045	0.002	9.450×10^{-6}	
Halsey	a	1.965	0.530	0.021	0.735 (0.014)*
	b	1.393	0.131	0.001	
Henderson	a	0.552	0.0842	0.008	0.885 (0.295)*
	b	0.350	0.0382	0.000	
Oswin	a	3.584	0.953	0.019	0.783 (0.041)*
	b	1.274	0.124	0.000	
Smith	a	-19.718	9.333	0.102	0.945 (0.704)*
	b	-72.743	13.932	0.006	

*X_m: Water content in the monolayer, C, K: Sorption constants, n: number of molecular layers, a, b: Empirical parameters. *The values are expressed as the statistic W (p-value).*

The evaluation of the effectiveness of a mathematical model aiming to fit experimental data is not an easy task. It is often necessary to consider different aspects such as the significance of the parameters, goodness of fit and normality of the residues. Therefore, one statistical index is not enough to assess the predictability of the model, being necessary to evaluate different parameters simultaneously [17]. According to Tables 4 and 5, it can be observed that the most of the parameters generated after fit of the BET and GAB models are not significant at all study temperatures. The larger uncertainty in both models is associated to the parameter C, which represents the monolayer region sorption heat. Although the BET and GAB models are more mechanistic models than the Halsey, Henderson, Oswin, and Smith models [11], the poor results obtained for the experimental fit of the water sorption in the freeze-dried sugarcane samples suggest that the assumptions used for deriving the equations do not probably work for freeze-dried sugarcane juice. In particular, these equations assume a homogeneous water sorption which is probably not true in the considered system [11]. The GAB model is more applicable to experimental data corresponding to type II isotherms [34].

Table 5. Statistical indices of the water sorption isotherm models fits.

Temperature 20 °C						
	BET	GAB	Halsey	Henderson	Oswin	Smith
R^2	0.952	0.976	0.988	0.989	0.989	0.872
MRPE	61.623	42.822	20.242	21.342	25.962	73.129
RMSE	5.409	3.768	2.588	2.636	2.593	8.335
MAE	4.551	3.299	2.410	1.783	2.279	7.004
AIC	45.284	40.947	34.437	34.659	34.459	48.472
BIC	44.451	40.114	33.813	34.034	33.835	47.848
ϕ	0.286	0.605	1.886	1.758	1.469	0.143
γ	5.290×10^{-9}	4.843×10^{-22}	1.950×10^{6}	1.268×10^{9}	3.370×10^{5}	7.996×10^{-1}
Temperature 25 °C						
R^2	0.943	0.948	0.939	0.937	0.939	0.798
MRPE	30.381	29.341	30.497	44.483	36.830	88.754
RMSE	5.224	4.964	5.437	5.635	5.525	9.809
MAE	4.022	3.903	4.127	4.586	4.342	8.251
AIC	44.866	44.254	43.345	43.775	43.539	50.428
BIC	44.033	43.421	42.721	43.149	42.915	49.803
ϕ	0.594	0.651	0.566	0.374	0.461	0.092
γ	3.055×10^{0}	6.675×10^{7}	1.863×10^{6}	1.322×10^{9}	5.403×10^{4}	1.657×10^{0}
Temperature 30 °C						
R^2	0.987	0.977	0.992	0.993	0.993	0.968
MRPE	20.578	31.693	20.242	17.949	18.962	24.186
RMSE	1.110	1.497	0.921	0.803	0.829	1.770
MAE	0.933	1.204	0.706	0.629	0.622	1.375
AIC	26.282	29.868	22.035	20.395	20.780	29.884
BIC	25.449	29.035	21.410	19.770	20.156	29.259
ϕ	4.321	2.059	5.321	6.890	6.317	2.261
γ	2.417×10^{0}	1.677×10^{-23}	1.131×10^{5}	8.915×10^{7}	7.226×10^{3}	3.221×10^{0}

R^2: Coefficient of determination, MRPE: Mean relative percentage error, RMSE: Root mean square error, MAE: Mean absolute error, AIC: Akaike information criterion, BIC: Bayesian information criterion.

It can be also observed that the worst results for the most of the applied mathematical models were obtained at 25 °C. From Table V, it can be concluded that the Henderson model is the only model with significant parameters at this temperature. Moreover, the residues originated after the fit of this model can be assumed to be normally distributed because the p-values obtained after the application of the Shapiro-Wilk test were higher than 0.05. This test can be used for checking the normality of data regardless of sample size [18]. In general, the Halsey and Oswin models resulted in significant parameters for temperatures different of 25 °C, whereas the Smith model did not accurately reproduce the experimental results at any temperature.

Depending on the statistical performance index considered, a specific model can provide the most accurate fittings (Table 5). The Halsey, Henderson, and Oswin models described more accurately experimental data at 20 °C and 30 °C. The main difference relies on the value of γ (higher for the Henderson model) which describes the precisions of the estimated parameters. The values obtained for the MRPE were relatively high (approximately 20%). This result can be associated to the low equilibrium moisture contents [17]. No model generated accurate fits at 25 °C as mentioned previously. The values of RMSE and MAE were slightly lower for the BET and GAB models due, probably to the larger number of parameters of these models (3) when comparing to the others (2). It was confirmed by the AIC and BIC values, which include the number of parameters in their formulation (see Equations 11 and 12) [35].

Figure 3 exhibits the curves obtained after fitting the Henderson model to experimental data at the three temperatures considered, with the 95% confidence and prediction intervals (CI and PI, respectively) are provided as well. It can be observed that at 20 and 25 °C, the greatest uncertainty was found with water activities ranging from 0.5 to 0.8. Moreover, greater uncertainty was found at 25 °C. The CI and PI were uniforms at 30 °C indicating that the model predictions were homogeneously accurate within the whole water activity ranges at this temperature.

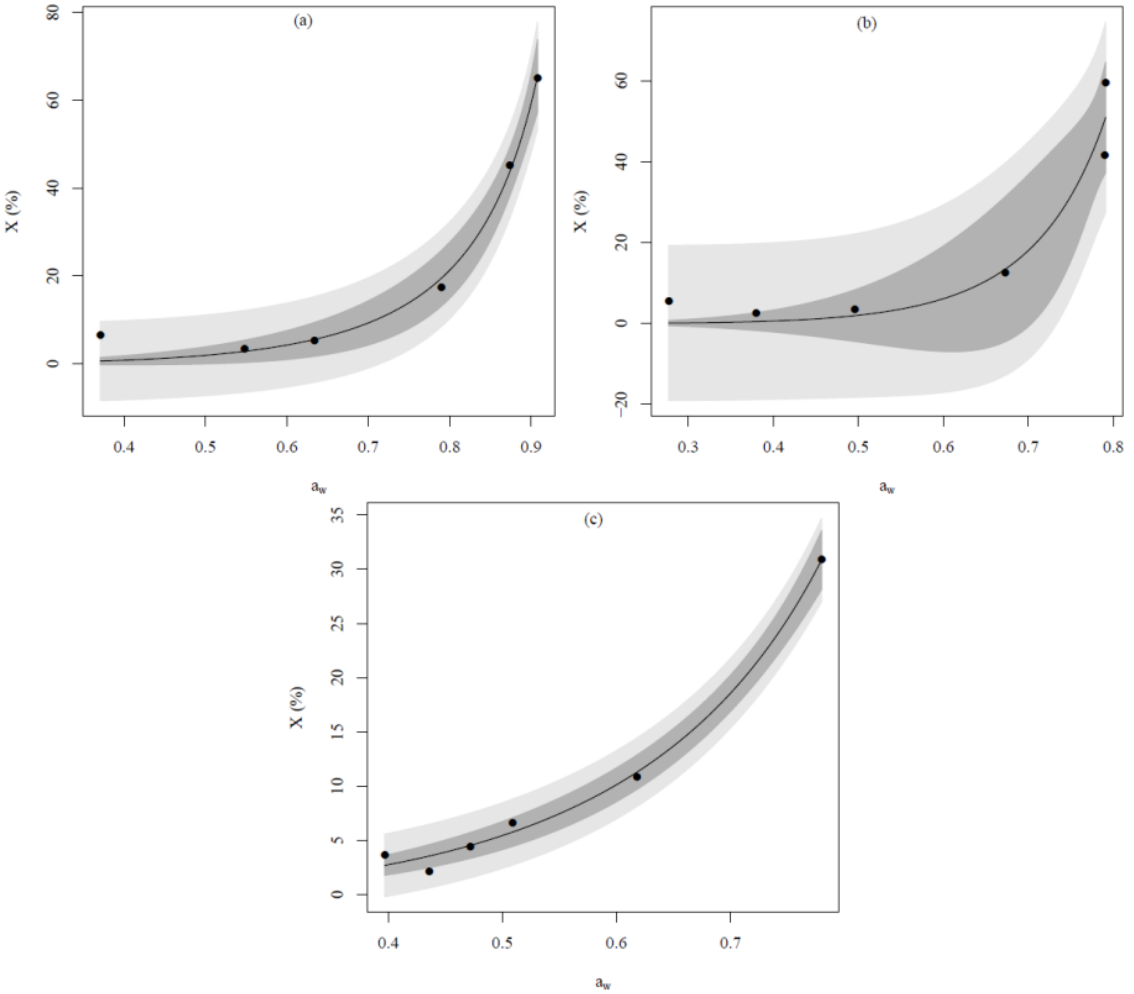

Figure 3: Curves of the fits of the Henderson model to experimental data at: (a) 20, (b) 25, and (c) 30 °C. The dark shadow corresponds to the 95% CI whereas light shadow corresponds to the 95% PI.

Figure 4 shows the results of the sorption isosteric heats as a function of equilibrium moisture contents. The ΔH_S values were negative, increasing with X. Therefore, the water sorption processes in freeze-dried sugarcane samples are exothermic as described in the literature for other samples [36]. This behavior is explained by solution heat containing liquid sugar molecules derived from sugarcane [37]. The water sorption in freeze-dried sugarcane samples tended asymptotically to values close to zero with the increase in the moisture content.

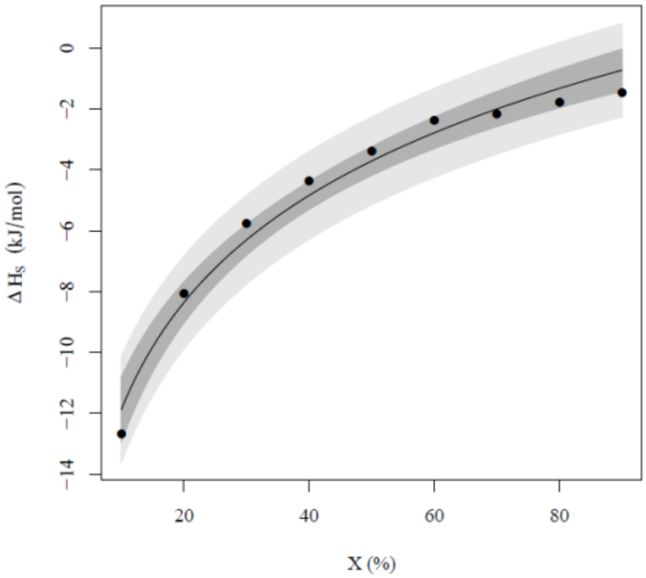

Figure 4: Curve obtained after fit of Equation 16 to net sorption isosteric heat data. The dark shadow corresponds to the 95% CI whereas the light shadow corresponds to the 95% PI.

The following empirical expression was obtained after fit of Equation 16 to the calculated data for the sorption isosteric heat. All the fitted parameters were statistically significant ($p<0.05$).

$$\Delta H = -16.700 \exp\left(-\frac{X}{30.658}\right) \tag{20}$$

From Equation 19, it can be obtained an Equation (Equation 21) for the net water sorption heat when take place changes of moisture contents from X_1 to X_2:

$$Q_{12} = -511.988 \left[\exp\left(-\frac{X_1}{30.658}\right) - \exp\left(-\frac{X_2}{30.658}\right)\right] \tag{21}$$

This equation can also be applied to study and optimize sugarcane powder dehydration.

4. CONCLUSION

The freeze-dried sugarcane sample exhibited higher phenolic compounds than *in natura* sugarcane samples. The water sorption isotherms of freeze-dried sugarcane powder were classified as type-III isotherms at all the study temperatures. After fit of the BET, GAB, Halsey, Henderson, Oswin and Smith mathematical models to experimental sorption curves, the Henderson model was considered to provide the best goodness-of-fit. The sorption isosteric heat was negative, suggesting an exothermic reaction that tended asymptotically to values close to zero with the increase in the moisture content. These results are important for predicting physical changes in the freeze-dried sugarcane powder as, water significantly affects structural transitions during food processing.

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