

Mathematical modeling of the sorption isotherms of three varieties of industrial cassava

Modelamiento Matemático de las isotermas de sorción de tres variedades de yuca industrial

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Abstract

A completely randomized design was used to model the sorption isotherms of three types of industrial cassava. The samples consisted of slices (3.6 cm × 0.6 cm × 0.5 cm) of three varieties of cassava: Corpoica Tai, Corpoica Gynes and Corpoica Veronica. Temperature was set at 20 °C, 30 °C and 45 °C. All experiments were performed in triplicate. Data were obtained through an experimental dynamic method to calculate desorption and adsorption isotherms. Results were analyzed for each temperature, and isotherms were calculated for each variety. Isotherms were statistically equal for all temperatures at a 95 % confidence level. The isotherms were adjusted based on mathematical models (GAB, BET, Smith, Oswin, Henderson, and Peleg). The GAB model was considered the most appropriate for data correlation.

Keywords: equilibrium moisture content; model adjustment; adsorption; desorption.

Resumen

Con el fin de modelar las isotermas de sorción de láminas (3.6 cm × 0.6 cm × 0.5 cm) de tres variedades de yuca industrial, se empleó un diseño completamente al azar en arreglo factorial con dos factores: temperatura (20 °C, 30 °C y 45 °C) y variedad (Corpoica Tai, Corpoica Gynes y Corpoica Veronica), con tres repeticiones. Para la obtención de los datos se empleó la técnica experimental del método dinámico para determinar las isotermas de desorción y adsorción. Los datos obtenidos fueron analizados para cada temperatura, determinándose las isotermas para las variedades estudiadas, las cuales fueron estadísticamente iguales entre sí para las tres temperaturas utilizadas aun nivel de confianza del 95%. Las isotermas fueron ajustadas a los modelos matemáticos de Gab, Bet, Smith, Oswin, Henderson y el modelo de Peleg y se determinó que el modelo de GAB es el más adecuado para correlacionar los datos obtenidos.

Palabras clave: humedad de equilibrio; ajuste del modelo; adsorción; desorción.

I. Introduction

Cassava or yucca (*Manihot esculenta* Crantz) belongs to the spurge family (*Euphorbiaceae*). Around 98 species of the genus *Manihot* have been described, however, only yucca is considered economically important and is grown in many parts. Also known as mandioca, this perennial plant is native to South America [1] and is quite common in tropical areas of about 90 countries in America, Asia and Africa.

Together with corn, sugarcane and rice, cassava is one of the most important source of energy in the tropics. Roots are the edible part of this plant although the foliage is used as animal feed, and as vegetables for human consumption in Africa [2].

According to the 2015 National Agricultural Survey, ENA, by its Spanish acronym [3], Colombia produced 518,482 tons of cassava in 2014, with average yields of 12.4 tons per hectare per year. The department of Meta is the main producer with 175.104 tons (33.6% of the total production) followed by the departments of Magdalena, Sucre, Bolivar, and among others.

In Colombia, cassava is mainly grown by small-scale farmers, with an average of planted areas ranging from one to five hectares per farm. Much of cassava production is oriented towards the fresh produce market. However, the Colombian government through its National Development Plan "Towards a Community State" developed a strategy

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aimed at strengthening the existing production chains and boost cassava production. Today, as a result of this governmental program, cassava production continues to increase substantially, as well as yields, in an effort to substitute the import of raw materials for the feed industry and the poultry industry [4].

Cassava is aimed mainly at four markets depending on its use: as a root for human consumption, as raw material for the food industry, as an intermediate product, and as raw material for the animal feed industry, where its use has increased significantly [4]. Drying and dehydration processes provide foods with lighter consistency as well as improved taste, smell and resistance, in addition to facilitate transport [5]. Drying-dehydration processes are also a useful tool for the development of new products for the agro-industrial sector [6].

Isotherms are defined as the relationship between the moisture content of foods and air temperature and relative humidity, which makes it essential for preservation of dehydrated foods. The equilibrium relative humidity of foods and the air relative humidity play an important role in processes related to drying, conservation and conditioning of food raw materials, in addition to being a useful tool to help structure storage and rehydration systems, and determining food stability [7].

Therefore, proper understanding of the rehydration kinetics is necessary for optimal storage conditions and reduce product loss.

II. Materials and Methods

A. Sample preparation

Raw materials consisted of samples of industrial cassava of the varieties Corpoica Tai, Corpoica Veronica and Corpoica Gynes, which were supplied by ASPROALGA, a local association of agricultural producers based on the department of Córdoba, Colombia. The samples were conditioned based on the shape and size typically used in drying processes.

The samples were cut into slices (3.6 cm long x 0.6 cm wide x 0.5 cm thick) using a lab scale cutting machine in order to allow better contact with the surrounding drying air.

B. Preparing sorption isotherms and mathematical modeling of data

Collection of experimental data needed to calculate the equilibrium curves for cassava samples was performed as follows.

The LabMaster-aw neo water activity meter with salt standards and 0 - 0.95 activity range was used in this

experiment. Each sample was placed in the sample analyzer together with the certified salts until the equilibrium was reached. This procedure was repeated for each of the salts.

Equilibrium curves were calculated using the method described by Rossi and Roa [8], which consists of plotting the equilibrium relative humidity on a dry basis vs the relative humidity of the air. The results obtained were adjusted to mathematical models (GAB, BET, Henderson, Peleg, Caurie, Smith, Oswin, Halsey and Iglesias-Chirife) as shown in Table I.

Table I. Mathematical models to be adjusted in the equilibrium humidity data for each cassava variety.

Name	Model
GAB	$X_{we} = \frac{X_m \times C_0 \times K_0 \times a_w}{(1 - K_0 \times a_w) \times (1 + ((c_0 - 1) \times K_0 \times a_w))}$
BET	$X_{we} = \frac{X_m \times C_0 \times a_w}{(1 - a_w)(1 + ((c_0 - 1) \times a_w))}$
Henderson	$X_{we} = 0.01 \times \left[\frac{-\log(1 - a_w)}{10^A} \right]^{1/B}$
Caurie	$X_{we} = \exp \left[a_w \times \ln(A) - \frac{1}{4.5 \times X_s} \right]$
Smith	$X_{we} = B + A \times \log(1 - a_w)$
Oswin	$X_{we} = A \times \left[\frac{a_w}{1 - a_w} \right]^B$
Halsey	$X_{we} = \left[\frac{A}{\ln \left(\frac{1}{a_w} \right)} \right]^{1/B}$
Iglesias - Chirife	$X_{we} = A + B \times \left(\frac{a_w}{1 - a_w} \right)$

Source: [7].

C. Data processing and statistical analysis

Data processing was performed through an analysis of variance in order to compare temperature and variety, and determine whether interaction occurs between these two factors.

Also, Tukey's range test (5% significance-level) was performed along with model assumption tests (normality, independence and homogeneity of variance). The evaluation of the adjustment quality resulting from the models proposed was performed based on factors such as linear regression coefficient (R²), sum of squared errors (SSE), and residual plot. The lowest SSE values (close to zero) as well as the highest values for R² (close to 1) were considered the most appropriate to choose the appropriate mathematical model [9]. The analysis was carried out using R Studio 1.0.44 software.

III. Results and discussion

The hygroscopic equilibrium of cassava samples was calculated by desorption and adsorption at temperatures of 20 °C, 30 °C and 45 °C as shown in Table II.

Table II.

Hygroscopic equilibrium moisture content per Kg water/Kg dry solid in samples of three cassava varieties at temperatures of 20 °C, 30 °C and 45 °C.

°C	Corpoica Tai		Corpoica Gynes		Corpoica Veronica	
	A _w	X _{bs}	A _w	X _{bs}	A _w	X _{bs}
20	0.989	1.568	0.960	1.882	0.989	3.545
	0.967	1.414	0.958	1.720	0.965	3.270
	0.954	1.192	0.881	1.394	0.889	2.988
	0.439	0.173	0.456	0.157	0.475	0.310
	0.152	0.125	0.156	0.103	0.159	0.243
	0.415	0.151	0.440	0.137	0.459	0.290
	0.700	0.203	0.717	0.221	0.706	0.381
	0.811	0.279	0.839	0.362	0.803	0.516
	0.884	0.303	0.891	0.432	0.865	0.674
30	0.965	1.599	0.962	1.880	0.943	2.572
	0.934	1.457	0.933	1.770	0.919	2.358
	0.822	0.904	0.859	1.520	0.847	1.931
	0.614	0.633	0.733	1.208	0.715	1.333
	0.157	0.178	0.164	0.087	0.168	0.142
	0.423	0.218	0.446	0.135	0.453	0.194
	0.746	0.332	0.747	0.240	0.722	0.339
	0.863	0.457	0.863	0.366	0.839	0.537
	0.927	0.589	0.920	0.497	0.902	0.750
45	0.989	1.637	0.980	1.944	0.961	4.085
	0.922	1.359	0.914	1.664	0.900	3.524
	0.823	0.674	0.819	1.018	0.803	2.345
	0.570	0.239	0.624	0.379	0.617	1.228
	0.163	0.061	0.212	0.156	0.203	0.332
	0.451	0.101	0.490	0.118	0.489	0.414
	0.749	0.196	0.742	0.200	0.725	0.519
	0.872	0.324	0.862	0.331	0.847	0.674
	0.949	0.513	0.932	0.495	0.916	1.048

Source: The authors

The above figure shows that that the equilibrium moisture values expressed in Kg water/Kg dry solid (dry basis) are higher for cassava of the variety Corpoica Veronica, while Corpoica Tai and Corpoica Gynes cassava varieties have similar values. Results for equilibrium moisture in Corpoica Tai cassava at temperatures of 20 °C, 30 °C and 45 °C are close, as occurs in the other varieties. These results are shown in Table III along with the analysis of variance (ANOVA). The analysis suggests a highly significant influence (at a 95% confidence level) of the variety variable on the equilibrium moisture content as well a significant influence of the variety-temperature interaction. The comparison of means test showed significant differences between cassava of the variety Corpoica Veronica and the other two varieties. Likewise, Corpoica Veronica cassava has the highest equilibrium moisture values.

Table III.

Analysis of variance for equilibrium moisture in cassava of the varieties.

Source	DF	Type III SS	Mean Square	F Value	Pr > F
VAR	2	0.23778135	0.11889068	20.71	<.0001
TEMP	2	0.05034241	0.02517121	4.39	0.0172
VAR*TEMP	4	0.27029042	0.06757261	11.77	<.0001

Source: Data provided by the authors

In Table 4, the parameters adjusted for the different mathematical equilibrium models, evaluated by nonlinear regression, of the experimental data of hygroscopic equilibrium of the laminae of the three varieties of cassava obtained by desorption and Adsorption for temperatures of 20 °C, 30 °C and 45 °C; With the respective linear regression coefficients (R^2) and the sum of the square errors (SSE).

Table IV indicates that the Gab and Caurie models better fit experimental data, while the remaining models, despite being used to describe hygroscopicity in various foods, showed the lowest adjustment to experimental data with respect to equilibrium moisture of industrial cassava, as shown by the regression coefficient values and the sum of squared errors.

Since the Gab model best fits experimental data, it can provide valuable information regarding the moisture content in the monomolecular layer (X_m), which is a fundamental parameter for storage conditions due to its high stability. On the other hand, X_m value indicates the presence of active sites suitable for water absorption [10].

The values of the parameters of the GAB model allow to interpret the adsorption behavior. When $C \gg 1$ and $k \ll 1$ it indicates the presence of structured molecules in both the monolayer and the multilayer, and their behavior differs from that of the molecules of the liquid fraction. If $k \approx 1$, the water molecules attached to the monolayer are not structured in a multilayer, and behave similarly to the molecules of the liquid fraction. When $C \approx 1$ there are no differences between the molecules of the monolayer and those of the multilayer. On the other hand, the larger the value of C , the greater the binding strength of the water in the monolayer (strongly bound water) and so the difference in enthalpy between the molecules of both the monolayer and the multilayer [10].

Similar studies with vegetables such as green onion, leeks, and green pepper, as well as dehydrated aromatic plants [11] and grains such as rice, corn and wheat [12] suggest that the GAB model provides a good description of experimental data to calculate equilibrium moisture content. In recent years the GAB model has been widely used to describe sorption isotherms of a variety of foods [13-15]; as well as their studies on foods from plants and animals [16-21].

Table IV.
Parámetros de las ecuaciones ajustadas de las tres variedades de yuca estudiadas, para las diferentes temperaturas.

		Corpoica Tai			Corpoica Gynes			Corpoica Veronica		
Model		20 °C	30 °C	45 °C	20 °C	30 °C	45 °C	20 °C	30 °C	45 °C
Gab	X _m	6,043	0,402	21,617	63,302	101,601	34,166	136,796	2,073	8,797
	C _o	0,059	2,261	0,012	0,012	0,026	0,013	0,012	0,621	0,156
	K _o	0,636	0,809	0,689	0,548	0,340	0,641	0,519	0,642	0,625
	R ²	0,980	0,916	0,945	0,899	0,955	0,910	0,945	0,981	0,786
	SSE	0,121	0,418	0,303	0,948	0,297	0,703	1,814	0,224	7,938
Bet	X _m	0,010	0,070	0,018	0,047	0,092	-----	0,022	0,177	0,196
	C _o	131031,055	626407,480	213525,429	342501,291	638256,064	-----	191343,722	1257657,075	848109,160
	R ²	-----	0,436	0,029	0,092	0,044	-----	-----	0,616	0,351
	SSE	7,589	2,813	5,679	8,531	6,304	-----	50,981	4,468	24,062
Herderson	A	-----	-----	-----	-----	-----	-----	-----	-----	-----
	B	-----	-----	-----	-----	-----	-----	-----	-----	-----
	R ²	-----	-----	-----	-----	-----	-----	-----	-----	-----
	SSE	-----	-----	-----	-----	-----	-----	-----	-----	-----
Caurie	A	43,592	25,534	110,036	34,018	12,868	59,044	27,649	21,785	33,377
	X _s	0,067	0,084	0,054	0,079	0,124	0,067	0,112	0,113	0,114
	R ²	0,981	0,919	0,948	0,901	0,937	0,913	0,946	0,978	0,787
	SSE	0,112	0,403	0,407	0,933	0,413	0,678	1,792	0,261	7,902
Smith	A	-0,714	-1,093	-0,888	-1,205	-1,318	-1,217	-1,683	-2,093	-3,041
	B	0,106	0,101	0,034	0,049	0,211	0,049	0,404	0,086	0,093
	R ²	0,906	0,906	0,882	0,820	0,872	0,863	0,784	0,968	0,774
	SSE	0,556	0,470	0,691	1,690	0,846	1,070	7,177	0,377	8,386
Oswin	A	0,467	0,503	0,440	0,585	0,758	0,562	1,265	0,857	1,227
	B	0,250	0,370	0,304	0,325	0,309	0,338	0,225	0,411	0,400
	R ²	0,825	0,880	0,807	0,744	0,844	0,803	0,706	0,942	0,744
	SSE	1,038	0,597	1,132	2,409	1,029	1,538	9,782	0,679	9,491
Halsey	A	-----	0,036	-----	-----	0,036	-----	-----	0,494	-----
	B	-----	0,044	-----	-----	0,044	-----	-----	2,111	-----
	R ²	-----	-----	-----	-----	-----	-----	-----	0,912	-----
	SSE	-----	13,309	-----	-----	26,643	-----	-----	1,025	-----
Iglesias - Chirife	A	0,627	0,487	0,526	0,634	-----	0,653	1,595	0,729	1,229
	B	0,005	0,048	0,012	0,029	-----	0,028	0,012	0,130	0,135
	R ²	0,367	0,710	0,520	0,427	-----	0,555	0,293	0,776	0,594
	SSE	3,761	1,450	2,813	5,384	-----	3,475	23,496	2,602	15,066

Source: The Authors

Figures 1-9 show experimental data adjustment as well as the experimental data related to equilibrium moisture based on water activity in the desorption-adsorption process of three types of cassava.

The behavior of equilibrium curves (desorption and adsorption) for all cassava varieties and for the three temperatures, resembles a type II isotherm. According to Barbosa-Cánovas et al. [22], type II isotherms are the most common in foods, and its sigmoidal shape is attributed to capillary effects and aqueous interactions on the surface.

This isotherm can be divided into three regions. In the first area, water is strongly bound to polar groups of polysaccharides in the food and has an enthalpy of vaporization considerably greater than that of pure water. This region is responsible for the moisture of the monolayer and has a water activity of around 0.2 to 0.3, therefore the rate of quality loss is negligible. In region B, water molecules are less bound than in the previous area and the energy of evaporation is slightly higher than that required to evaporate

pure water, while the properties of the solvent in the region C are very similar to those of pure water [23].

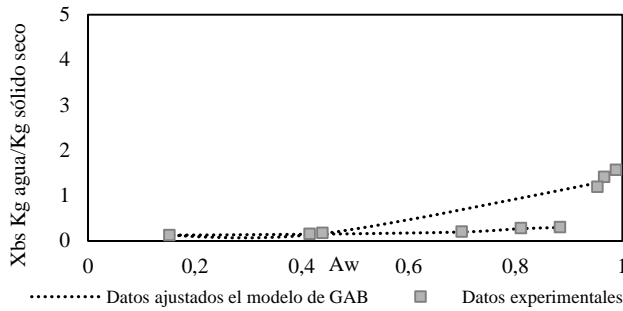


Figure 1. Sorption curves for Corpoica Tai cassava. 20°C.
Source: Data provided by the authors.

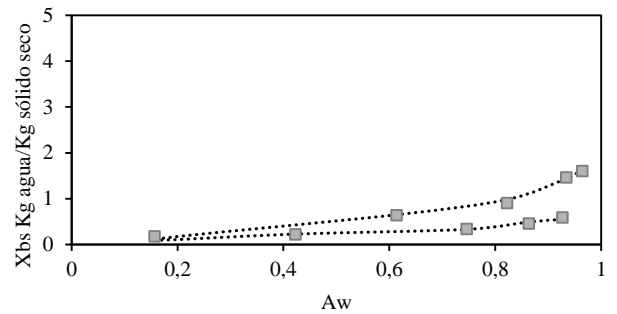


Figure 2. Sorption curves for Corpoica Tai cassava. 30°C.
Source: Data provided by the authors.

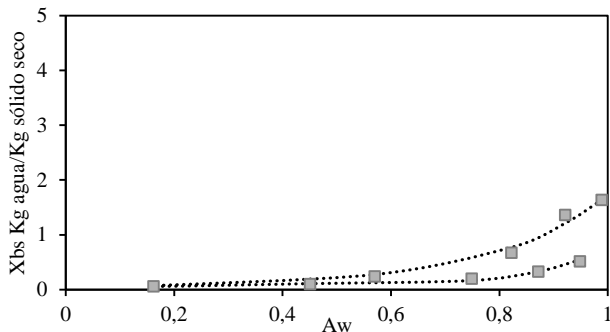


Figure 3. Sorption curves for Corpoica Tai cassava. 45°C.
Source: Data provided by the authors.

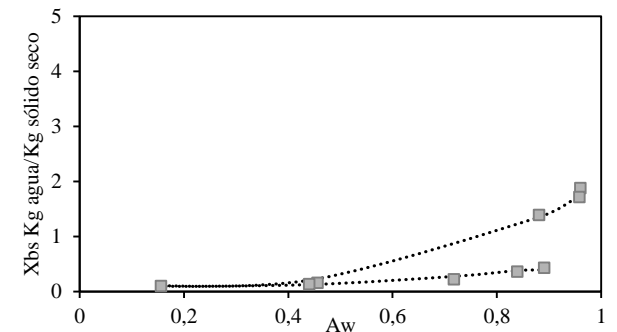


Figure 4. Sorption curves for Corpoica Gynes cassava. 20°C.
Source: Data provided by the authors.

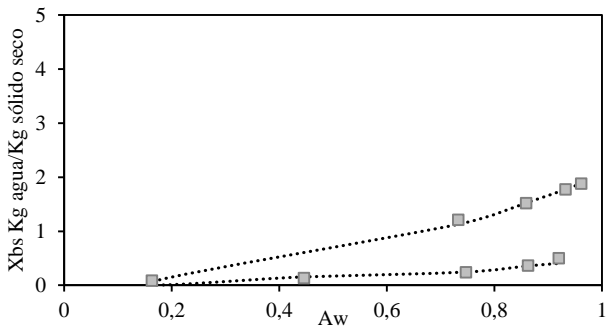


Figure 5. Sorption curves for Corpoica Gynes cassava. 30°C.
Source: Data provided by the authors.

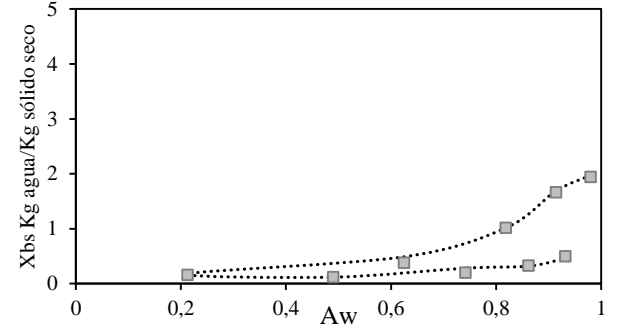


Figure 6. Sorption curves for Corpoica Gynes cassava. 45°C.
Source: Data provided by the authors.

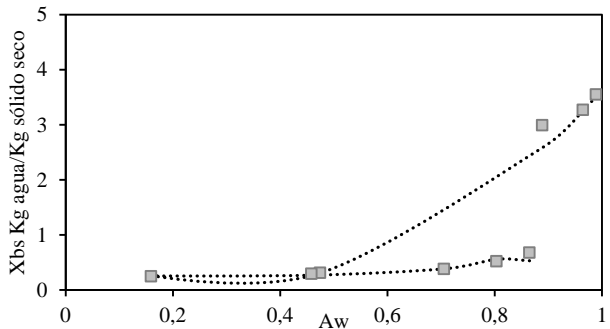


Figure 7. Sorption curves for Corpoica Veronica cassava. 20°C.
Source: Data provided by the authors.

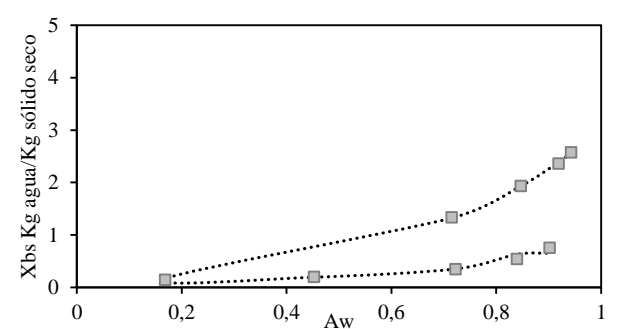


Figure 8. Sorption curves for Corpoica Veronica cassava. 30°C.
Source: Data provided by the authors.

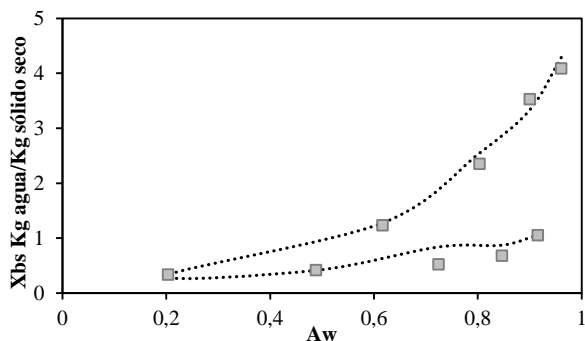


Figure 9. Sorption curves for Corpoica Veronica cassava. 45°C.
Source: Data provided by the authors.

Similar behaviors (Type II) were reported for samples of cassava flour by authors [24-26]; tomato pulp [27]; potato slices [28]; bananas [29]; corn starch [30]; and cassava starch [31].

IV. Conclusions

The equilibrium moisture content for cassava of the varieties Corpoica Tai, Corpoica Gynes and Corpoica Veronica showed statistically significant differences at a level of significance of 5% while the equilibrium moisture content for temperatures of 45 °C, 55 °C, and 70°C had no statistically significant differences.

The behavior of desorption-adsorption isotherms for the three varieties of cassava is properly described by the GAB and Caurie models. However, the GAB model best fits the behavior of the experimental equilibrium data.

The behavior of the equilibrium curves (desorption-adsorption) for the three varieties of cassava and for all temperatures, resembles a type II isotherm, which is the most common in foods. The sigmoidal shape of type II isotherms is attributed to capillary effects and aqueous interactions on the surface.

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