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Sorption Isotherms of Two Varieties of *Amaranthus* at 25°c: Comparison of Water Sorption Characteristics and Mathematical Models

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Abstract: In this study statistical methodology is used to determined similar varieties of *Amaranthus* varieties and to model the behaviour of the moisture content as a function of the water activity (a_w). Different equations proposed in the literature are studied. When analyzing the equations relating the moisture content (m.c.) and the a_w, estimates of the parameters were obtained by fitting a nonlinear model for each variety Using the criteria of minimum S, E or P we conclude that the G. A. B. (Guggenheim andersen and de Boer) and Oswin equation provide the best fits. For *Amaranthus Cruentus* the best fit is given by Oswin and Bradley model, according to P and E criteria, respectively. However, the order of the difference with respect to the goodness of fit statistics using G. A. B. model is negligible. Since the S goodness of fit criterion seems to be reasonable to select the equation in this setting, we use the S measure in order to choose a model. The S statistic for the G. A. B. model is 60% larger on the for *Amaranthus Cruentus* than on the *Amaranthus Mantegazzianus*.

Key words: Amaranth, sorption isotherms

INTRODUCTION

Grain *amaranthus* which was one of the basic foods in pre-Columbian times fell into obsolescence with the collapse of Indian cultures following the conquest. Corn and bean became two of the leading crops that feed the world, while *amaranthus* faded into obscurity[1]. In America it survived only in small pockets of cultivation in scattered mountain area of Mexico and the Andes. In recent years it have been rediscovery as a crop with high potential to increase the world food production lies on the fact that it can grown in desert areas and that seed contains protein of unusual quality[2]. *Amaranthus* is commonly included as an ingredient in cereals based foods like cookers, crackers, breads, breakfast cereals, muffins and also in drinks and beverages[3]. Also, *amaranthus* is been investigated for oil since it is a potential source of squalene[4,5]. Also *amaranthus* flour is investigated[6].

Like others cereals, *amaranthus* is susceptible to microbial growth and mycotoxins production during storage. Bresler *et al.*[7], reported the natural occurrence of zearalelone in grains of *amaranthus* species and many species of toxigenic fungi. Therefore it is essential the knowledge of water sorption isotherms inorder to establish humidity bound to inhibit microbial growth and mycotoxins production during storage. Many authors reports studies about chemical composition of flour and seeds[8-11] but studies on the post harvest handling, specially on the effect of moisture on grain quality and storage, are little available in literature. Pollio *et al.*[12] determined water vapour adsorption and desorption isotherms at 35 C, 45 C and 65 C of *Amaranthus cruentus*. Experimental curves were fitted by Guggenheim anderson and de Boer (G. A. B.) equation and the isosteric heat was calculated. They did not compared sorption behaviour of different varieties and they did not reported moisture content to avoid microbial growth under storage conditions. Also, Pagano *et al.* [13] fitted G. A B. equation to sorption data of *Amaranthus cruentus* L. obtained from literature, originated from data of different sources, determined over a wide range of temperatures and with diverse experimental techniques. In the particular case of 25 C the fit, for adsorption isotherms which is the goal of this study, the fit was done with eight observations.

The aim of this study is to determine adsorption isotherms of two species of *amaranthus* grain (*Amaranthus cruentus* and *A. mantegazzianus*) in order to establish storage conditions to prevent spoilage during it.

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MATERIALS AND METHODS

Water Sorption Characteristics: The samples used in this research corresponded to two varieties of amaranths denominated *Amaranthus cruentus* and *A. mantegazzianus*. Samples were received with approximately 8 % moisture dry basis (d. b.) and stored at 5 C until the analysis was carried out. The isopiestic method was used and the range of a_w considered was 0.60-0.90 which is the most important for microbial growth.

Approximately 2 g samples were stored over constant relative humidity solutions in dessicators at 25±1 C under vacuum conditions and weighed periodically until equilibrium was attained (40-50 days). The saturated salts solutions were Sodium bromide (NaBr), Sodium chloride (NaCl), Ammonium sulphate ($(NH_4)_2SO_4$), Potassium chloride (KCl) and Barium chloride ($BaCl_2$) whose a_w values were reported by Kitic *et al.*[14] and Chirife *et al.* [15].

In order to inhibit fungal growth at high a_w, grains were dipped in Mercury chloride ($HgCl_2$) solution al 0.1%. Immediately, the grains were dried under an air stream at ambient temperature in order to restore their initial moisture. This treatment does not affect sorption characteristics[15]. After this treatment, grains a_w were about 0.55 which is below the initial value used in the isotherms determination. A_w was measured by means of an electronic hygrometer (Novasina Thermoconstanter Humidat TH2). Once equilibrium was attained, moisture contents (m. c.) were determined by drying in a vacuum oven at 100±1C during 8 h (variation in m .c ≤ 0.01%). Bertoni *et al.*[9] used this condition without mention time. All measurements were done by quintuplicate and the whole isotherms were determined by duplicate.

Statistical Methodology: We designed the study by considering three independent data sets of different size in order to compare the water sorption characteristics of the two varieties and also to fit and validate different models used in the literature for other cereals.

Comparison Between Varieties: With the first data set of size 50 (25 observations for each variety) we performed a two-way analysis of variance, i.e.

$$Y_{ijk} = \mu+\alpha_i+\beta_j+\gamma_{ij}+\varepsilon_{ijk} \quad 1 \le i \le 2,\ 1 \le j \le 5,\ 1 \le k \le 5 \qquad (1)$$

where i denotes the variety, j the a_w and k the index of the replicate performed for each variety at each a_w level. Y_{ijk} is the observed moisture content and ε_{ijk} is the measurement error of the k-th experimental unit the i-th variety at the j-th a_w level. It is assumed that

$$\sum_{i=1}^{2}\alpha_i = \sum_{j=1}^{5}\beta_j = \sum_{i=1}^{2}\gamma_{ij} = \sum_{j=1}^{5}\gamma_{ij} = 0$$

Table 1: Sorption data (average) of two different amaranth varieties at 25°C (Moisture content expressed as % dry basis) (standard deviations in brackets)

	Moisture Content (% dry basis)	
a_w	Cruentus	Mantegazzianus
0.577	11.373 (.0550)	11.557 (.2020)
0.751	14.779 (.2464)	14.814 (.1213)
0.803	17.284 (.1758)	16.595 (.3380)
0.842	19.329 (.3401)	19.120 (.1192)
0.903	22.404 (.3917)	22.830 (.1739)

To check if there is any difference between varieties, the hypothesis H_A: $\alpha_i = 0$; $1 \le i \le 2$ has to be tested. Before treating this problem, the existence of interaction should be tested, i.e. the hypothesis H_{AB} : $\gamma_{ij} = 0$; $1 \le i \le 2$, $1 \le j \le 5$. If H_{AB} is rejected, then moisture content and a_w interact for the varieties considered. In this setting, H_A has no sense because it does not indicate the lack of differences between varieties and therefore only an analysis at each a_w level can be performed.

The main assumption of the model, equation 1, is that the measurement errors are independent and identically distributed with zero location parameter and homogeneous and constant scale parameter. An additional hypothesis is the normal or Gaussian distribution of the errors, which was not rejected with the Shapiro-Wilk statistic (p = 0.4992). Under normality, the tests to be performed are the usual test statistics in analysis of variance models based on square sums of residuals, which lead to *F* statistics[17].

Both tests assume that the scale is constant and is highly sensitive to failures of this assumption. The Levene test to check the homoscedasticity of the data yielded a p-value equal to 0.6426.

Thus, the usual ANOVA based on the *F* statistic [18] was carried out and discussed.

Unfortunately, interactions were strongly significant (p-value=0.0001) not allowing to reach jointly significant differences among the two varieties. In Table 1 sorption data (m.c. in % dry basis) of the two varieties are presented.

Using either Tukey's multiple comparisons, Bonferroni method or Scheffé procedure, significant differences between the two varieties are detected with global level 0.05. This difference is detected at a_w=0.803.

Model Fit: Different equations for water sorption isotherms were proposed in the literature[19,20] We have studied the fit of the following equations:

Bradley[22] equation:

$$M = b_0 + b_1 \log(-\log(a_w))$$

Halsey[23] equation:

$$M = \exp(b_0 + b_1 \log(-\log(a_w)))$$

Oswin[24] equation:

$$M = \exp(b_0 + b_1 \log(a_w/(1-a_w)))$$

Chirife *et al.*[21] equation:

$$M = \exp(b_0 + b_1 \log(b_2 - \log(a_w)))$$

Henderson[25] equation:

$$M = \exp(b_0 + b_1 \log(-\log(1-a_w)))$$

Hailwood and Horrobin[26] or G. A. B. equation:

$$M = 1/(b_0 + b_1 a_w + b_2(1/a_w))$$

In all of them M denotes the m.c., we give the form of the equation we have used in order to model m.c. as a function of the a_w. These equations were fitted using the second data set.

In order to evaluate the goodness of fit and to avoid cross-validation methods, the third data set was used. The three criteria introduced in Boente *et al.*[27] were considered. They can be described as follows:

The mean square of the deviations

$$S = \frac{\sum_{i=1}^{n} e_i^2}{n}$$

The mean relative percentage deviation in modulus [27]

$$P = \frac{\sum_{i=1}^{n} |e_i|/M_i}{n} \times 100$$

The mean relative error[28].

$$E = \frac{\sum_{i=1}^{n} e_i^2/M_i^2}{n} \times 100$$

where e_i denotes the residual at the i-th observation.

RESULTS

When analyzing the equations relating the m.c. and the a_w, estimates of the parameters were obtained by fitting a nonlinear model for each variety.

In Table 2 we report the values of the estimated parameters for each equation together with their standard deviations.

In Fig. 1 we have plotted, for instance, the observed data and the fitted isotherm for the G. A. B. equation for each variety. Figure 2 shows the raw residuals of this fit

Table 2: Estimated parameters and their standard deviation

	Variety	Coefficients	Estimate	Standard Deviation
Bradley	Cruentus	B0	5.9507	0.1596
		B1	-6.9901	0.1009
	Mantegazzianus	B0	5.9507	0.1899
		B1	-7.1071	0.1201
Halsey	Cruentus	B0	2.1156	0.0109
		B1	-0.4371	0.0060
	Mantegazzianus	B0	2.1182	0.0098
		B1	-0.4420	0.0054
Oswin	Cruentus	B0	2.2373	0.0075
		B1	0.3903	0.0044
	Mantegazzianus	B0	2.2415	0.0073
		B1	0.3945	0.0042
Chirife	Cruentus	B0	2.0959	0.0181
		B1	-0.4479	0.0261
		B2	-0.0008	0.0047
	Mantegazzianus	B0	2.1022	0.0159
		B1	-0.4509	0.0231
		B2	-0.0002	0.0042
Henderson	Cruentus	B0	2.4268	0.0077
		B1	0.7816	0.0122
	Mantegazzianus	B0	2.4336	0.0091
		B1	0.7889	0.0144
GAB	Cruentus	Bo	0.2317	0.0145
		B1	-0.1866	0.0094
		B2	-0.0165	0.0055
	Mantegazzianus	B0	0.2569	0.0168
		B1	-0.2033	0.0109
		B2	-0.0263	0.0064

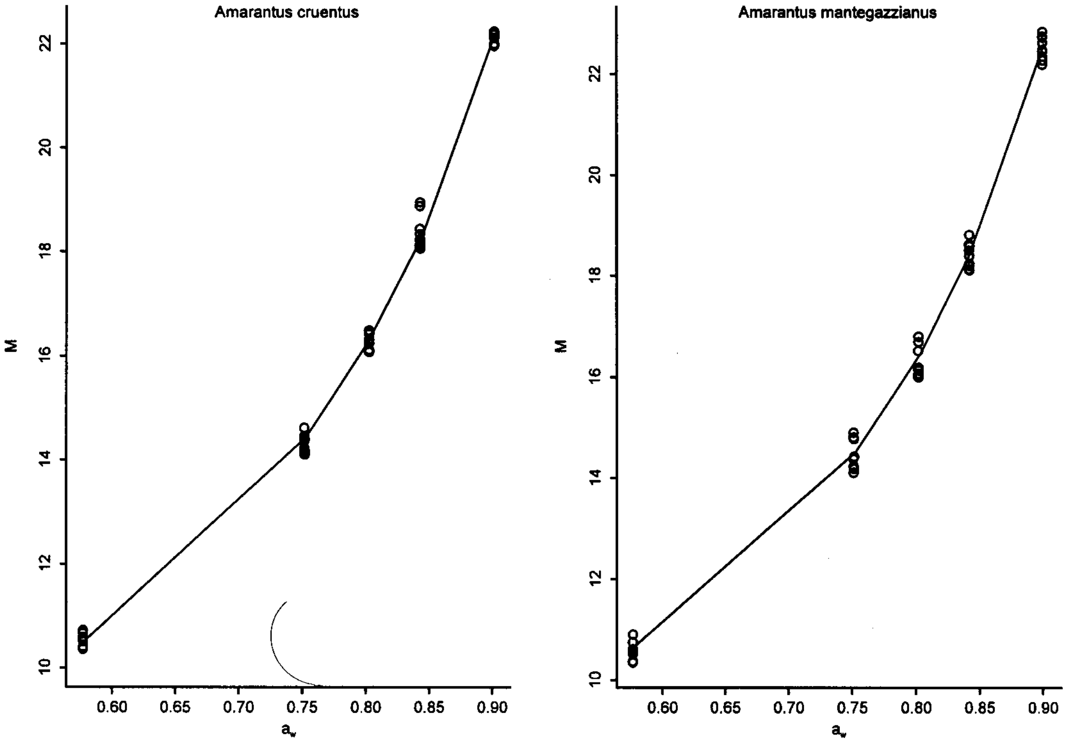

Fig. 1: Experimental data and the fitted isotherm for the G. A. B. Equation

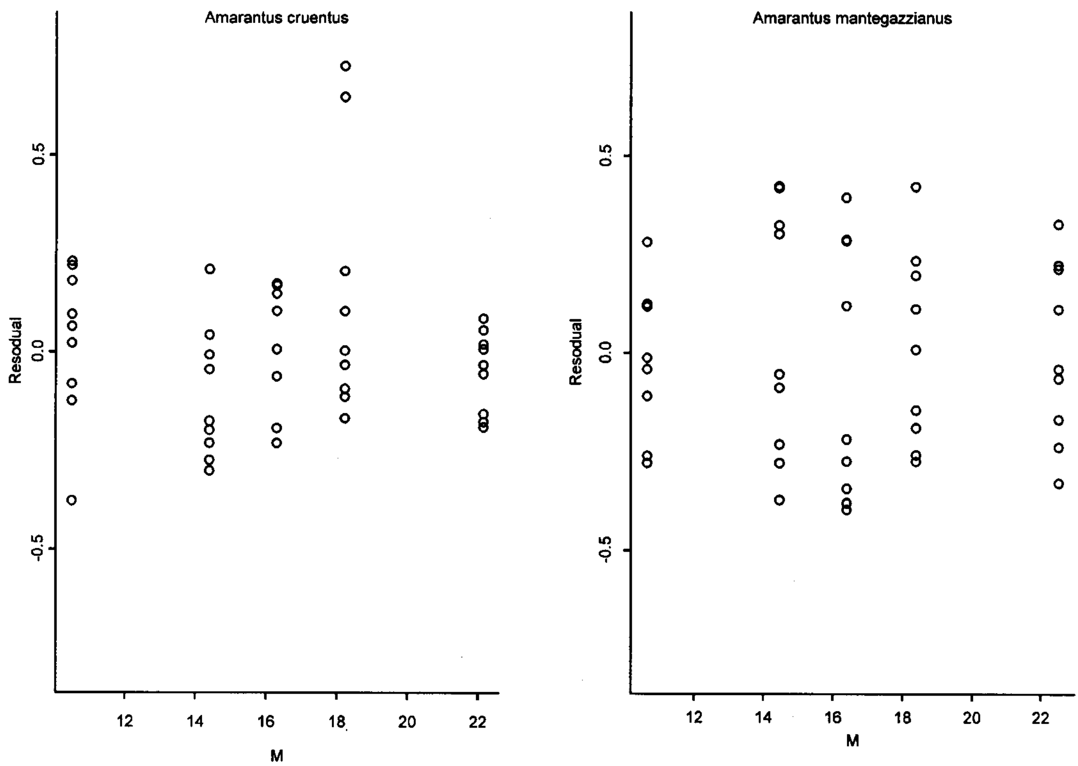

Fig. 2: Raw residuals of the fit with G AB equation

Table 3: Values of the goodness of fit measures evaluated on the third data set

	Cruentus			Mantegazzianus		
Equation	S	P	E	S	P	E
Bradley	1.0671	5.7694	0.5551	0.7421	4.4370	0.4064
Halsey	1.0739	5.6777	0.4239	0.6372	4.4228	0.2581
Oswin	1.0435	5.6655	0.4501	0.6313	4.4267	0.2876
Chirife	1.1557	6.0436	0.4758	0.7041	4.7636	0.2990
Henderson	1.1002	5.8572	0.5853	0.7713	4.5792	0.4382
GAB	0.9903	5.6882	0.4583	0.5903	4.4062	0.2806

showing the lack of trend. The S goodness of fit criterion seems therefore reasonable to select the equation. However, Table 3 reports the values of S, P and E obtained for each equation and variety evaluated on the third data set. The results are consistent among the measures, since for all the criteria G. A. B equation is the best fit for *Amaranthus Mantegazzianus*, while for *Amaranthus Cruentus* provides one of the best fits. More precisely, it is the best fit with respect to the S measure, being the third one for the P criterion and the second for the E one. Note that P and E criteria provide different model adequacies between varieties. For *Amaranthus Cruentus* the best fit is given by Oswin and Bradley model, according to P and E criteria, respectively. However, the order of the difference with respect to the goodness of fit statistic using G. A. B. model is negligible. It is worth noticing that for the S measure, which is the one to be taken into account in this setting, the S statistic for the G. A. B. model is 60% larger on the for *Amaranthus Cruentus* than on the *Amaranthus Mantegazzianus*.

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