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Water Sorption of *Amaranthus cruentus* L. Seeds Modelled by GAB Equation

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ABSTRACT

The GAB (Guggenheim, Andersen, and de Boer) equation was adjusted to literature data of sorption of *Amaranthus cruentus* L. (M_e vs. a_w for adsorption and desorption) determined at 25, 30, 35, 40, 45, 50, 55, 65, 70, and 90°C, in the range of water activity from 0.029 to 0.979. To quantify the goodness of fit, the correlation coefficient (R^2), the sum of squares (RSS), the standard error of the estimate (S_y), the mean relative deviation (MRD) and the plots of residuals were analysed. The three theoretical parameters of the GAB model (M_o, C, and K) gave a good correlation ($R^2 > 0.9817$, RSS < 0.0297, MRD < 0.138, $S_y < 0.0143$, and random residuals-plots) in the range of a_w from 0.029 to 0.979, of interest in seed storage and processing. However this correlation does not consider the effect of temperature (T) on coefficient values. In a second stage, parameters M_o and K were adjusted at each temperature. Very low variances were obtained in the range 25–65°C for desorption and in the range 25–55°C for adsorption. These results suggested that M_o and K remain almost constant and a correlation with T is not justified. On the contrary sense, parameter C showed stronger variation with T. This was explained by the analysis of sensitivity for the influence of C

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on moisture content. On this basis, the relation C–T was proposed by an Arrhenius-type relation [$C = A.\exp(B/T)$] and this function was incorporated to the original GAB model to re-estimate the parameters A, B, M_o, and K. The developed modification provides a generalised and precise expression of GAB model for Amaranth.

Key Words: Amaranth; Sorption; Desorption; Isotherms; GAB model.

INTRODUCTION

Amaranth genus (Amaranthaceae family) involves more than 50 species.[1] Among edible ones it can be mentioned five American species: *Amaranthus cruentus* L., *Amaranthus caudatus* L., *Amaranthus dibins martext thelling*, *Amaranthus hyponchondriacus* L., and *Amaranthus. mantegazzianus*.[1]

In the last years, this grain has been rediscovered because of its extraordinary differential properties for human consumption, like high lysine content, good balance in other aminoacids, high content of proteins (14–18%), vitamins and minerals and high proportion of squalene in the oil compared to other vegetable oils.[2] The potential complementary nature of amaranth protein has been studied by combining amaranth with wheat, sorghum, and maize in compound flours. In the same sense its starch components are distinctive.[3]

Amaranth grain can be used in breakfast cereals, soups, breads, cookies, pancakes, and as ingredient in confections.[4,5] Also, the popped grain provides opportunities for processors to develop innovative products like candies and nougats.[6] The composition of *A. cruentus* L. grains, based on 100 g (dry basis), is 16.8 g protein, 3.1 g ash, 7.7 g fat, 10.5 g water, and 73 g starch.[6] Compared with other cereals like wheat, corn, rice, and oats, amaranth grains have higher content of proteins, fiber, calcium, and iron and provide more calories. The quality of proteins is very remarkable. The content of essential aminoacids of amaranth grains is comparable with the corresponding for soybeans (4 g isoleucine, 6 g leucine, 5.5 g lysine, 3.5 g treonine, 1 g tryptophane, 4.5 g valine, based on 100 g of protein).[6]

Successful amaranth grain production requires a good knowledge of both pre-harvest and post-harvest characteristics to prevent quality losses. The crop should be harvested as soon as possible after a frost—usually about 10 days—to reduce grain loss from shattering[4] and must be dried below 10–12% moisture content for safe storage. Excessive thermal processing has been shown to reduce the quality of amaranth grain.[3,7]

To optimise grain conditioning operations and equipment design, the characteristics of the relationship between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH) and its dependence with temperature must be comprehended.

Moisture sorption isotherms describe the interaction between moisture content (M_e) and relative humidity, usually called water activity (a_w) in food science studies. Many theoretical, semi-theoretical and empirical equations have been developed in order to model the sorptional equilibrium of grains.

GAB (Guggenheim, Anderson, and de Boer) equation, derived from the model of BET (Brunauer, Emmet, and Teller) for physical adsorption, has been widely adopted, mainly for starchy products,[8] cereals and oilseeds.[9] Shatadal and Jayas,[10] in a review of moisture sorption isotherms, recognized GAB equation as the most satisfactory theoretical isotherm equation. They found it suitable for describing the effect of temperature on the sorption behavior of several food components in the temperature range of 25–80°C and, remarking the popularity of GAB equation in Europe, suggested that more studies should be done to derive the parameters of GAB equation for different cereal grains.

Also, Van den Berg,[11] from the analysis of approximately 75 equations, concluded that GAB equation should be used due its important advantages over the others, like: (a) it has a sound theoretical background, because derives from the Langmuir and BET theories of physical adsorption; (b) it provides a good description of almost all food isotherms in the wide range 0–0.9 of water activity; (c) it is a simple expression with only three parameters that can be used easily in engineering design; (d) its parameters have physical meaning to comprehend the complexity of water sorption; and (e) it is able to describe the effect of temperature on the isotherms by equating its parameters through the Arrhenius model.

ASAE Standard D254.5,[12] after its revision,[13] also includes the GAB equation as accepted prediction method. Guggenheim, Anderson, and de Boer equation has been also recommended by Bakker-Arkema[14] for use in the simulation of drying.

Notwithstanding, this isotherm does not include the temperature term; then it can only describe the relationship between a_w and moisture content at fixed temperatures. In that respect, trying to improve its performance, Iglesias and Chirife[15] modelled M_o (monolayer moisture content) as an Arrhenius type relationship with temperature. In the same sense, Jayas and Mazza[16] modified one parameter of the GAB model to incorporate the effect of temperature when studying water sorption by oats.

Calzetta Resio et al.[17] used the GAB model to estimate the isosteric heat of sorption of amaranth starch in the range from 25 to 50°C. Pollio et al.[18] also studied the sorption equilibrium of amaranth grains in order to predict the isosteric heat of sorption but at only three temperatures (35, 45, and 65°C). Lema et al.[19] presented experimental data of adsorption and desorption of water over amaranth in the range 25 to 55°C. Tosi et al.[1] reported data of water sorption on amaranth grains (*A. cruentus* L. variety) in the range from 40 to 90°C.

As very little information about sorptional equilibrium of amaranth grains is available in literature and the GAB model proved to be a valuable tool for the analysis of sorption and desorption on foods, the objectives of this work were: (i) to study the adjustment of GAB equation to sorption data of amaranth obtained from literature; (ii) to analyse the effect of temperature on GAB parameters; and (iii) to develop a simple modification of GAB equation that incorporates the above mentioned effect.

MATERIALS AND METHODS

Sources of Sorption Data

Experimental data of water sorption (M_e vs. a_w) of the species *A. cruentus* L. were taken from literature[1,18,19] for desorption/adsorption at 25, 30, 35, 40, 45, 50, 55, 65, 70, and 90°C in the range of water activity from 0.029 to 0.979. Table 1 presents all the data sets with their individual temperature and water activity ranges. The total number of data points available was 147. All the data were original experimental points either cited precisely in tables or read from experimental points on figures. The collected data were obviously classified in two groups: adsorption and desorption; however some of them were not possible to be identified as desorption or adsorption data, then these points were

Table 1. Sources of sorption data of amaranth seeds (*Amaranthus cruentus* L. variety) for the fitting of GAB equation.

Temperature range (°C)	Water activity range (dec.)	Type of data[a]		No. of points	Method[b]	Reference	Year	Data set no.
25–55	0.114–0.979	Ads.	Fig.	53	Grav./sss.	[19]	2001	1
25–55	0.114–0.979	Des.	Fig.	52	Grav./sss.	[19]	2001	2
35–65	0.029–0.875	Des.	Tab.	26	Grav./sss.	[18]	1998	3
40–90	0.20–0.80	Ave.	Fig.	16	Grav./sas.	[1]	1994	4

[a]Ads., adsorption; Des., desorption; Ave., average; Fig., data from Figure; Tab., data from Table.
[b]Grav./sss., gravimetric with saturated salt solutions; Grav./sas., gravimetric with saturated acid solutions.

considered as average results. Table 2 summarizes the complete data sets and shows that—as drying has been generally of more interest of study than rehydration—a higher amount of data points for desorption are available in literature.

The published data of water sorption on amaranth grains were obtained by static gravimetric methods with different atmospheres surrounding the product (Table 1). The experimental determination of isotherms using the static gravimetric method involved the exposition for long times of grain samples supported in small baskets into glass desiccators containing either saturated salt solutions or sulfuric-acid solutions to maintain constant vapor pressure at constant temperatures. Lema et al.[19] used saturated salts and amaranth grains with initial moisture content in the range 28–31% (d.b.) for desorption experiences. For adsorption, they used dry grains with moisture content between 2–4% (d.b.). Tosi et al.[1] worked with natural dried grains which were exposed to saturated solutions of sulfuric acid that provided water activities between 0.2 and 0.8. These authors measured the a_w level with an humidimeter (Hanna, HI 8564 Model). Pollio et al.[18] obtained the isotherms by the gravimetric method using saturated salt solutions for dehydrating small samples of amaranth grains (harvested with 9% d.b. moisture content and hydrated to 21% d.b.) in vacuum desiccators. These researchers measured the corresponding a_w levels with a hygrometer (Thermoconstanter Humidal TH2, Novasina AB, Zurich, Switzerland) while the moisture content was measured gravimetrically after vacuum drying. Equilibrium conditions were obtained when the change in sample mass among three successive measures was less than 0.001 g[19] or 0.005 g.[1] The moisture content of samples at this stage was determined by drying in oven either at 95°C during 48 hours[19] or at 130°C during 1 hour[1] or at 70°C and 6.7 kPa over magnesium perchlorate.[18] The time to reach equilibrium varied from 10 to 12 d depending on relative humidity and temperature.[19] The differences among the reported data would be attributed to differences in grain maturity and history, and to the different techniques used for measuring EMC–ERH.[9,21]

Mathematical Modelling and Fitting Method

The whole set of published data were modelled by the Guggenheim–Anderson–de Boer isotherm (GAB) that has the following form:

$$M_e = \frac{M_o\, C\, K\, a_w}{(1 - K\, a_w)(1 - K\, a_w + C\, K\, a_w)} \tag{1}$$

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Table 2. Collection of sorption equilibrium values of amaranth seeds (*Amaranthus cruentus* L. variety).

Temperature T (°C)	Equilibrium moisture content M_e (dec.)	Water activity a_w (dec.)	Type of data[a]	Reference	Data set no.
25	0.0234	0.1145	Ads.	[19]	1
25	0.0366	0.2274	Ads.		
25	0.0496	0.3265	Ads.		
25	0.0648	0.4291	Ads.		
25	0.0887	0.6342	Ads.		
25	0.1096	0.7385	Ads.		
25	0.1343	0.8274	Ads.		
25	0.1938	0.9573	Ads.		
25	0.0459	0.1145	Des.	[19]	2
25	0.0637	0.2274	Des.		
25	0.0794	0.3265	Des.		
25	0.0884	0.4291	Des.		
25	0.1158	0.6342	Des.		
25	0.1298	0.7385	Des.		
25	0.1500	0.8274	Des.		
25	0.1938	0.9573	Des.		
30	0.0390	0.1167	Ads.	[19]	1
30	0.0503	0.2217	Ads.		
30	0.0635	0.3267	Ads.		
30	0.0773	0.4317	Ads.		
30	0.1062	0.6283	Ads.		
30	0.1250	0.7383	Ads.		
30	0.1530	0.8217	Ads.		
30	0.2268	0.9617	Ads.		
30	0.0562	0.1167	Des.	[19]	2
30	0.0710	0.2217	Des.		
30	0.0873	0.3267	Des.		
30	0.1024	0.4317	Des.		
30	0.1319	0.6283	Des.		
30	0.1495	0.7383	Des.		
30	0.1734	0.8217	Des.		
30	0.2268	0.9617	Des.		
35	0.0297	0.1148	Ads.	[19]	1
35	0.0398	0.2139	Ads.		
35	0.0597	0.3235	Ads.		
35	0.0698	0.4330	Ads.		
35	0.0929	0.6278	Ads.		
35	0.1150	0.7513	Ads.		
35	0.1306	0.8296	Ads.		
35	0.2073	0.9791	Ads.		
35	0.0454	0.1148	Des.	[19]	2
35	0.0587	0.2139	Des.		

(*continued*)

Table 2. Continued.

Temperature T (°C)	Equilibrium moisture content M_e (dec.)	Water activity a_w (dec.)	Type of data[a]	Reference	Data set no.
35	0.0733	0.3235	Des.		
35	0.0903	0.4330	Des.		
35	0.1120	0.6278	Des.		
35	0.1285	0.7513	Des.		
35	0.1442	0.8296	Des.		
35	0.2073	0.9791	Des.		
35	0.0360	0.1120	Des.	[18]	3
35	0.0549	0.2160	Des.		
35	0.0713	0.2900	Des.		
35	0.0816	0.3630	Des.		
35	0.0913	0.4420	Des.		
35	0.1011	0.5540	Des.		
35	0.1094	0.6050	Des.		
35	0.1440	0.7490	Des.		
35	0.1740	0.8130	Des.		
35	0.2065	0.8550	Des.		
40	0.0302	0.1148	Ads.	[19]	1
40	0.0438	0.2122	Ads.		
40	0.0622	0.3304	Ads.		
40	0.0736	0.4435	Ads.		
40	0.0993	0.6313	Ads.		
40	0.1133	0.7670	Ads.		
40	0.1244	0.8400	Ads.		
40	0.0424	0.1148	Des.	[19]	2
40	0.0571	0.2122	Des.		
40	0.0751	0.3304	Des.		
40	0.0887	0.4435	Des.		
40	0.1056	0.6313	Des.		
40	0.1273	0.7670	Des.		
40	0.1391	0.8400	Des.		
40	0.0580	0.2000	NA	[1]	4
40	0.0866	0.4000	NA		
40	0.1270	0.6000	NA		
40	0.1800	0.8000	NA		
45	0.0307	0.1138	Ads.	[19]	1
45	0.0429	0.2034	Ads.		
45	0.0592	0.3224	Ads.		
45	0.0707	0.4379	Ads.		
45	0.0939	0.6086	Ads.		
45	0.1131	0.7500	Ads.		
45	0.1253	0.8138	Ads.		
45	0.1563	0.9759	Ads.		
45	0.0408	0.1138	Des.	[19]	2
45	0.0544	0.2034	Des.		

Table 2. Continued.

Temperature T (°C)	Equilibrium moisture content M_e (dec.)	Water activity a_w (dec.)	Type of data[a]	Reference	Data set no.
45	0.0699	0.3224	Des.		
45	0.0859	0.4379	Des.		
45	0.1093	0.6086	Des.		
45	0.1299	0.7500	Des.		
45	0.1453	0.8138	Des.		
45	0.0341	0.1130	Des.	[18]	3
45	0.0417	0.1910	Des.		
45	0.0648	0.3160	Des.		
45	0.0778	0.3890	Des.		
45	0.0922	0.5320	Des.		
45	0.1006	0.6110	Des.		
45	0.1369	0.7730	Des.		
45	0.1709	0.8360	Des.		
45	0.1961	0.8750	Des.		
50	0.0292	0.1140	Ads.	[19]	1
50	0.0447	0.1895	Ads.		
50	0.0532	0.3140	Ads.		
50	0.0681	0.4333	Ads.		
50	0.0888	0.5825	Ads.		
50	0.1117	0.7368	Ads.		
50	0.1222	0.7842	Ads.		
50	0.0393	0.1140	Des.	[19]	2
50	0.0512	0.1895	Des.		
50	0.0674	0.3140	Des.		
50	0.0800	0.4333	Des.		
50	0.0984	0.5825	Des.		
50	0.1169	0.7368	Des.		
50	0.1279	0.7842	Des.		
50	0.0466	0.2000	NA	[1]	3
50	0.0800	0.4000	NA		
50	0.1130	0.6000	NA		
50	0.1670	0.8000	NA		
55	0.0226	0.1138	Ads.	[19]	1
55	0.0345	0.2103	Ads.		
55	0.0471	0.3241	Ads.		
55	0.0625	0.4379	Ads.		
55	0.0797	0.6207	Ads.		
55	0.1144	0.7517	Ads.		
55	0.1281	0.8207	Ads.		
55	0.0289	0.1138	Des.	[19]	2
55	0.0376	0.1897	Des.		
55	0.0558	0.3172	Des.		
55	0.0679	0.4379	Des.		

(*continued*)

Table 2. Continued.

Temperature T (°C)	Equilibrium moisture content M_e (dec.)	Water activity a_w (dec.)	Type of data[a]	Reference	Data set no.
55	0.0905	0.5914	Des.		
55	0.1144	0.7517	Des.		
55	0.1281	0.8207	Des.		
65	0.0076	0.0290	Des.	[18]	3
65	0.0277	0.1080	Des.		
65	0.0499	0.2850	Des.		
65	0.0708	0.4950	Des.		
65	0.0953	0.6660	Des.		
65	0.1101	0.7470	Des.		
65	0.1393	0.7990	Des.		
70	0.0400	0.2000	NA	[1]	4
70	0.0733	0.4000	NA		
70	0.1030	0.6000	NA		
70	0.1530	0.8000	NA		
90	0.0300	0.2000	NA	[1]	4
90	0.0600	0.4000	NA		
90	0.0930	0.6000	NA		
90	0.1400	0.8000	NA		

[a]Ads., adsorption; Des., desorption; NA, not accounted.

The non-linear module of Systat package[20] was used to fit the equation to the sorption data. This procedure is an algorithm for minimum sum-of-squares regression of m nonlinear functions with n variables. The goodness of fit of the model was quantified through the correlation coefficient (R^2), the sum of squares (RSS), the standard error of the estimate (S_y) and the mean relative deviation (MRD).[22] The sum of squares (RSS) is defined as follows:

$$\mathrm{RSS} = \sum_{i=1}^{m} (M_e - \hat{M}_e)^2 \tag{2}$$

where M_e is the measured value; $\hat{M}_e$ is the value estimated through the fitting equation and m is the number of data points.

The standard error of the estimate (S_y) is the conditional standard deviation of the dependent variable and has the form:

$$S_y = \sqrt{\frac{\sum_{j=1}^{m} (M_e - \hat{M}_e)^2}{\mathrm{df}}} = \sqrt{\frac{\mathrm{RSS}}{\mathrm{df}}} \tag{3}$$

where df are the degrees of freedom of the fitting equation.

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The MRD in an absolute value that was used because gives a clear idea of the mean divergence of the estimated data respect to the measured data:

$$\mathrm{MRD} = \frac{1}{m}\sum_{i=1}^{m}\frac{|M_e - \hat{M}_e|}{M_e} \tag{4}$$

The plotting of the residuals ($M_e - \hat{M}_e$) in function of the independent variable a_w was also used as a measure of the adjustment in the range of analysis.

In general, low values of R^2, high values of RSS, S_y, and MRD, and clear patterns in the residual plots mean that the model is not able to explain the variation in the experimental data.

Table 3 shows the obtained values of the parameters M_o, C, and K of Eq. (1) for the complete data set with the corresponding standards errors (ASE) and percent standard error (ASE%) of the parameters. This fitting can only be used to describe the average sorption behavior because it was originated from data of different sources, determined over a wide range of temperatures and with diverse experimental techniques (Fig. 1). Fitting individual data sets, more sensitive tests of the adequacy and characteristics of the GAB equation can be performed than fitting the whole data set, due to the great dissemination of the experimental points. Table 4 shows the results of the fitting of the grouped data for desorption, adsorption and "average." These results can describe the individual processes of desorption and adsorption, while the average can be used in general applications.[23] From these results, it can also be noted that the hysteresis effect is significant over all the water activity range. Figure 2 shows the comparison between the curves for desorption, adsorption, and average predicted by the GAB equation at 50°C. Very similar graphs with comparable magnitude of hysteresis effect were obtained at 25, 30, 35, 40, 45, and 55°C, demonstrating that temperature has no strong influence on hysteresis. This behavior has also been observed by Sun and Woods[24] in a review of sorption data for wheat. On the other hand, these results confirm that the theoretical desorption curves are positioned above the adsorption curves for all the a_w range. The regression for "average" data, as shown in Fig. 2 for data at 50°C, lie between adsorption and desorption curves when a_w is between 0.1 and 0.5.

Besides, GAB equation was fitted for desorption and adsorption at each individual temperature. The original data in which desorption or adsorption were not identified (termed here as "average") were assumed to be desorptive for low water activities and

Table 3. Parameters for the fitting of GAB equation for water sorption of amaranth grains for the whole data set in the range of temperature from 25 to 90°C and water activity from 0.029 to 0.979.

Parameter			Statistics of fitting				
M_o	C	K	Number of points	R^2	RSS	S_y	MRD
0.0634 ASE = 0.0035 ASE% = 5.5	11.1997 ASE = 2.2202 ASE% = 19.8	0.7218 ASE = 0.0196 ASE% = 2.7	147	0.9817	0.0293	0.0143	0.1380

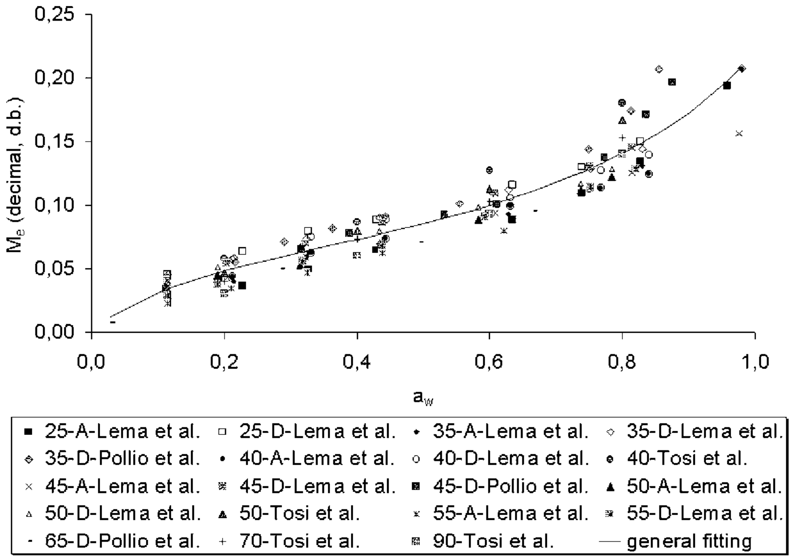

Figure 1. Moisture sorption isotherms of *Amaranthus cruentus* L. grains from literature.

adsorptive at high water activities.[23] Then, these points were included into the subgroups adsorption or desorption at their corresponding temperature. The results of these adjustments are presented in Table 5. As can be seen, R^2 values are very high and RSS, S_y, and ASE% (except for C) are low for all the temperatures and both for desorption and adsorption. Values at 70 and 90°C were not adjusted because each set consisted of only four data. These results clearly demonstrate the adequacy of the GAB model to describe M_e vs. a_w relationship for amaranth seeds.

Comparison with Published Data for Other Starchy Foods

Calzetta Resio et al.,[17] working in the range of 25–50°C with amaranth starch isolated from amaranth seeds, reported values of M_o and C varying from 0.102 to 0.09 and from 16.8 to 9.7, respectively, while K varied between 0.81 and 0.80, showing no clear variation trend with temperature. These values are not very different from those obtained here, in spite of the differences in composition and structure of the tested materials. This could mean that the starchy components of the seed determine, to a great extent, its sorption characteristics.

Continuing the analysis of the adequacy of GAB model through the study of the residual plots, Figs. 3 and 4 show clear patterns, in agreement with the behavior observed by Chen and Jayas[9] for high-protein and high-starch materials. These authors explained this phenomenon by the sigmoid shape of the sorption curve that cannot be adequately tracked by most adsorption models.

Lomauro et al.[8] confirmed that nearly 80% of the isotherms of starchy foods can be described by the GAB equation. These authors have reported values of the GAB

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Table 4. Fitted parameters for GAB equation for desorption, adsorption, and average in the range of temperature from 25 to 90°C and water activity from 0.029 to 0.979.

	Parameter			Statistics of fitting				
	M_o	C	K	Number of points	R^2	RSS	S_y	MRD
Desorption	0.0637 ASE = 0.0037 ASE% = 5.8	15.1820 ASE = 3.7544 ASE% = 24.7	0.7320 ASE = 0.0218 ASE% = 3.0	78	0.9867	0.0122	0.0127	0.1216
Adsorption	0.0544 ASE = 0.0036 ASE% = 6.6	10.5661 ASE = 2.7185 ASE% = 25.7	0.7511 ASE = 0.0200 ASE% = 2.7	53	0.9895	0.0053	0.0103	0.0833
Average	0.0753 ASE = 0.0263 ASE% = 34.9	5.8055 ASE = 3.8359 ASE% = 66.1	0.7265 ASE = 0.1312 ASE% = 18.1	16	0.9872	0.9274	0.0134	0.0969

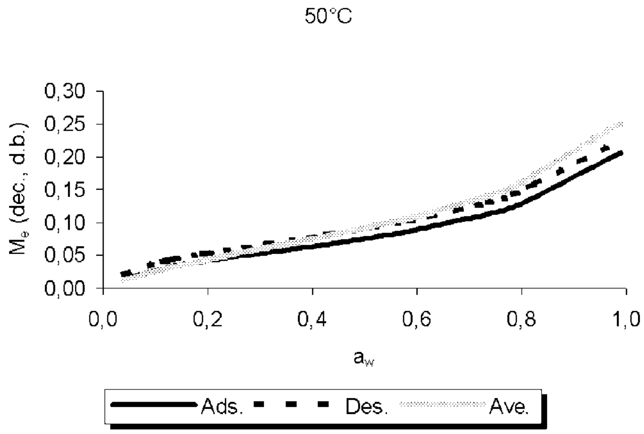

Figure 2. The influence of different kinds of data on the isotherms at 50°C of *Amaranthus cruentus* L. grains predicted by GAB equation.

parameters for starchy foods (Table 6) comparable to those observed in this work for amaranth.

In a similar fashion, Tolaba et al.,[25] in a study of water sorption on quinoa grains (with characteristics of composition analogous to those of amaranth), found comparable values for K, which varies slightly between 0.6 and 0.8, while M_o showed a moderate dependence with temperature. These results confirm the similitude in sorption behaviour among products with similar compositions.

Temperature Dependence of the Guggenheim, Anderson, and de Boer Equation

Table 5 shows that M_o varied between 0.070 (at 25°C) and 0.044 (at 65°C) for desorption (with standard deviation of 0.013), while for adsorption it varied between 0.052 (at 25°C) and 0.049 (at 55°C) (with standard deviation of 0.014). Parameter K presented a slight variation between 0.676 (at 25°C) and 0.858 (at 65°C) for desorption (with standard deviation of 0.105) and between 0.778 (at 25°C) and 0.787 (at 55°C) for adsorption (with a standard deviation of 0.125).

Analysing the parameters M_o and K, it can be noted that both show a slight variation along the temperature range. Both for adsorption and desorption, the percent standard errors of estimation (ASE, %) of the parameters M_o and K are notably low compared with those corresponding to C. In virtue of this, both M_o and K can be considered approximately constant in the range of temperature from 25 to 65°C. Then, it is not justified to explore a correlation with temperature. In this sense, Van den Berg,[11] Maroulis et al.[26] and Kiranoudis et al.[27] have also proposed to consider M_o constant with temperature and these authors analysed the effect of temperature only on the other parameters. Besides, Van den Berg[11] studying the water sorption isotherms of various foods and related products—including starchy foods—informed that the influence of temperature on the isotherm is described by C and—to a lesser extent—by K.

Table 5. Fitted parameters of GAB equation for desorption and adsorption at different temperatures from 25 to 90°C and water activity from 0.029 to 0.979.

T (°C)	M_o (d.b.)	ASE_{Mo}	ASE_{Mo} (%)	C	ASE_C	ASE_C(%)	K	ASE_K	ASE_K (%)	R^2	RSS	S_y
						Desorption						
25	0.070	0.003	3.6	19.913	3.330	16.7	0.676	0.014	2.1	1	3.2×10^{-5}	0.002
30	0.078	0.002	2.5	21.490	2.833	13.2	0.689	0.010	1.4	1	2.3×10^{-5}	0.002
35	0.077	0.011	14.3	10.792	4.846	44.9	0.678	0.050	7.4	0.991	2.4×10^{-3}	0.049
40	0.082	0.006	7.3	13.956	1.818	13.0	0.540	0.040	7.4	1	3.5×10^{-5}	0.002
45	0.056	0.005	8.9	17.242	6.822	39.6	0.807	0.030	3.7	0.997	6×10^{-4}	0.007
50	0.076	0.008	10.5	11.587	2.030	17.5	0.580	0.061	10.5	0.999	5.2×10^{-5}	0.003
55	0.065	0.005	7.1	7.800	0.971	12.5	0.664	0.031	4.7	1	1.1×10^{-5}	0.002
65	0.044	0.005	11.4	12.841	5.121	39.9	0.858	0.048	5.6	0.998	1×10^{-4}	0.005
						Adsorption						
25	0.052	0.002	3.7	7.352	0.948	12.9	0.778	0.009	1.2	1	2.0×10^{-5}	0.002
30	0.056	0.001	2.4	16.424	2.455	14.9	0.789	0.007	0.8	1	2.1×10^{-5}	0.002
35	0.051	0.003	5.8	13.015	3.841	29.5	0.776	0.015	1.9	0.999	9.1×10^{-5}	0.004
40	0.086	0.010	11.8	7.588	0.862	11.4	0.494	0.056	11.3	1	1.3×10^{-5}	0.002
45	0.073	0.003	4.4	8.155	0.729	8.9	0.587	0.016	2.8	1	1.2×10^{-5}	0.001
50	0.054	0.019	35.2	10.671	12.52	117.3	0.813	0.144	17.7	0.985	1.3×10^{-3}	0.015
55	0.049	0.006	13.0	7.313	2.286	31.3	0.787	0.048	6.1	0.999	4.8×10^{-5}	0.003

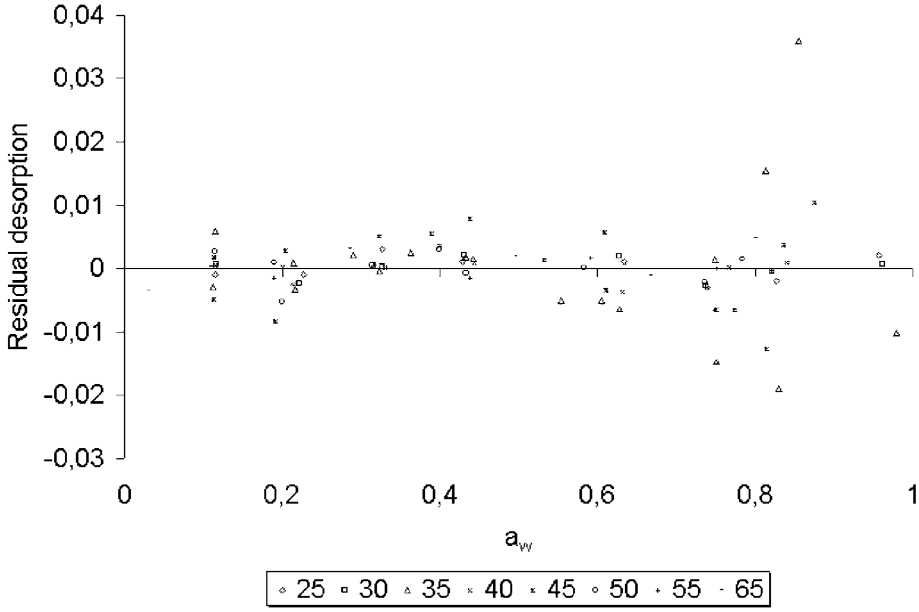

Figure 3. Residual plot from the adjustment of GAB equation [Eq. (1)] for desorption data of *Amaranthus cruentus* L. at eight temperatures.

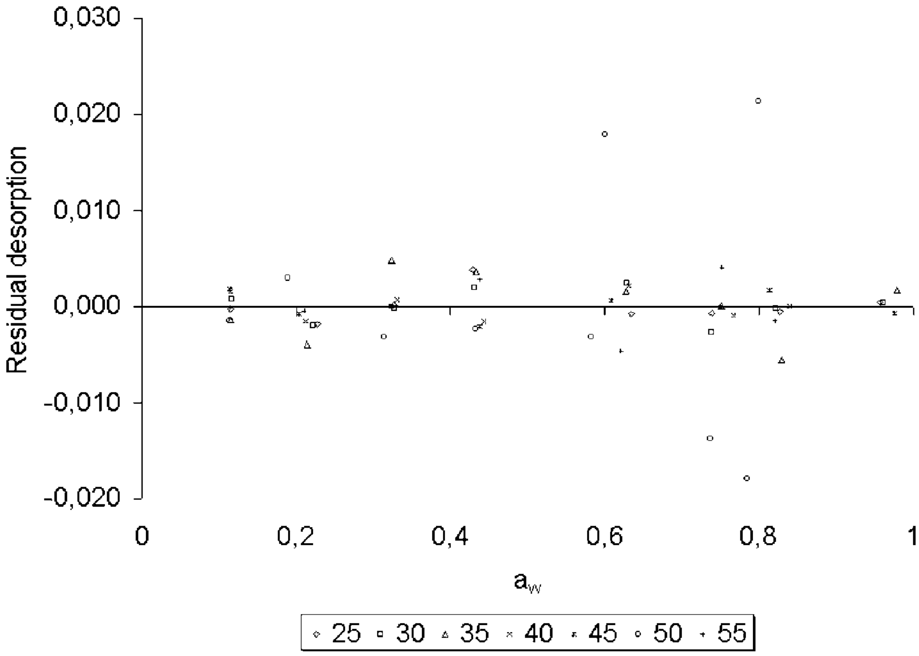

Figure 4. Residual plot from the adjustment of GAB equation [Eq. (1)] for adsorption data of *Amaranthus cruentus* L. at seven temperatures.

Table 6. Constants for GAB isotherms of starchy foods reported by Lomauro et al.[8]

		Desorption					Adsorption				
Product	T (°C)	a_w range	M_o (d.b.)	C	K	P^* (%)	a_w range	M_o (d.b.)	C	K	P^* (%)
Barley	25	0.26–0.96	0.074	101.24	0.811	4.16	0.43–0.96	0.070	30.14	0.827	3.54
Wheat	25	0.24–0.96	0.076	77.69	0.807	3.82	0.26–0.96	0.070	104.60	0.825	3.79
Rice	4.4	0.19–0.92	0.163	7.44	0.421	3.62	0.10–0.96	0.072	5.49	0.735	7.81
Rapeseed	25	0.48–0.92	0.035	28.97	0.913	4.39	0.52–0.92	0.032	18.01	0.923	3.44
Corn flour	25	0.42–0.98	0.073	16.11	0.801	5.06	0.46–0.98	0.067	14.49	0.822	5.35

Note: P^*, mean relative deviation modulus.

Respect to the values of C of this work, it can be observed in Table 5 that this parameter presents an evident dependence on temperature with a variable behavior along the temperature range. In order to study the relation C vs. T, the sensitivity of M_e respect to C was analysed through the partial derivation of Eq. (1) respect to C, following the procedure proposed by Gely and Giner:[28]

$$\frac{\delta M_e}{\delta C} = \frac{M_o K a_w (1 - K a_w + C K a_w) - M_o C K^2 a_w{}^2}{(1 - K a_w)(1 - K a_w + C K a_w)^2} \tag{5}$$

Figures 5 and 6, for desorption and adsorption respectively, were plotted to show the response of Eq. (5) to different values of C, using the mean values for M_o and K given in Table 5. It can be observed the remarkable effect of C on $\delta M_e/\delta C$. It can also be noted that this effect decreases strongly with the increase of C, being irrelevant for values higher than 100. However, for the values of C obtained in this work (between approximately 7 to 22 for desorption and 7 to 17 for adsorption), the effect of C on the derivative is obvious. So, a value for C most accurate than its arithmetic mean is desirable for an overall better performance of the GAB model.

In this sense, an Arrhenius-type expression[9,11,26,27,29] was proposed to describe the C–T relationship:

$$C = A \exp\left(\frac{B}{T + 273.16}\right) \tag{6}$$

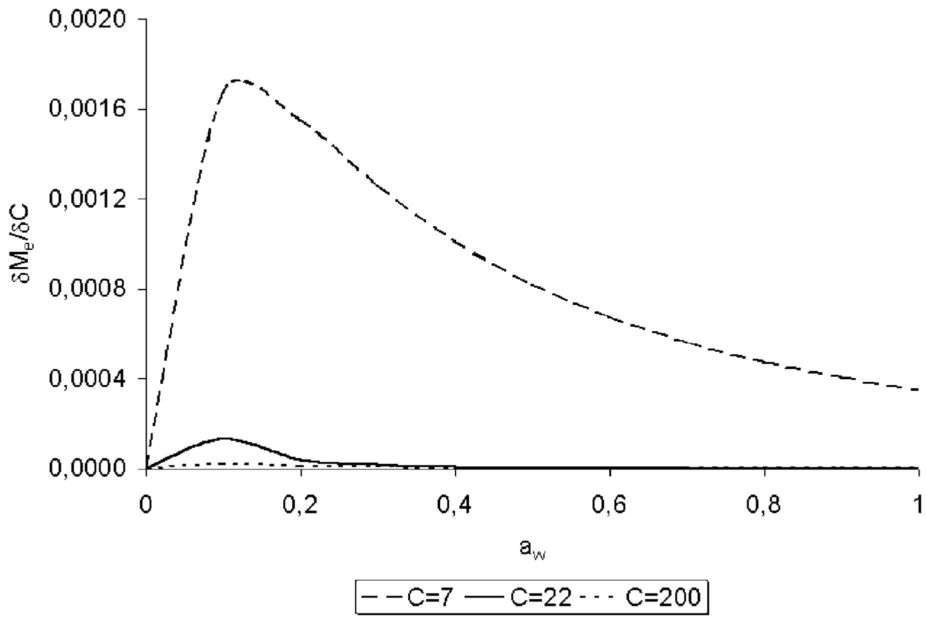

Figure 5. Test of sensitivity of M_e against C through the partial derivative, for water desorption of *Amaranthus cruentus* L. seeds.

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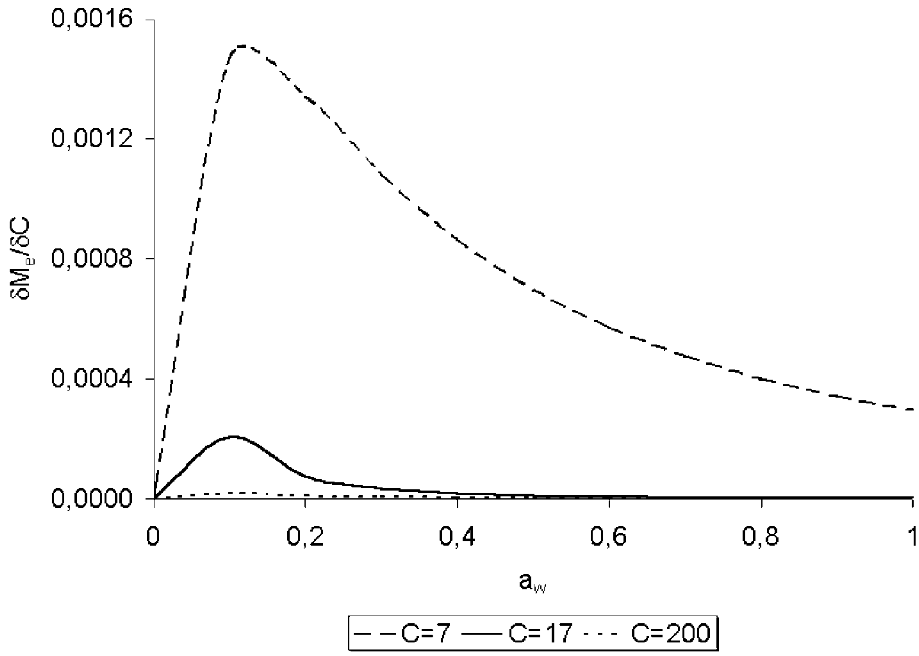

Figure 6. Test of sensitivity of M_e against C through the partial derivative, for water adsorption of *Amaranthus cruentus* L. seeds.

With the aim to generalise the GAB isotherm, the model of Eq. (6) was included into the original GAB isotherm presented in Eq. (1), obtaining a comprehensive four-parameter expression that contemplates the temperature effect on water sorption data:

$$M_e = \frac{M_o A \exp[(B)/(T + 273.16)] K a_w}{(1 - K a_w)[1 - K a_w + A \exp[(B)/(T + 273.16)] K a_w]} \tag{7}$$

Through the non-linear module of Systat,[20] the parameters of Eq. (7) were re-estimated for the fitting of all the desorption and adsorption data. In both cases, coefficients of correlation R^2 higher than 0.983 were obtained (Table 7). This showed both the accuracy of Eq. (7) and the lack of bias in the prediction of the influence of a_w on M_e.

The residual plots (Figs. 7 and 8) were uniformly scattered, remarking the goodness of fit of this proposed modification.

The following graphs (Figs. 9 and 10) were drawn to compare the experimental and calculated [through Eq. (7)] values for desorption and adsorption of water from Amaranth grains. In both cases, it can be observed that the points are regularly distributed around a line at 45°.

In spite of the overall accuracy of Eq. (7) over the whole temperature range, the fitting of any data set for a unique temperature to the three-parameter version always delivers more accurate results. This is shown in Fig. 11 that presents the data sets for 40°C and the

Table 7. Parameters of the generalized GAB isotherm for sorption of water of *Amaranthus cruentus* L. seeds.

	Desorption	Adsorption
Parameter		
A	13.66	7.10
B	2.88	11.83
M_o	0.064	0.064
K	0.731	0.712
Number of points	86	61
R^2	0.986	0.983
S_y	0.013	0.014
RSS	0.013	0.011
MRD	0.129	0.103

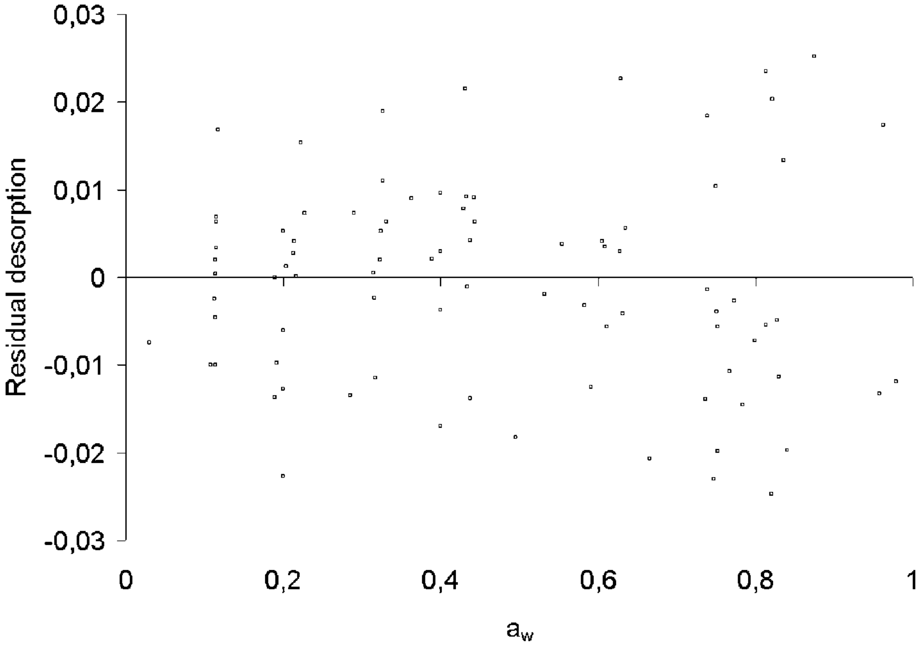

Figure 7. Residual plot from the generalised GAB equation [Eq. (7)] for water desorption on *Amaranthus cruentus* L. in the range from 25 to 90°C.

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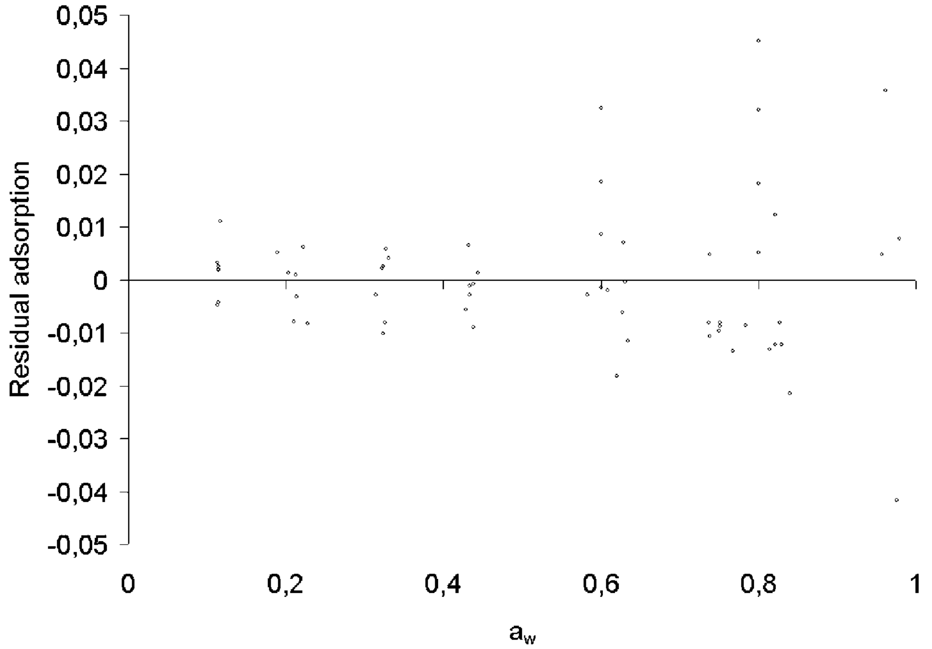

Figure 8. Comparison between experimental and calculated [by Eq. (7)] moisture content for desorption of water of *Amaranthus cruentus* L. at eight temperatures.

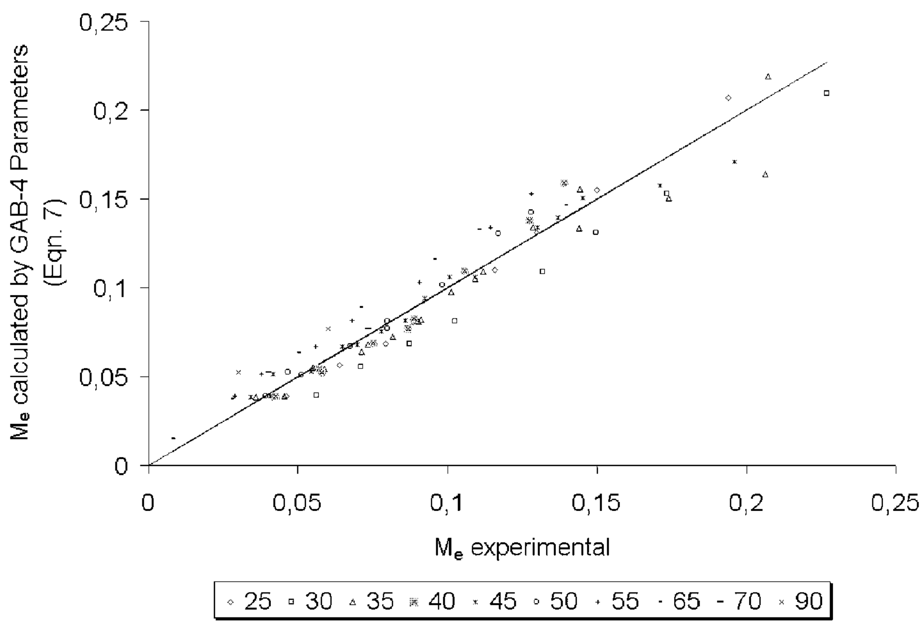

Figure 9. Residual plot from the generalised GAB equation [Eq. (7)] for water adsorption on *Amaranthus cruentus* L. in the range from 25 to 90°C.

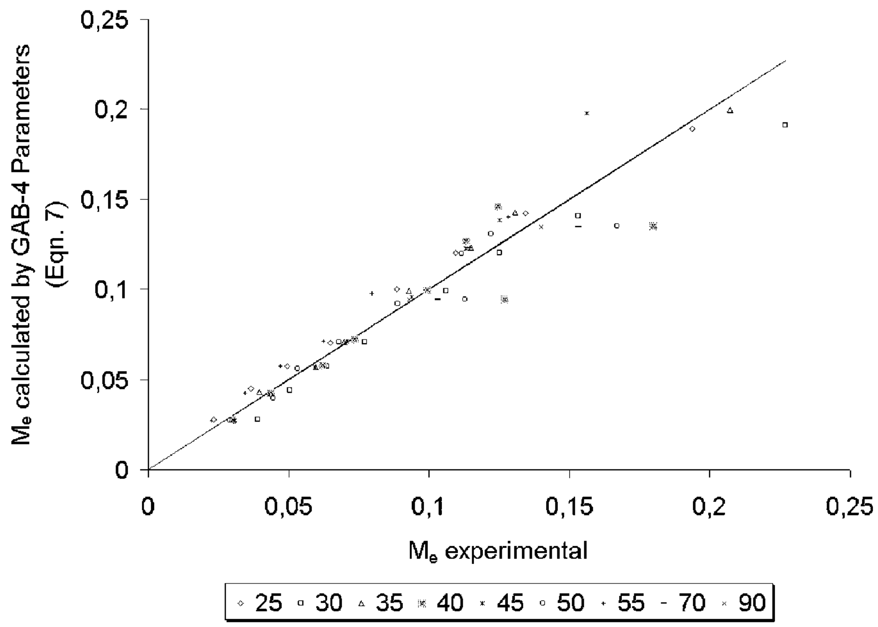

Figure 10. Comparison between experimental and calculated [by Eq. (7)] moisture content for adsorption of water of *Amaranthus cruentus* L. at seven temperatures.

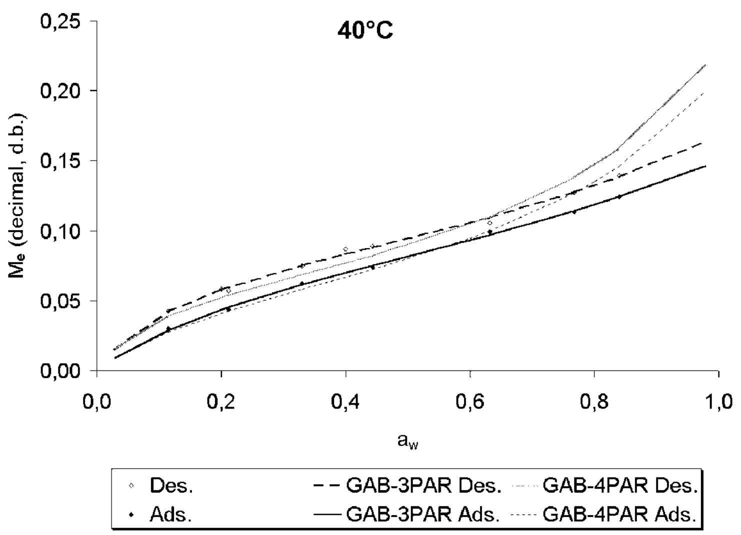

Figure 11. Data sets of moisture sorption isotherms of *Amaranthus cruentus* L. grains at 40°C and predicted curves by the three-parameter [Eq. (1)] and four-parameter [Eq. (7)] versions of GAB equation. *Key:* Des., desorption; GAB-3PAR Des., GAB-4PAR Des.: GAB model for desorption with three and four parameters, respectively Ads., GAB-3PAR Ads., GAB-4PAR Ads.: GAB model for adsorption with three and four parameters, respectively.

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values predicted by the three-parameter [Eq. (1)] and four-parameter [Eq. (7)] versions of GAB equation.

CONCLUSIONS

From the analysis of the present work, the following conclusions can be drawn:

Guggenheim, Anderson, and de Boer isotherm describes closely the sorption data of water on *Amaranthus cruentus* L. seeds in the temperature range from 25°C to 90°C.

Monolayer moisture content (M_o) shows a slight decrease with the increase of temperature, and can be considered constant in the range from 25°C to 90°C.

Parameter K also presents a very slow variation with temperature; consequently, it can be set constant in the range of analysis.

Both for desorption and adsorption, the parameter C shows a strong dependence on temperature.

The generalised GAB expression with four parameters—that considers the influence of temperature—describes adequately the sorption data in the range from 25 to 90°C.

NOTATION

A, B	parameters of Eq. (6)
ASE	standard error of estimation of parameter
a_w	water activity
C	parameter of GAB equation
df	degrees of freedom
EMC	equilibrium moisture content
ERH	equilibrium relative humidity
K	parameter of GAB equation
m	number of data points
M_e	dimensionless equilibrium moisture content
$\hat{M}_e$	estimated value
M_o	mono-layer moisture content
MRD	mean relative deviation
P^*	mean relative deviation modulus
R^2	correlation coefficient
RSS	sum of squares
S_y	standard deviation of estimate
T	temperature

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