

ADSORPTION ISOTHERMS OF PEAR AT SEVERAL TEMPERATURES

by

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The moisture adsorption isotherms of pear were determined at 15 °C, 30 °C, and 45 °C using the standard static gravimetric method over a range of water activity from 0.112 to 0.920. The experimental data were fitted with isotherm equations recommended in ASAE Standard D245.5. In order to find which equation gives the best results, large number of numerical experiments were performed. After that, several statistical criteria proposed in scientific literature for estimation and selection of the best sorption isotherm equations were used. For each equation and experimental data set, the average performance index was calculated and models were ranked afterwards. After that, some statistical rejection criteria were checked (D'Agostino-Pearson test of normality, single-sample run test and significance and precision of the model parameters). The performed statistical analysis shows that the Guggenheim-Anderson-de Boer equation has the highest value of average performance index, but higher correlation between pair of parameters leads to lower precision of estimated parameters.

Key words: *adsorption isotherms, pear, statistical analysis*

Introduction

The food sorption isotherm describes the thermodynamic relationship between water activity and the equilibrium of moisture content at constant temperature and pressure. The moisture sorption isotherms are extremely important in modelling the drying process, in design and optimization of drying equipment, in predicting shelf-life stability, in calculating moisture changes which may occur during storage and in selecting appropriate packaging material [1]. Also, the knowledge of the sorption data is essentially useful to predict microbiological, enzymatic and chemical stability of food materials. Experimentally determination and modeling of sorption isotherms of food materials has attracted numerous researches because their values are used in industrial purposes. Sorption isotherms are usually classified according to their shape in five different types: I, II, III, IV, and V [2, 3]. The sorption isotherms for most foods are non-linear and generally with sigmoid shape. A new classification system which was used to divide sorption isotherms into classes and that is applied on 115 sorption isotherms for different agricultural products and/or food materials were given in [4].

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Several researches have reported sorption data for pear at different temperatures and water activities. Kiranoudis *et al.* [5] determined sorption isotherms of pear at two temperatures 25 °C and 45 °C, Guine *et al.* [6] determined desorption isotherms of pear at 20, 25, and 30 °C, while Lahsasni *et al.* [7] determined sorption isotherms of prickly pear fruit at three temperatures 30 °C, 40 °C, and 50 °C over a range of relative humidity from 0.05 to 0.90. New researches were conducted by Guine [8], which determined desorption isotherms for two varieties of pears for temperatures of 20, 30, and 40 °C, and Djendoubi *et al.* [9], which determined desorption isotherms of pear at three temperatures 30, 45, and 60 °C at water activities between 0.07-0.98.

Numerous isotherm equations are available in scientific literature for approximate experimental data of sorption isotherm on food materials [10-12]. Popovski and Mitrevski [13-19] proposed seven methods for generating new sorption isotherm models. van den Berg and Bruin [20], classified the 77 sorption isotherm equations into three groups: theoretical, partially theoretical, and fully empirical. Some of them take into account the effect of temperature. The modified Chung-Pfost, modified Henderson, modified Halsey, modified Oswin and Guggenheim-Anderson-de Boer (GAB) equations were recommended as standard equations in ASAE Standard D245.5 for approximation of sorption isotherms data [21].

Generally, sorption isotherm equations are selected on the basis of several statistical criterions. In scientific literature, for the goodness of fit of experimental sorption data and selection of the best isotherm equation, following criterions are used: correlation coefficient, (r), coefficient of determination, (R^2), root mean squared error, ($RMSE$), and the mean relative deviation, (MRD). The selection of a sorption isotherm equation with graphical evaluation of the residual randomness is also popular [3, 22].

The results of comparative statistical analysis based on serial statistical criterion between the transcendental and cyclometric sorption isotherm models; transcendental and trigonometric sorption isotherm models for approximation of experimental equilibrium data of some fruits were presented in [23, 24]. The results of statistical evaluation of some four parameters sorption isotherm models for approximation of experimental equilibrium data of some vegetables were presented in [25].

The objectives of this study were:

- experimental determination of adsorption isotherms of pear at 15 °C, 30 °C, and 45 °C for a range of water activity from 0.112 to 0.920, and
- evaluation of suitability of isotherm equations recommended in ASAE Standard D245.5 and compares their goodness of fit based on several statistical criterions.

Material and methods

Fresh pears of the variety William with an average initial moisture content of 85% wet basis were used in experimental determination of adsorption isotherms. The pears were peeled and sliced in thin slices in order to obtain uniform samples with thickness of 4 ± 10^{-1} mm, before being reduced to a cylinder with diameter of 30 ± 10^{-1} mm. Several measurements were made using a caliper and only samples with a tolerance of $\pm 5\%$ were used. The representative samples taken for determination of sorption isotherms were pre-dried to final moisture content in a convective dryer at air drying temperature of 60 °C, and air drying velocity of 1 m/s for a period of 7 hours.

The equilibrium moisture content of pears was determined at 15 °C, 30 °C, and 45 °C using static gravimetric method, developed and standardized in the European COST 90 Project

[26]. Ten saturated salt solutions LiCl, CH₃COOK, MgCl, K₂CO₃, Mg(NO₃)₂, NaBr, SrCl₂, NaCl, KCl, and BaCl₂ prepared according to the recommendation of Greenspan [27], were used to give defined constant water activity from 0.112 to 0.920. Two dry samples were placed on holder into each of the ten glass jars and exposed to atmospheres of various relative humidity. At water activities, $a_w > 0.60$, small quantity of crystalline thymol was placed in the glass jar in order to prevent microbial spoilage of the sample of pear [26]. The glass sorption jars were placed and kept in the temperature controlled cabinet type SANYO MCO-15AC, maintained at the temperature 15 °C, 30 °C, and 45 °C with an accuracy of ± 0.1 °C (fig. 1). Three replications were made at each temperature and relative humidity, using a two samples per replication and the average values of equilibrium moisture content have been calculated. The change of samples mass was determined by electrical balance type KERN PLJ360-3M, with precision of 0.001 g every 7 days. The equilibrium between samples and their environment was reached after 21 days as evidenced by the constant weight after two successive weighing of the samples. The equilibrium moisture content of the samples was determined gravimetrically by drying in an oven at temperature of 105 °C and atmospheric pressure for 24 h.



Figure 1. Temperature controlled cabinet and glass jars used in the experiments

Statistical criterion for selection of sorption isotherm model

In scientific literature for estimation and selection of best sorption equation, several statistical criteria were proposed [3, 22]. The value of performance index, (ϕ), which is calculated on the basis of values of coefficient of determination, (R^2), the $RMSE$, and the MRD , is the first statistical criterion for selection of isotherm sorption equation [22]:

$$R^2 = \frac{SS_M - SS_E}{SS_M}, \quad RMSE = \sqrt{MS_E}, \quad MRD = \frac{1}{n} \sum_{i=1}^n \left| \frac{E_i}{X_i} \right| \quad (1)$$

$$MS_E = \frac{SS_E}{n - k}, \quad SS_M = \sum_{i=1}^n (X_i - \bar{X}_i)^2, \quad SS_E = \sum_{i=1}^n E_i^2 \quad (2)$$

$$E_i = X_{i \text{ exp}} - X_{i \text{ cal}}, \quad \bar{X}_i = \frac{1}{n} \sum_{i=1}^n X_i$$

$$\phi = \frac{R^2}{RMSE \cdot MRD} \quad (3)$$

Higher values of ϕ , indicate that the sorption equation better approximates the experimental sorption data.

The D'Agostino-Pearson's test of normality is the most effective procedure for assessing a goodness of fit for a normal distribution. This test is based on the individual statistics for testing of the residual population of skewness, (z_1) and kurtosis, (z_2). This test is the second statistical criterion as adequate of sorption equation and it is based on the following equations [28]:

$$SE_m = \sum_{i=1}^n \varepsilon_i^m, \text{ for } m=2,3,4 \quad \varepsilon_i = E_i - \bar{E}, \quad s = \sqrt{\frac{SE_2}{n-1}} \quad (4)$$

$$m_3 = \frac{nSE_3}{(n-1)(n-2)}, \quad m_4 = \frac{n(n+1)SE_4}{(n-1)(n-2)(n-3)} - \frac{3SE_2^2}{(n-2)(n-3)} \quad (5)$$

$$A_1 = \frac{m_3(n-2)}{s^3 \sqrt{n(n-1)}} \sqrt{\frac{(n+1)(n+3)}{6(n-2)}}, \quad B_1 = \frac{3(n^2 + 27n - 70)(n+1)(n+3)}{(n-2)(n+5)(n+7)(n+9)} \quad (6)$$

$$C_1 = \sqrt{2(B_1 - 1)} - 1, \quad D_1 = \sqrt{C_1}, \quad E_1 = \frac{1}{\sqrt{\ln(D_1)}}, \quad F_1 = \frac{A_1 \sqrt{C_1 - 1}}{\sqrt{2}} \quad (7)$$

$$G_2 = \frac{24n(n-2)(n-3)}{(n+1)^2(n+3)(n+5)}, \quad H_2 = \frac{(n-2)(n-3)|m_4|}{s^4(n-1)(n+1)\sqrt{G_2}} \quad (8)$$

$$J_2 = \frac{6(n^2 - 5n + 2)}{(n+7)(n+9)} \sqrt{\frac{6(n+3)(n+5)}{n(n-2)(n-3)}}, \quad K_2 = 6 + \frac{8}{J_2} \left(\frac{2}{J_2} + \sqrt{1 + \frac{4}{J_2^2}} \right) \quad (9)$$

$$L_2 = \frac{1 - \frac{2}{K_2}}{1 + H \sqrt{\frac{2}{K_2} - 4}} \quad (10)$$

$$z_1 = E_1 \ln(F_1 + \sqrt{F_1^2 + 1}), \quad z_2 = \left(\frac{2}{9K_2} \right)^{\frac{1}{2}} \left(1 - \frac{2}{9K_2} - \sqrt[3]{L_2} \right) \quad (11)$$

The test statistic for the D'Agostino-Pearson test of normality is computed with equation:

$$\chi^2 = z_1^2 + z_2^2 \quad (12)$$

The χ^2 statistics has a chi-squared distribution with 2 degrees of freedom (*df*). The tabled critical 0.05 chi-square value for *df*=2 is $\chi_{0.05}^2 = 5.99$. Therefore, if the computed value of chi-square is equal to, or greater than, either of the aforementioned values, the null hypothesis can be rejected at the appropriate level of significance [28] *i. e.* the sorption equation should be rejected.

Because the χ^2 statistics is not recommended individually as an adequate measure of the effectiveness of a sorption equation to describe the experimental data, additional criterion has to be introduced.

The single-sample run test is one of a numerous statistical procedures that have been developed for evaluating whether or not the distribution of series is random. This test is the third statistical criterion for effectiveness of sorption equation. The test evaluates the number of runs in a series in which, on each trial, the outcome must be one of *k* = 2 alternatives. In this test, the number of positive and negative residuals, *n*₁ and *n*₂, and the number of times the sequence of residuals changes sign, (*g*), are used to calculate the following test statistic [28]:

$$z_r = \frac{|g - g_1| - 0.5}{\sigma_r}, \quad g_1 = \frac{2n_1 n_2}{n_1 + n_2} + 1, \quad \sigma_r = \sqrt{\frac{2n_1 n_2 (2n_1 n_2 - n_1 - n_2)}{(n_1 + n_2)^2 (n_1 + n_2 - 1)}} \quad (13)$$

If the computed value of, (z_r), is greater than the tabled critical two-tailed value $z_{0.05} = 1.96$, the null hypothesis should be rejected [28], *i. e.* the sorption equation should be rejected.

A fourth statistical criterion for selection of sorption isotherm equation is the evaluation of significance and precision of the model constant. That can be done with constructing of individual confidence intervals (CI). If the estimated value of parameters is out of the 95% confidence interval, the model contains irrelevant parameters for approximation of experimental data *i. e.* sorption isotherm equation should be rejected.

Results and discussion

The experimental values for the equilibrium moisture content of pear at each water activity for the three different temperatures given in tab. 1 were fitted with isotherm equations recommended in ASAE Standard D245.5 [21]. Because the regression methods (indirect non-linear or direct non-linear), estimation method, the initial step size, the start values of parameters, convergence criterion and form of the function have significant influence on accuracy of estimated parameters [29], a large number of numerical experiments were performed.

Table 1. Equilibrium moisture content of pear*

15 °C		30 °C		45 °C	
a_w	X_{eq} [kg/kg d.b.]	a_w	X_{eq} [kg/kg d.b.]	a_w	X_{eq} [kg/kg d.b.]
0.113	0.011 ± 0.000	0.113	0.007 ± 0.000	0.112	0.008 ± 0.000
0.234	0.018 ± 0.000	0.216	0.016 ± 0.001	0.195	0.018 ± 0.000
0.333	0.040 ± 0.001	0.324	0.040 ± 0.000	0.311	0.040 ± 0.000
0.432	0.083 ± 0.001	0.432	0.080 ± 0.001	0.432	0.074 ± 0.001
0.559	0.159 ± 0.000	0.514	0.119 ± 0.000	0.469	0.091 ± 0.002
0.607	0.197 ± 0.002	0.560	0.145 ± 0.002	0.520	0.107 ± 0.000
0.741	0.325 ± 0.001	0.691	0.250 ± 0.000	0.640	0.172 ± 0.001
0.756	0.350 ± 0.002	0.751	0.320 ± 0.003	0.745	0.265 ± 0.000
0.859	0.600 ± 0.001	0.836	0.495 ± 0.001	0.817	0.395 ± 0.002
0.920	0.904 ± 0.003	0.900	0.813 ± 0.002	0.880	0.653 ± 0.002

* mean and standard deviation based on $N = 3$ replications

The method of indirect non-linear regression and estimation methods of Quasi-Newton, Simplex, Simplex and quasi-Newton, Hooke-Jeeves pattern moves, Hooke-Jeeves pattern moves and quasi-Newton, Rosenbrock pattern search, Rosenbrock pattern search and quasi-Newton, Gauss-Newton and Levenberg-Marquardt from computer program Statistica [30], were used to approximate the experimental data. On the basis of experimental data, and each equation from tab. 2, the average values of the coefficient R^2 , $RMSE$, MRD , and ϕ , were calculated. When the value for the coefficient R^2 was different, the greatest value was accepted as relevant.

After that, the equations were ranked on the basis of average values of performance index, (ϕ_a), (tab. 3). From tab. 3 it is evident that the GAB model, has the highest value of average performance index, $\phi_a = 755.9$. In agreement with the first statistic criterion, this model correlates the experimental values of adsorption isotherms of pear better than other models. From all

models, modified Chung-Pfost has the smallest value of performance index, $\phi_a = 5.035$. So, this model exhibited the worst ability to correlate the experimental equilibrium data of pear.

Table 2. Equations for fitting the equilibrium sorption data

Name of model	Equation	References
Modified Chung-Pfost	$X_{eq} = -\frac{1}{B} \ln \left[-\frac{(t+C) \ln(a_w)}{A} \right]$	[1]
Modified Halsey	$X_{eq} = \left[-\frac{\exp(A+Bt)}{\ln(a_w)} \right]^{1/C}$	[1]
Modified Oswin	$X_{eq} = (A+Bt) \left(\frac{a_w}{1-a_w} \right)^C$	[1]
Modified Henderson	$X_{eq} = \left[-\frac{\ln(1-a_w)}{A(t+C)} \right]^{1/B}$	[1]
Guggenheim-Anderson-de Boer	$X_{eq} = \frac{X_m K C a_w}{(1-K a_w)(1-K a_w + K C a_w)}$ $X_m = x_{m0} \exp\left(\frac{\Delta H_x}{RT}\right) \quad K = K_0 \exp\left(\frac{\Delta H_k}{RT}\right)$ $C = C_0 \exp\left(\frac{\Delta H_c}{RT}\right)$	[1]

Table 3. Statistic summary of the regression analysis

Name of model	R_a^2	$RMSE_a$	MRD_a	ϕ_a	Rank
Modified Chung-Pfost	0.888	0.094	1.934	5.035	5
Modified Halsey	0.990	0.028	0.682	88.39	4
Modified Oswin	0.996	0.017	0.330	519.2	3
Modified Henderson	0.996	0.015	0.136	675.4	2
GAB	0.999	0.009	0.167	755.9	1

Table 4. Rejection criteria for sorption models

Name of model	χ_a^2	z_{ra}	Rejection criteria
Modified Chung-Pfost	2.709	1.466	–
Modified Halsey	1.501	1.636	–
Modified Oswin	1.204	1.412	–
Modified Henderson	3.804	0.639	–
GAB	3.840	0.639	–

– not rejected

In tab. 4, the computed average values for, (χ^2) , and, (z_r) , are given. It is obvious that all equations have average value of, (χ^2) , and, (z_r) , smaller than the tabled critical value. In accordance with the proposed statistical criteria, these models-equations are able to correlate the experimental values of sorption isotherms of pear with 0.9-2.8% average root mean

squared error, with excluding of the modified Chung-Pfost equation which in comparison with the other equations have a high average value of root mean squared error, 9.4%

Because all equations “survived” the second and third statistical criteria, only the first statistical criterion is relevant for selection of best sorption equation. In accordance with this statistical criterion, the GAB equation has the highest value of performance index in comparison with the others, so this equation was taken for further statistical evaluation – verification of the fourth statistical criterion. The values of GAB model parameters were estimated by fitting the equation to experimental data using Gauss-Newton estimation method which minimizes the sum squares errors, while the 95% confidence intervals of the estimated parameters were determined by using the **nlparci** (beta, resid,'jacobian', **J**) function of the Statistics Toolbox of Matlab®8.3, [31]. The significance of each of the estimated parameters was evaluated through (t) test statistic. The estimated values of parameters, 95% confidence intervals and two-tailed p-value of estimated parameters at three different temperatures are given in tab. 5.

Table 5. Estimated values of parameters, 95% confidence intervals and p value

t [°C] and 95% CI	Value of parameters					
	X_{m0}	K_0	C_0	ΔH_x	ΔH_k	ΔH_c
15 °C	0.124	0.278	0.183	1083.465	2843.341	2754.322
95% CI	(0.051-0.198)	(0.262-0.295)	(0.031-0.334)	(-329.882-2496.812)	(2701.663-2985.018)	(768.839-4739.805)
p value	$5.100 \cdot 10^{-3}$	$1.596 \cdot 10^{-9}$	$2.500 \cdot 10^{-2}$	$1.128 \cdot 10^{-1}$	$4.825 \cdot 10^{-10}$	$1.348 \cdot 10^{-2}$
30 °C	0.099	0.289	0.196	582.095	3038.901	3791.733
95% CI	(0.067-0.131)	(0.280-0.299)	(0.074-0.319)	(-238.624-1402.813)	(2957.235-3120.567)	(2223.314-5360.152)
p value	$1.680 \cdot 10^{-4}$	$2.390 \cdot 10^{-11}$	$7.230 \cdot 10^{-3}$	$1.374 \cdot 10^{-1}$	$6.449 \cdot 10^{-12}$	$7.230 \cdot 10^{-4}$
45 °C	0.080	0.303	0.261	143.766	3165.113	4285.862
95% CI	(0.068-0.092)	(0.298-0.307)	(0.163-0.360)	(-253.731-541.264)	(3126.640-3205.586)	(3287.961-5283.763)
p value	$1.013 \cdot 10^{-6}$	$1.252 \cdot 10^{-13}$	$4.170 \cdot 10^{-4}$	$4.210 \cdot 10^{-1}$	$3.575 \cdot 10^{-14}$	$1.932 \cdot 10^{-5}$

X_{m0} [kg.kg⁻¹]: parameter to express temperature dependence of X_m , K_0 : Arrhenius type parameter to express temperature dependence of K , C_0 : Arrhenius type parameter to express temperature dependence of C , ΔH_x [Jmol⁻¹]: parameter to express temperature dependence of X_m , ΔH_k [Jmol⁻¹]: difference in enthalpy between bulk liquid and multilayer, ΔH_c [Jmol⁻¹]: difference in enthalpy between monolayer and multilayer

From tab. 5 it is evident that the calculated two-tailed p-values for all parameters are extremely small (much less than 0.05) with exclusion for parameter ΔH_x . One of the reasons for this might be the applied method of indirect non-linear regression analysis, considering the fact that the successful application of GAB equation depends on the regression method employed on the experimental data [32, 33]. Although, the method of direct non-linear regression has several advantages over indirect non-linear regression method [32, 33], from numerical experiments it should be noted that extremely low two-tailed p-value for each of the parameters were obtained with application on direct non-linear regression method. But, in this case, the individual confidence intervals for some parameters were much wider. Other reason for the low p-value of parameters is a high correlation between pair of parameters: (X_{m0} ; ΔH_x), (K_0 ; ΔH_k) (C_0 ; ΔH_c), due to internal compensation on values of parameters in Arrhenius type relationships. On other side it is also known that the non-linear regression applied to models with Arrhenius type relationships generates very highly correlated parameters, elongated confidence intervals and low precision or high uncertainties of parameters [33].

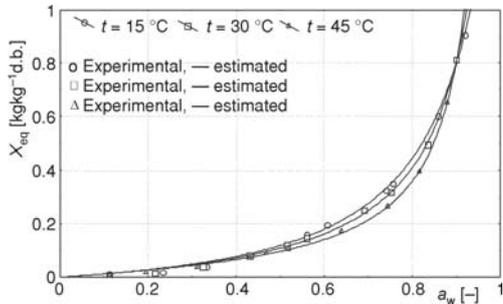


Figure 2. Experimental and calculated equilibrium moisture content for different temperatures

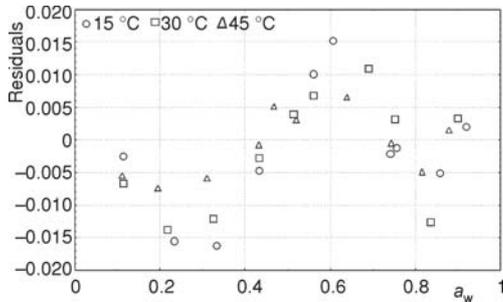


Figure 3. Residuals plot of sorption data for pear at 15 °C, 30 °C, and 45 °C (GAB equation)

The experimental and estimated values for equilibrium moisture content for pears at three temperatures are shown on fig. 2.

The adsorption isotherms of pear have a shape typical of high-sugar content foods according to the BET classification *i. e.* type III (J-shaped). According to BET theory, a type III isotherm appears when the binding energy of the first layer is lower than the binding energy between water molecules [34]. But, for water activity lower than 0.11, it is difficult to conclude that the isotherms follow type III of the pattern [35]. The values of equilibrium moisture content for pear decreased with an increase in temperature, at constant water activity, but up to water activity of 0.85 for all temperatures, curves are crossing. The intersection point of isotherms depends on the type of sugar present, sugar size distribution and composition of the food [36]. Since this process is known to be endothermic, more sugar is dissolved and thus more water is held by food products at higher temperatures. Because the pear is fruit with high pectin and sugars contents, there was intersection point with increase in temperature. Similar results were reported for the isotherms of pear [37, 38], apple [39], raisins [40], figs,

prunes, and apricots [32, 41], grapes and apricot [42], and mango [43].

In fig. 3 the residuals of the dependent variable X_{eq} obtained by the GAB model, are plotted against the corresponding independent variable a_w , for three temperatures. Analysis of the residuals did not indicate abnormal distribution.

Conclusions

The moisture adsorption isotherms of pear at three temperatures (15, 30, and 45 °C) and ten different water activity were experimentally determined with the gravimetric static method. The adsorption isotherms of pear according to the BET classification exhibit Type III (J-shaped), typical of high sugar foods. All isotherms were very similar in shape, and for the water activity of up to 0.85 curves are crossing. For approximation of experimental equilibrium data, the modified Chung-Pfost, modified Halsey, modified Oswin, modified Henderson, and GAB equations were used. According to the performed statistical analysis, it was concluded that the GAB equation has a high value of performance index and so it has a best fit to experimental data, while the modified Chung-Pfost equation exhibited the worst ability to correlate the experimental equilibrium data of pear in accordance to the lowest value of performance index. But, from fourth statistical criterion it was concluded that the parameters in GAB equation have extremely low p -value as a result of high correlation between pair of parameters (X_{m0} ; ΔH_x), (K_0 ; ΔH_k) (C_0 ; ΔH_c) due to internal compensation on values of parameters in Arrhenius type relation-

ships. Therefore, the single statistical criterion can not be used to select the sorption isotherm equation.

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Nomenclature

a_w	– water activity	R^2	– coefficient of determination
A_1-F_1	– auxiliary variables for calculation of the skewness test statistics	$RMSE$	– root mean squared error
C	– Guggenheim constant	SS_E	– sum of squares of errors about regression
CI	– confidence interval	SS_M	– sum of squares of errors adjusted for the mean
C_0	– Arrhenius type parameter to express temperature dependence of C_0	SS_m	– auxiliary variables for the calculation of the normality test statistic
E_i	– residual, [kgkg^{-1}]	s	– standard deviation of errors about the residual mean
G_1-L_1	– auxiliary variables for calculation kurtosis test statistics	T, t	– temperature, [K], [$^{\circ}\text{C}$]
g	– residual change	z_1, z_2	– statistic for testing the skewness and kurtosis of the residual population
g_1	– mean of the sampling distribution of runs in a random series	z_r	– statistic for testing the randomness of the moisture residual series
ΔH_c	– difference in enthalpy between monolayer and multilayer, [Jmol^{-1}]	X_i	– moisture content, [kgkg^{-1}]
ΔH_k	– difference in enthalpy between bulk liquid and multilayer, [Jmol^{-1}]	X_m	– monolayer moisture content, [kgkg^{-1}]
ΔH_x	– parameter to express temperature dependence of X_m , [Jmol^{-1}]	X_{m0}	– parameter to express temperature dependence of X_m , [kgkg^{-1}]
K	– parameter in GAB equation, factor correcting properties of the multilayer molecules relative to the bulk liquid	<i>Greek symbols</i>	
k	– number of parameter estimates	ε	– error about the residual mean
K_0	– Arrhenius type parameter to express temperature dependence of K_0	χ^2	– statistic for testing the normality of the moisture residuals
MRD	– mean relative deviation	ϕ	– measure for the goodness of fit
MS_E	– mean square errors	σ_r	– expected standard deviation of the sampling distribution of runs in a random series
m_3	– third moment about the mean for the residual population-skewness	<i>Subscripts</i>	
m_4	– fourth moment about the mean for the residual population-kurtosis	a	– average
n	– number of experimental points	c	– calculated
n_1, n_2	– number of positive and negative residuals	e	– experimental
R	– universal gas constant, [$\text{Jmol}^{-1}\text{K}^{-1}$]	eq	– equilibrium

References

- [1] Gal, S., The Need for, and Practical Applications of Sorption Data, in: *Physical Properties of Foods* (Ed. R. Jowitt, F. Escher, B. Hallstrom, H. Meferet, W. Spiess, G. Vos), Elsevier Applied Science, London, 1987, pp. 13-25
- [2] Brunauer, S., *et al.*, On a Theory of the van der Waals Adsorption of Gases, *Journal of the American Chemical Society*, 62 (1940), 1, pp. 1723-1732
- [3] Basu, S., *et al.*, Models for Sorption Isotherms for Foods: A Review, *Drying Technology*, 24 (2006), 8, pp. 917-930
- [4] Blahovec, J. S., Yanniotis, S., Modified Classification of Sorption Isotherms, *Journal of Food Engineering*, 91 (2009), 1, pp. 72-77

- [5] Kiranoudis, C.T., et al., Drying Kinetics of Some Fruits, *Drying Technology*, 15 (1997), 5, pp. 1399-1418
- [6] Guine, R. P. F., Castro, J. A. A. M., Experimental Determination and Computer Fitting of Desorption Isotherms of D. Joaquina Pears, *Food and Bioproducts Processing*, 80 (2002) 3, pp. 149-154
- [7] Lahsasni, S., et al., Adsorption-Desorption Isotherms and Heat of Sorption of Prickly Pear Fruit (*Opuntia ficus indica*), *Energy Conversion and Management*, 45 (2004), 2, pp. 249-261
- [8] Guine, R. P. F., Sorption Isotherms of Pears Using Different Models, *International Journal of Fruit Science*, 9 (2009) 1, pp. 11-22
- [9] Djendoubi, M. N., et al., Moisture Desorption Isotherms, Isosteric Heats of Desorption and Glass Transition of Fresh Pear and Apple: Experimental and Mathematical Investigation, *Proceedings on CD*, 3rd European Drying Conference – EuroDrying'2011, Palma, Balearic Island, Spain, 2011
- [10] Boquet, R., et al., Equations for Fitting Water Sorption Isotherms of Foods, II. Evaluation of Various Two-Parameter Models, *Journal of Food Technology*, 13 (1978), 4, pp. 319-327
- [11] Boquet, R., et al., Equations for Fitting Water Sorption Isotherms of Foods, III. Evaluation of Various Three-Parameter Models, *Journal of Food Technology*, 14 (1979), 4, pp. 527-534
- [12] Chirife, J., Iglesias, H. A., Equations for Fitting Water Sorption Isotherms of Foods: Part 1 – a Review, *Journal of Food Technology*, 13 (1978), 2, pp. 159-174
- [13] Popovski, D., Mitrevski, V., Some New Four Parameter Model for Moisture Sorption Isotherms, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 3 (2004), 3, pp. 698-701
- [14] Popovski, D., Mitrevski, V., A Method for Extension of the Water Sorption Isotherm Models, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 3 (2004), 6, pp. 799-803
- [15] Popovski, D., Mitrevski, V., A Method for Generating Water Sorption Isotherm Models, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 4 (2005), 3, pp. 945-948
- [16] Popovski, D., Mitrevski, V., A Generator of Water Desorption Isotherm Models, *Proceedings on CD*, 11th Polish Drying Symposium, Poznan, Poland, 2005
- [17] Popovski, D., Mitrevski, V., Method of Free Parameter for Extension of the Water Sorption Isotherm Models, *Proceedings on CD*, 32nd International Conference of Slovak Society of Chemical Engineering, Tatranske Matliare, Slovakia, 2005
- [18] Popovski, D., Mitrevski, V., Two Methods for Generating New Water Sorption Isotherm Models, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 5 (2006), 3, pp. 1407-1410.
- [19] Popovski, D., Mitrevski, V., Trigonometric and Cyclometric Models of Water Sorption Isotherms, *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 6 (2006), 1, pp. 1711-1718
- [20] van den Berg, C., Bruin, S., Water Activity and its Estimation in Food Systems: Theoretical Aspects, Chapter No. 1 of Water Activity, in: *Influences on Food Quality* (Ed. L. B. Roeland, G. F. Stewart), Academic Press, New York-London, 1981
- [21] ***, ASAE Standard, D245.5, St. Joseph, Mich., USA, 1999, pp. 512-528
- [22] Ruiz-Lopez, I. I., Herman-Lara, E., Statistical Indices for the Selection of Food Sorption Isotherm Models, *Drying Technology*, 27 (2009), 6, pp. 726-738
- [23] Mitrevski, V., et al., Comparison between the Transcendental and Cyclometric Sorption Isotherm Models, *Journal on Processing and Energy in Agriculture*, 16 (2012), 1, pp. 1-5
- [24] Mitrevski, V., et al., Comparison between the Transcendental and Trigonometric Sorption Isotherm Models, *Proceedings on CD*, 18th International Drying Symposium, IDS 2012, Xianmen, China, 2012
- [25] Mitrevski, V., et al., Statistical Evaluation of Some Four Parameters Sorption Isotherm Models, *Proceedings on CD*, 4th European Drying Conference, EuroDrying 2013, Paris, France, 2013
- [26] Wolf, W., et al., Standardization of Isotherm Measurements (COST-project 90 and 90 bis), in: *Properties of Water in Foods* (Ed. D. Simatos, J. L. Multon), Dordrecht, 1985, pp. 661-677
- [27] Greenspan, L., Humidity Fixed Points of Binary Saturated Aqueous Solutions, *Journal of Research of National Bureau of Standards – A Physics and Chemistry*, 81A (1977), 1, pp. 89-96
- [28] Sheskin, D. J., Handbook of Parametric and Nonparametric Statistical Procedures, 5th ed., CRC Press, Boca Raton, Fla., USA, 2011
- [29] Popovski, D., Mitrevski, V., Numerical Experiments with the GAB Model, *Proceedings on CD*, 30th International Conference of Slovak Society of Chemical Engineering, Tatranske Matliare, Slovakia, 2003
- [30] ***, Statistica (Data Analysis Software System), v.10.0, Stat-Soft, Inc, USA, 2011
- [31] ***, Statistics Toolbox of Matlab® 8.3, The MathWorks Inc., Natick, MA, USA, 2013
- [32] Maroulis, Z. B., et al., Application of the GAB Model to the Moisture Sorption Isotherms for Dried Fruits, *Journal of Food Engineering*, 7 (1988), 1, pp. 63-78

- [33] Samaniego-Esquerria, C. M., *et al.*, Comparison of Regression Methods for Fitting the GAB Model to the Moisture Isotherms of Some Dried Fruit and Vegetables, *Journal of Food Engineering*, 11 (1981), 2, pp. 115-133
- [34] Leung, H. K., Water Activity and other Colligative Properties of Foods, in: Physical and Chemical Properties of Foods (Ed. M. R. Okos), 1986, pp. 138-185
- [35] Mulet, A., *et al.*, Equilibrium Isotherms and Isotheric Heats of Morel (*Morchella Esculenta*), *Journal of Food Engineering*, 53 (2002), 1, pp. 75-81
- [36] Weisser, H., Influence of Temperature on Sorption Equilibria, in: Properties of Water in Foods (Ed. D. Simatos, J. L. Multon), Dordrecht, 1985, pp. 95-118
- [37] Lahsasni, S., *et al.*, Moisture Adsorption-Desorption Isotherms and Heat of Sorption of Prickly Pear Fruit Cladode (*Opuntia Ficus Indica*) at Different Temperatures, *Energy Conversion and Management*, 44 (2003), 6, pp. 923-926
- [38] Barroca, M. J., *et al.*, Sorption Isotherms of Portuguese Varieties of Pears, *Proceedings on CD, 7th Meeting on Food Chemistry, Portugal, 2005*
- [39] Roman, G. N., *et al.*, Moisture Equilibrium in Apples at Several Temperatures: Experimental Data and Theoretical Considerations, *Journal of Food Science*, 47 (1982) 5, pp. 1484-1488
- [40] Saravacos, G. D., *et al.*, Effect of Temperature on the Water Adsorption Isotherms of Sultana Raisins, *Journal of Food Science*, 51 (1986), 2, pp. 381-383
- [41] Tsami, E., *et al.*, Water Sorption Isotherms of Raisins, Currants, Figs, Prunes and Apricots, *Journal of Food Science*, 55 (1990), 6, pp. 1594-1597
- [42] Ertekin, F. K., Atil, G., Sorption Isotherms and Isotheric Heat Sorption for Grapes, Apricots, Apples and Potatoes, *LWT Food Science and Technology*, 37 (2004), 4, pp.429-438
- [43] Falade, K. O., *et al.*, Adsorption Isotherm and Heat of Sorption of Fresh and Osmo-Oven Dried Plantain Slices, *European Food Research Technology*, 217 (2003), 3, pp. 230-234