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Complete List of Authors:	Mitrevski, Vangelce; Faculty of Technical Sciences, Heat and Mass Transfer Lutovska, Monika; Faculty of Technical Sciences, Pavkov, Ivan; Faculty of Agriculture, Department of Agricultural Engineering Mijakovski, Vladimir; Faculty of Technical Sciences, Popovski, Filip; Faculty of Technical Sciences,

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THE POWER SERIES AS WATER SORPTION ISOTHERM MODELS

VANGELCE MITREVSKI[1,3], MONIKA LUTOVSKA[1], IVAN PAVKOV[2], VLADIMIR MIJAKOVSKI[1] and FILIP POPOVSKI[1]

[1]Faculty of Technical Sciences, University St. Kliment Ohridski, Ivo Lola Ribar nn, 7000 Bitola, Republic of Macedonia
[2]Faculty of Agriculture, University of Novi Sad, Trg Dositeja Obradovica, 21000 Novi Sad, Republic of Serbia

[3]Corresponding author: Vangelce Mitrevski

Address: University St. Kliment Ohridski, Faculty of Technical Sciences, Ivo Lola Ribar nn,
7000 Bitola, Republic of Macedonia

TEL: +389 47 207 702
FAX: +389 47 203 370
EMAIL: vangelce.mitrevski@uklo.edu.mk

ABSTRACT

In this study a power series which can generate different families of new water sorption isotherm models were presented. The experimental obtained values for adsorption isotherms of pear for three different temperatures 15, 30 and 45 °C and ten water activities, from 0.112 to 0.920, were fitted with newly generated sorption isotherm models and plus referent Anderson model known in the literature as Guggenheim-Anderson-de Boer (GAB) model. In order to find which model gives the best results for approximation of experimental sorption data, several statistical criteria proposed in scientific literature were used. For each model 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, confidence intervals of estimated parameters, significance and precision of the model parameters). The performed statistical analysis shows that the two new generated three-parameter models M32 and M34 gave the best fit to the sorption data of pear than the referent three parameters Anderson model.

PRACTICAL APLICATIONS

In scientific literature many sorption isotherm models were developed by researchers for approximation of sorption data of food materials. It is known that the most of these models are empirical, semi-empirical and theoretical and that some of them are one, two, three, four and more parameters models, and that have different success for approximation of experimental sorption data due to complex nature of food materials. This study have intends to developed of a generator which can generate different families of new three parameters water sorption isotherm models, which have better statistical success for approximation of sorption data of food materials in whole range of water activity in comparison with referent three parameters Anderson model.

INTRODUCTION

A food moisture sorption isotherm describes the thermodynamic relationship between water activity (a_w) and the equilibrium of moisture content (X_{eq}) of food material at constant temperature and pressure. It is well known that moisture sorption isotherms of food 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 (Gal, 1987). Also, the knowledge of the sorption data is essentially useful to predict microbiological, enzymatic and chemical stability of food materials. Many sorption models are available in scientific literature for approximate experimental data of sorption isotherm on food materials (Boquet *et al*. 1978; Boquet *et al*. 1979; Chirife and Iglesias 1978; Lewicki 1998). Popovski and Mitrevski (2004, 2004a, 2005, 2005a, 2005b, 2006, 2006a) proposed seven methods for generating of new sorption models. These models are developed based on different rational, exponential, logarithmic, trigonometric or cyclometric functions. Each of those generated models has some success in approximation of equilibrium moisture data of a given type of food material and in appropriate range of water activity. Van den Berg and Bruin (1981) gave a survey of seventy seven models classified into three groups: theoretical, partially theoretical, and fully empirical. Among them is the power series of Jaroniec (Jaroniec 1975):

$$X_{eq} = \exp\left(\sum_{i=1}^{n} P_i \ln^{i-1} a_w\right) \tag{1}$$

which represents a family of water sorption isotherm models. The first member of this family is two-parameter model (P_1, P_2) of McGavacak and Patric (McGavacak and Patric 1920)

$$X_{eq} = P_1 a_w{}^{P_2} \tag{2}$$

The objectives of this study were:

(a) generalization of the Jaroniec power series (1). Obtained of a generator which can generate different families of new water sorption isotherm models and

(b) evaluation of suitability of generated isotherm models 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 a uniform samples with thickness of 4±0.1 mm, before being reduced to a cylinder form with diameter of 20±0.1 mm. Several measurements were made using a calliper and only samples with a tolerance of ±5 % were used. (Mitrevski *et al.* 2014). 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 $m.s^{-1}$ for a period of **7** hours. The equilibrium moisture content of pears was determined at 15, 30 and 45°C using static gravimetric method (Rahman and Sablani 2009). Ten saturated salt solutions L_iCl, CH_3COOK, MgCl, K_2CO_3, $Mg(NO_3)_2$, NaBr, $SrCl_2$, NaCl, KCl and $BaCl_2$ were used to obtained defined constant water activity from 0.112 to 0.920. The glass sorption jars were placed and kept in the temperature controlled cabinet type SANYO MCO-15AC, maintained at the temperature 15, 30 and 45°C with an accuracy of ±0.1 °C. Three replications were made at each temperature and relative humidity, using 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.

Generator of sorption isotherm models

In the power series (1), Jaroniec used the logarithmic function $\ln(a_w)$. Instead of $\ln(a_w)$, we can use any monotonous function $F(a_w)$ with constant sign into the interval [0,1]. In that way, the Jaroniec power series (1) can be generalized as

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \, F^{i-1}(a_w)\right] \tag{3}$$

For $F(a_w)$ in equation (3) different rational, exponential, logarithmic, trigonometric or cyclometric functions were used. In addition ten examples are given:

- $$F(a_w) = \frac{1}{1+a_w} \tag{4}$$

$$X_{eq} = \exp\left(\sum_{i=1}^{n} \frac{P_i}{(1+a_w)^{i-1}}\right) \tag{5}$$

- $$F(a_w) = \frac{1+a_w}{1+2a_w} \tag{6}$$

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \left(\frac{1+a_w}{1+2a_w}\right)^{i-1}\right] \tag{7}$$

- $F(a_w) = \exp(a_w)$ (8)

$$X_{eq} = \exp\left(\sum_{i=1}^{n} P_i \exp^{i-1} a_w\right) \tag{9}$$

- $F(a_w) = \exp(1-a_w)$ (10)

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \exp^{i-1}(1-a_w)\right] \tag{11}$$

- $F(a_w) = \ln(1+a_w)$ (12)

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \ln^{i-1}(1+a_w)\right] \tag{13}$$

- $F(a_w) = \dfrac{a_w}{\ln(1+a_w)}$ (14)

$$X_{eq} = \exp\left\{\sum_{i=1}^{n} P_i \left[\frac{a_w}{\ln(1+a_w)}\right]^{i-1}\right\} \tag{15}$$

- $F(a_w) = \dfrac{a_w}{\sin a_w}$ (16)

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \left(\frac{a_w}{\sin a_w}\right)^{i-1}\right] \tag{17}$$

- $F(a_w) = \dfrac{\sin a_w}{a_w}$ (18)

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \left(\frac{\sin a_w}{a_w}\right)^{i-1}\right] \tag{19}$$

- $F(a_w) = \dfrac{\arcsin a_w}{a_w}$ (20)

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \left(\frac{\arcsin a_w}{a_w}\right)^{i-1}\right] \tag{21}$$

- $$F(a_w) = \frac{a_w}{\arctan a_w} \tag{22}$$

$$X_{eq} = \exp\left[\sum_{i=1}^{n} P_i \left(\frac{a_w}{\arctan a_w}\right)^{i-1}\right] \tag{23}$$

To examine the statistical efficiency of the above mentioned families, a comparison of their three-parameter models were made:

(1) → $$X_{eq} = \exp(P_1 + P_2 \ln a_w + P_3 \ln^2 a_w) \tag{24}$$

(5) → $$X_{eq} = \exp\left[P_1 + \frac{P_2}{1+a_w} + \frac{P_3}{(1+a_w)^2}\right] \tag{25}$$

(7) → $$X_{eq} = \exp\left[P_1 + P_2 \frac{1+a_w}{1+a_w} + P_3\left(\frac{1+a_w}{1+2a_w}\right)^2\right] \tag{26}$$

(9) → $$X_{eq} = \exp(P_1 + P_2 \exp a_w + P_3 \exp^2 a_w) \tag{27}$$

(11) → $$X_{eq} = \exp\left[P_1 + P_2 \exp(1-a_w) + P_3 \exp^2(1-a_w)\right] \tag{28}$$

(13) → $$X_{eq} = \exp\left[P_1 + P_2 \ln(1+a_w) + P_3 \ln^2(1+a_w)\right] \tag{29}$$

(15) → $$X_{eq} = \exp\left\{P_1 + P_2 \frac{a_w}{\ln(1+a_w)} + P_3\left[\frac{a_w}{\ln(1+a_w)}\right]^2\right\} \tag{30}$$

(17) → $$X_{eq} = \exp\left[P_1 + P_2 \frac{a_w}{\sin a_w} + P_3\left(\frac{a_w}{\sin a_w}\right)^2\right] \tag{31}$$

(19) → $$X_{eq} = \exp\left[P_1 + P_2 \frac{\sin a_w}{a_w} + P_3\left(\frac{\sin a_w}{a_w}\right)^2\right] \tag{32}$$

(21) → $$X_{eq} = \exp\left[P_1 + P_2 \frac{\arcsin a_w}{a_w} + P_3\left(\frac{\arcsin a_w}{a_w}\right)^2\right] \tag{33}$$

$$(23) \rightarrow \qquad X_{eq} = \exp\left[P_1 + P_2 \frac{a_w}{\arctan a_w} + P_3\left(\frac{a_w}{\arctan a_w}\right)^2\right] \tag{34}$$

As referent, the popular model of Anderson were used (Anderson 1946):

$$X_{eq} = \frac{P_1 a_w}{(1 - P_2 a_w)(1 - P_3 a_w)} \tag{35}$$

known in the literature as GAB model, according to Guggenheim (Guggenheim 1966), Anderson (Anderson 1946) and de Boer (de Boer 1953).

Statistical criterion for selection of sorption isotherm model

Statistical analysis is a very useful tool in many engineering problems in order to obtain certain statistical parameters. Generally, several statistical criterions or statistical parameters are used for selection of sorption isotherm models. In scientific literature, for the goodness of fit of experimental sorption data and selection of the best isotherm model, following statistical 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 model with graphical evaluation of the residual randomness is also popular (Basu *et al*. 2006; Ruiz-Lopez and Herman-Lara 2009). In this study, several statistical criterions were used for selection of the most appropriate sorption model (Ruiz-Lopez and Herman-Lara 2009).

The value of performance index, (ϕ), which is calculated on the basis of values of coefficient of determination, (R^2), the root mean squared error, (RMSE), and the mean relative deviation, (MRD), is the first statistical criterion for selection of isotherm sorption model (Ruiz-Lopez and Herman-Lara 2009):

$$\phi = \frac{R^2}{\mathrm{RMSE} \cdot \mathrm{MRD}} \tag{36}$$

Higher values of performance index, (ϕ), indicate that the sorption model 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) and is the second statistical criterion as adequate of sorption model. The test statistic for the D'Agostino-Pearson test of normality is computed with equation (Sheskin 2008):

$$\chi^2 = z_1^2 + z_2^2 \tag{37}$$

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 $\chi^2_{0.05} = 5.99$. 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 (p>0.95), i.e. the sorption model should be rejected (Sheskin 2008). Because the χ^2 statistics is not recommended individually as an adequate measure of the effectiveness of a sorption model to describe the experimental sorption data, one must use additional statistical criterion.

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 model. 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 (Sheskin 2008):

$$z_r = \frac{|g - g_1| - 0.5}{\sigma_r},\ g_1 = \frac{2n_1 n_2}{n_1 + n_2} + 1,\ \sigma_r = \sqrt{\frac{2n_1 n_2 (2n_1 n_2 - n_1 - n_2)}{(n_1 + n_2)^2 (n_1 + n_2 - 1)}} \tag{38}$$

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 (p>0.95), i.e. the sorption model should be rejected (Sheskin 2008).

A fourth statistical criterion for selection of sorption isotherm model is the evaluation of significance and precision of the model constant. That can be done with constructing of individual confidence intervals (CI) and with calculated of two-tailed p-value of estimated parameters. If the estimated value of parameters is out of the 95% confidence interval or estimated two-tailed p-value according to (t) test of statistic is (p<0.05) the model contains irrelevant parameters for approximation of experimental sorption data i.e. sorption isotherm model should be rejected.

RESULTS AND DISCUSSION

For statistical evaluation of new generated sorption isotherm models and referent Anderson model the experimental obtained values for the equilibrium moisture content of pear for ten water activity and three different temperatures (Table 1) were used (Mitrevski *et al*. 2014).

TABLE 1.

Because the regression method, 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 (Popovski and Mitrevski 2003; Mitrevski *et al*. 2014), a large number of numerical experiments were performed. 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 StatSoft Statistica (Statsoft Inc., Tulsa, OK, http://www.statsoft.com), were used in numerical experiments. On the basis of experimental sorption data of pear and each model, the average values of: coefficient of determination, (R^2), root mean squared error, (RMSE), mean relative deviation, (MRD), and performance index, (ϕ), were calculated. When the value for coefficient of determination was different, the greatest value was accepted as relevant. After that, the sorption models were ranked on the basis of average values of performance index, (ϕ_a), (Table 2).

From Table 2 it is evident that the Anderson model i.e. GAB model (M35), has the highest value of average performance index, ϕ_a = 776.807. In agreement with the first statistic criterion, this model correlates the experimental values of sorption data of pear better than other models. From all models, new generated model M26 has the smallest value of performance index, ϕ_a = 24.169. So, this model exhibited the worst ability to correlate the experimental equilibrium data of pear according to first statistical criterion.

TABLE 2.

In Table 3, the computed average values for, (χ^2), and, (z_r), are given. It is obvious that all models have average value of, (χ^2), and, (z_r), smaller than the tabled critical value ($\chi^2_{0.05}$ = 5.99; $z_{0.05}$ = 1.96). In accordance with the proposed statistical criteria, these models are able to correlate the experimental values of sorption isotherms of pear with 0.9÷4.3 % average root mean squared error.

TABLE 3.

Because all models "survived" the second and third statistical criteria, the forth statistical criterion is relevant for selection of the best sorption model. The values of the model parameters were estimated by fitting the models to experimental sorption data of pear 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 (The MathWorks Inc., Natick, MA, USA, 2013). The significance of each of the estimated parameters (P_1, P_2, P_3) 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 Table 4.

TABLE 4.

From Table 4 it is evident that the calculated two-tailed p-values for all parameters at three different temperatures are extremely small (much less than $p<0.05$) for all models, with excluding on models M32 and M34. According to fourth statistical criterion these model contains unhelpful parameters for the approximation of the experimental sorption data of pear i.e. these models have no significant estimate parameters. For models M32 and M34 the p-values for all parameters are higher than critical ($p>0.05$) for all three temperatures. So, from statistical view point these models are able to approximate sorption data of pear at three temperatures in whole range of water activity. But, from the first statistical criterion the model M34 have the higher value of average performance index (ϕ_a = 87.418) in comparison with the model M32 (ϕ_a = 71.969), so this model better approximates experimental sorption data of pear. As shown in Fig.1 and Fig.2, a good match was found between experimental and calculated values of equilibrium moisture content for pear with the models M32 and M34.

FIGURE 1.

FIGURE 2.

CONCLUSIONS

In this study a generalization of the Jaroniec power series (1) was made. The power series (3) that can generate many families of new water sorption models was presented. Several statistical criterions proposed in scientific literature were used for selection of sorption isotherm models. From statistical evaluation of the generated models, according to proposed statistical criterions, it can be concluded that two presented new three-parameter models M32 and M34 give better results than the referent three parameters Anderson model (M35). These models may be successfully used for approximation of sorption data of food materials in the whole range of water activity.

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Tables

TABLE 1. EQUILIBRIUM MOISTURE CONTENT OF PEAR*

5°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

TABLE 2. STATISTIC SUMMARY OF THE REGRESSION ANALYSIS*

Number of model (equation)	R_a^2	$RMSE_a$	MRD_a	ϕ_a	Rank
M24	0.986	0.029	0.375	96.158	5
M25	0.989	0.027	0.419	91.384	6
M26	0.974	0.043	1.155	24.169	12
M27	0.995	0.019	0.429	129.768	2
M28	0.990	0.036	0.424	66.819	10
M29	0.992	0.024	0.402	106.259	4
M30	0.994	0.024	0.399	108.961	3
M31	0.993	0.022	0.590	78.517	8
M32	0.993	0.025	0.563	71.969	9
M33	0.991	0.027	0.732	53.034	11
M34	0.993	0.022	0.541	87.418	7
M35	0.999	0.009	0.181	776.807	1

* "a" average value calculated for three temperatures

TABLE 3. REJECTION CRITERIA FOR SORPTION MODELS*

Model-equation	χ_a^2	z_{ra}	Rejection criteria
M24	1.520	0.831	-
M25	1.396	0.913	-
M26	1.378	1.006	-
M27	1.635	0.975	-
M28	1.387	0.944	-
M29	1.409	0.944	-
M30	1.460	0.975	-
M31	1.646	0.975	-
M32	1.672	0.944	-
M33	1.628	0.944	-
M34	1.684	0.975	-
M35	1.010	0.831	-

* "a" average value calculated for three temperature, "-" not rejected

TABLE 4. ESTIMATED VALUES OF PARAMETERS, 95% CONFIDENCE INTERVALS AND p VALUES*

Model (equation)	Temperature	Parameter	Value	95% CI	p
M24	15°C	P_1	0.259	(0.137, 0.381)	**1.545E-3**
		P_2	4.865	(4.044, 5.687)	**2.000E-6**
		P_3	1.427	(0.698, 2.156)	**2.407E-3**
	30°C	P_1	0.262	(0.083, 0.441)	**1.046E-2**
		P_2	5.072	(3.960, 6.183)	**1.300E-5**
		P_3	1.510	(0.600, 2.421)	**5.750E-3**
	45°C	P_1	0.138	(-0.095, 0.371)	2.039E-1
		P_2	5.055	(3.743, 6.368)	**3.900E-5**
		P_3	1.526	(0.595, 2.457)	**6.096E-3**
M25	15°C	P_1	17.32	(11.29, 23.35)	**2.540E-4**
		P_2	-47.68	(-68.07, -27.29)	**8.790E-4**
		P_3	27.21	(10.05, 44.37)	**7.167E-3**
	30°C	P_1	18.70	(11.02, 26.39)	**6.960E-4**
		P_2	-51.90	(-77.47, -26.34)	**1.964E-3**
		P_3	30.21	(9.096, 51.32)	**1.170E-2**
	45°C	P_1	19.28	(11.04, 27.51)	**8.730E-4**
		P_2	-54.18	(-80.88, -27.47)	**1.974E-3**
		P_3	32.05	(10.62, -53.47)	**9.505E-3**
M26	15°C	P_1	-2.822	(-3.488, -2.155)	**2.100E-5**
		P_2	0.263	(0.165, 0.361)	**3.960E-4**
		P_3	-0.006	(-0.009, 0.003)	**2.024E-3**
	30°C	P_1	-3.141	(-3.820, -2.461)	**1.200E-5**
		P_2	0.325	(0.205, 0.445)	**3.710E-4**
		P_3	-0.009	(0.014, 0.004)	**2.598E-3**
	45°C	P_1	-3.466	(-4.062, -2.870)	**3.000E-6**
		P_2	0.379	(0.257, 0.500)	**1.570E-4**
		P_3	-0.012	(-0.017, -0.006)	**1.638E-3**
M27	15°C	P_1	-6.552	(-9.387, -3.717)	**9.410E-4**
		P_2	2.713	(0.102, 5.324)	**4.366E-2**
		P_3	-0.058	(-0.655, -0.538)	8.229E-1
	30°C	P_1	-5.848	(-9.208, -2.487)	**4.487E-3**
		P_2	1.830	(-1.348, 5.009)	2.155E-1
		P_3	0.185	(-0.560, 0.930)	5.750E-1
	45°C	P_1	-5.028	(-8.161, -1.895)	**6.755E-3**
		P_2	0.820	(-2.246, 3.886)	5.471E-1
		P_3	0.449	(-0.293, 1.191)	1.958E-1
M28	15°C	P_1	7.263	(5.048, 9.477)	**1.110E-4**
		P_2	-8.725	(-12.05, -5.401)	**4.420E-4**
		P_3	1.757	(0.531, 2.982)	**1.162E-2**
	30°C	P_1	7.897	(5.020, 10.77)	**3.370E-4**
		P_2	-9.581	(-13.79, -5.377)	**1.020E-3**
		P_3	2.005	(0.502, 3.508)	**1.607E-2**
	45°C	P_1	8.158	(5.003, 11.31)	**4.840E-4**
		P_2	-10.11	(-14.56, -5.664)	**1.035E-3**

		P_3	2.184	(0.663, 3.706)	**1.152E-2**
M29	15°C	P_1	-3.794	(-5.703, -1.885)	**2.210E-3**
		P_2	0.484	(-6.463, 7.432)	8.737E-1
		P_3	7.886	(1.572, 14.20)	**2.130E-2**
	30°C	P_1	-3.615	(-5.845, -1.385)	**6.433E-3**
		P_2	-0.919	(-9.303, 7.465)	8.030E-1
		P_3	9.631	(1.765, 17.50)	**2.314E-2**
	45°C	P_1	-3.434	(-5.478, -1.390)	**5.371E-3**
		P_2	-2.276	(-10.35, 5.799)	5.264E-1
		P_3	11.07	(3.129, 19.01)	**1.319E-2**
M30	15°C	P_1	3.355	(-19.18, 25.89)	7.352E-1
		P_2	-19.18	(-52.88, 14.53)	2.204E-1
		P_3	11.85	(-0.740, 24.44)	6.136E-2
	30°C	P_1	9.945	(-17.88, 37.77)	4.259E-1
		P_2	-29.90	(-71.90, 12.10)	1.362E-1
		P_3	16.15	(0.312, 31.98)	**4.669E-2**
	45°C	P_1	16.27	(-11.03, 43.57)	2.015E-1
		P_2	-39.99	(-81.74, 1.765)	5.793E-2
		P_3	20.08	(4.139, 36.02)	**2.055E-2**
M31	15°C	P_1	-58.69	(-116.0, -1.368)	**4.602E-2**
		P_2	85.79	(-17.18, 188.8)	8.947E-2
		P_3	-30.38	(-76.59, 15.83)	1.639E-1
	30°C	P_1	-43.52	(-112.1, 25.09)	1.773E-1
		P_2	57.12	(-66.91, 181.1)	3.122E-1
		P_3	-16.92	(-72.93, 39.10)	4.983E-1
	45°C	P_1	-25.65	(-94.31, 43.01)	4.063E-1
		P_2	23.72	(-101.3, 148.8)	6.674E-1
		P_3	-1.432	(-58.32, 55.46)	9.542E-1
M32	15°C	P_1	0.861	(-52.73, 51.00)	9.698E-1
		P_2	18.53	(-96.77, 133.8)	7.153E-1
		P_3	-22.73	(-86.76, 41.30)	4.290E-1
	30°C	P_1	18.36	(-45.64, 82.37)	5.193E-1
		P_2	-18.90	(-160.3, 122.5)	7.612E-1
		P_3	-2.827	(-80.84, 75.18)	9.341E-1
	45°C	P_1	37.44	(-28.51, 103.4)	2.213E-1
		P_2	-60.32	(-204.9, 84.28)	3.568E-1
		P_3	19.49	(-59.70, 98.68)	5.789E-1
M33	15°C	P_1	-48.46	(-69.46, -27.47)	**9.470E-4**
		P_2	72.72	(37.26, 108.2)	**1.859E-3**
		P_3	-27.28	(-42.21, -12.32)	**3.486E-3**
	30°C	P_1	-47.75	(-72.37, -22.13)	**3.130E-3**
		P_2	70.90	(26.98, 114.8)	**6.568E-3**
		P_3	-26.28	(-45.07, -7.498)	**1.297E-2**
	45°C	P_1	-45.34	(-71.67, -19.00)	**4.743E-3**
		P_2	66.12	(20.33, 111.9)	**1.124E-2**
		P_3	-24.04	(-43.92, - 4.163)	**2.434E-2**
M34	15°C	P_1	-20.56	(-50.38, 9.270)	1.472E-1
		P_2	19.86	(-30.86, 70.59)	3.853E-1

		P_3	-2.700	(-24.26, 18.85)	7.756E-1
	30°C	P_1	-12.06	(-48.01, 23.89)	4.535E-1
		P_2	4.393	(-57.27, 66.06)	8.710E-1
		P_3	4.271	(-22.14, 30.68)	7.135E-1
	45°C	P_1	-2.419	(-38.22, 33.38)	8.775E-1
		P_2	-12.93	(-74.97, 49.12)	6.373E-1
		P_3	11.93	(-14.91, 38.77)	3.282E-1
M35	15°C	P_1	0.014	(0.071, 0.135)	**1.310E-4**
		P_2	0.175	(-0.030, 0.799)	6.427E-2
		P_3	0.023	(0.857, 0.965)	**1.600E-9**
	30°C	P_1	0.106	(0.070, 0.143)	**2.420E-4**
		P_2	0.114	(-0.413, 0.640)	6.259E-1
		P_3	0.965	(0.934, 0.996)	**2.390E-11**
	45°C	P_1	0.112	(0.083, 0.140)	**3.500E-5**
		P_2	-0.320	(-0.823, 0.183)	1.763E-1
		P_3	1.003	(0.987, 1.018)	**1.250E-13**

* Bold numbers indicate that estimated parameters are insignificant

Figures

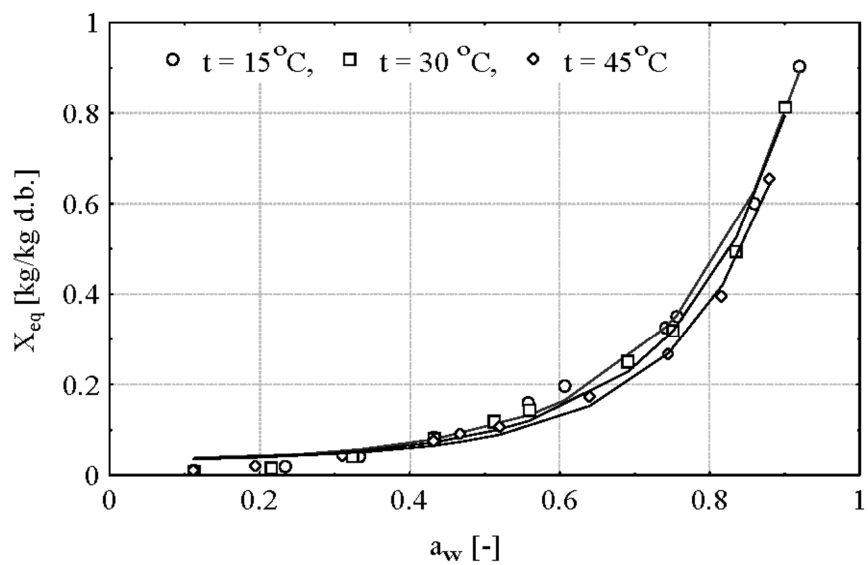


FIG. 1. EXPERIMENTAL AND CALCULATED SORPTION ISOTHERMS FOR PEAR - MODEL M32

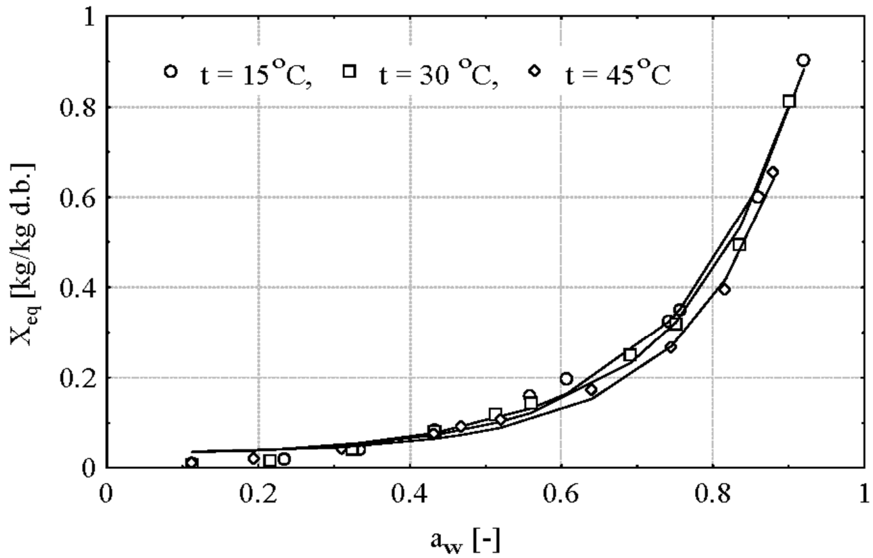


FIG. 2. EXPERIMENTAL AND CALCULATED SORPTION ISOTHERMS FOR PEAR - MODEL M34

Tables

TABLE 1.
EQUILIBRIUM MOISTURE CONTENT OF PEAR*

5°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

TABLE 2.
STATISTIC SUMMARY OF THE REGRESSION ANALYSIS*

Number of model (equation)	R_a^2	$RMSE_a$	MRD_a	ϕ_a	Rank
M24	0.986	0.029	0.375	96.158	5
M25	0.989	0.027	0.419	91.384	6
M26	0.974	0.043	1.155	24.169	12
M27	0.995	0.019	0.429	129.768	2
M28	0.990	0.036	0.424	66.819	10
M29	0.992	0.024	0.402	106.259	4
M30	0.994	0.024	0.399	108.961	3
M31	0.993	0.022	0.590	78.517	8
M32	0.993	0.025	0.563	71.969	9
M33	0.991	0.027	0.732	53.034	11
M34	0.993	0.022	0.541	87.418	7
M35	0.999	0.009	0.181	776.807	1

* "a" average value calculated for three temperatures

TABLE 3.
REJECTION CRITERIA FOR SORPTION MODELS*

Model-equation	χ_a^2	z_{ra}	Rejection criteria
M24	1.520	0.831	-
M25	1.396	0.913	-
M26	1.378	1.006	-
M27	1.635	0.975	-
M28	1.387	0.944	-
M29	1.409	0.944	-
M30	1.460	0.975	-
M31	1.646	0.975	-
M32	1.672	0.944	-
M33	1.628	0.944	-
M34	1.684	0.975	-
M35	1.010	0.831	-

* "a" average value calculated for three temperature, "-" not rejected

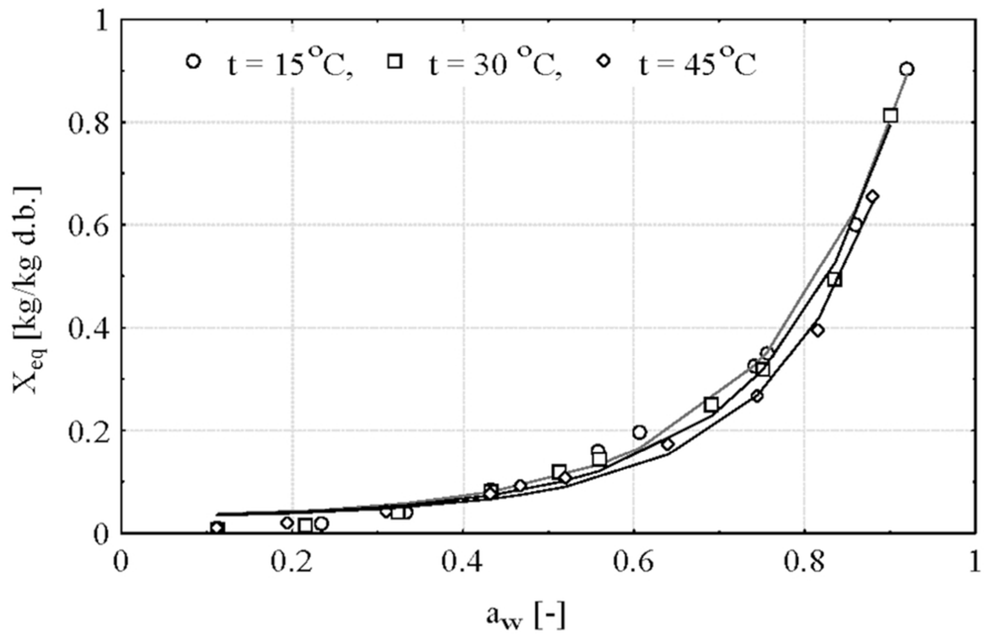
TABLE 4.
ESTIMATED VALUES OF PARAMETERS, 95% CONFIDENCE INTERVALS AND p VALUES*

Model (equation)	Temperature	Parameter	Value	95% CI	p
M24	15°C	P_1	0.259	(0.137, 0.381)	**1.545E-3**
		P_2	4.865	(4.044, 5.687)	**2.000E-6**
		P_3	1.427	(0.698, 2.156)	**2.407E-3**
	30°C	P_1	0.262	(0.083, 0.441)	**1.046E-2**
		P_2	5.072	(3.960, 6.183)	**1.300E-5**
		P_3	1.510	(0.600, 2.421)	**5.750E-3**
	45°C	P_1	0.138	(-0.095, 0.371)	2.039E-1
		P_2	5.055	(3.743, 6.368)	**3.900E-5**
		P_3	1.526	(0.595, 2.457)	**6.096E-3**
M25	15°C	P_1	17.32	(11.29, 23.35)	**2.540E-4**
		P_2	-47.68	(-68.07, -27.29)	**8.790E-4**
		P_3	27.21	(10.05, 44.37)	**7.167E-3**
	30°C	P_1	18.70	(11.02, 26.39)	**6.960E-4**
		P_2	-51.90	(-77.47, -26.34)	**1.964E-3**
		P_3	30.21	(9.096, 51.32)	**1.170E-2**
	45°C	P_1	19.28	(11.04, 27.51)	**8.730E-4**
		P_2	-54.18	(-80.88, -27.47)	**1.974E-3**
		P_3	32.05	(10.62, -53.47)	**9.505E-3**
M26	15°C	P_1	-2.822	(-3.488, -2.155)	**2.100E-5**
		P_2	0.263	(0.165, 0.361)	**3.960E-4**
		P_3	-0.006	(-0.009, 0.003)	**2.024E-3**
	30°C	P_1	-3.141	(-3.820, -2.461)	**1.200E-5**
		P_2	0.325	(0.205, 0.445)	**3.710E-4**
		P_3	-0.009	(0.014, 0.004)	**2.598E-3**
	45°C	P_1	-3.466	(-4.062, -2.870)	**3.000E-6**
		P_2	0.379	(0.257, 0.500)	**1.570E-4**
		P_3	-0.012	(-0.017, -0.006)	**1.638E-3**
M27	15°C	P_1	-6.552	(-9.387, -3.717)	**9.410E-4**
		P_2	2.713	(0.102, 5.324)	**4.366E-2**
		P_3	-0.058	(-0.655, -0.538)	8.229E-1
	30°C	P_1	-5.848	(-9.208, -2.487)	**4.487E-3**
		P_2	1.830	(-1.348, 5.009)	2.155E-1
		P_3	0.185	(-0.560, 0.930)	5.750E-1
	45°C	P_1	-5.028	(-8.161, -1.895)	**6.755E-3**
		P_2	0.820	(-2.246, 3.886)	5.471E-1
		P_3	0.449	(-0.293, 1.191)	1.958E-1
M28	15°C	P_1	7.263	(5.048, 9.477)	**1.110E-4**
		P_2	-8.725	(-12.05, -5.401)	**4.420E-4**
		P_3	1.757	(0.531, 2.982)	**1.162E-2**
	30°C	P_1	7.897	(5.020, 10.77)	**3.370E-4**
		P_2	-9.581	(-13.79, -5.377)	**1.020E-3**
		P_3	2.005	(0.502, 3.508)	**1.607E-2**
	45°C	P_1	8.158	(5.003, 11.31)	**4.840E-4**

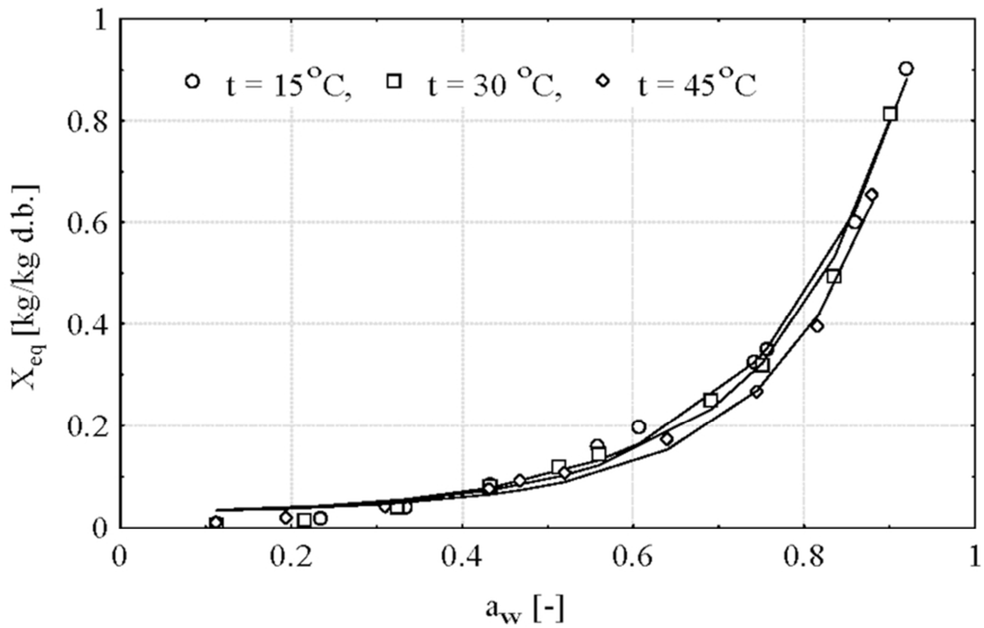
		P_2	-10.11	(-14.56, -5.664)	**1.035E-3**
		P_3	2.184	(0.663, 3.706)	**1.152E-2**
M29	15°C	P_1	-3.794	(-5.703, -1.885)	**2.210E-3**
		P_2	0.484	(-6.463, 7.432)	8.737E-1
		P_3	7.886	(1.572, 14.20)	**2.130E-2**
	30°C	P_1	-3.615	(-5.845, -1.385)	**6.433E-3**
		P_2	-0.919	(-9.303, 7.465)	8.030E-1
		P_3	9.631	(1.765, 17.50)	**2.314E-2**
	45°C	P_1	-3.434	(-5.478, -1.390)	**5.371E-3**
		P_2	-2.276	(-10.35, 5.799)	5.264E-1
		P_3	11.07	(3.129, 19.01)	**1.319E-2**
M30	15°C	P_1	3.355	(-19.18, 25.89)	7.352E-1
		P_2	-19.18	(-52.88, 14.53)	2.204E-1
		P_3	11.85	(-0.740, 24.44)	6.136E-2
	30°C	P_1	9.945	(-17.88, 37.77)	4.259E-1
		P_2	-29.90	(-71.90, 12.10)	1.362E-1
		P_3	16.15	(0.312, 31.98)	**4.669E-2**
	45°C	P_1	16.27	(-11.03, 43.57)	2.015E-1
		P_2	-39.99	(-81.74, 1.765)	5.793E-2
		P_3	20.08	(4.139, 36.02)	**2.055E-2**
M31	15°C	P_1	-58.69	(-116.0, -1.368)	**4.602E-2**
		P_2	85.79	(-17.18, 188.8)	8.947E-2
		P_3	-30.38	(-76.59, 15.83)	1.639E-1
	30°C	P_1	-43.52	(-112.1, 25.09)	1.773E-1
		P_2	57.12	(-66.91, 181.1)	3.122E-1
		P_3	-16.92	(-72.93, 39.10)	4.983E-1
	45°C	P_1	-25.65	(-94.31, 43.01)	4.063E-1
		P_2	23.72	(-101.3, 148.8)	6.674E-1
		P_3	-1.432	(-58.32, 55.46)	9.542E-1
M32	15°C	P_1	0.861	(-52.73, 51.00)	9.698E-1
		P_2	18.53	(-96.77, 133.8)	7.153E-1
		P_3	-22.73	(-86.76, 41.30)	4.290E-1
	30°C	P_1	18.36	(-45.64, 82.37)	5.193E-1
		P_2	-18.90	(-160.3, 122.5)	7.612E-1
		P_3	-2.827	(-80.84, 75.18)	9.341E-1
	45°C	P_1	37.44	(-28.51, 103.4)	2.213E-1
		P_2	-60.32	(-204.9, 84.28)	3.568E-1
		P_3	19.49	(-59.70, 98.68)	5.789E-1
M33	15°C	P_1	-48.46	(-69.46, -27.47)	**9.470E-4**
		P_2	72.72	(37.26, 108.2)	**1.859E-3**
		P_3	-27.28	(-42.21, -12.32)	**3.486E-3**
	30°C	P_1	-47.75	(-72.37, -22.13)	**3.130E-3**
		P_2	70.90	(26.98, 114.8)	**6.568E-3**
		P_3	-26.28	(-45.07, -7.498)	**1.297E-2**
	45°C	P_1	-45.34	(-71.67, -19.00)	**4.743E-3**
		P_2	66.12	(20.33, 111.9)	**1.124E-2**
		P_3	-24.04	(-43.92, - 4.163)	**2.434E-2**
M34	15°C	P_1	-20.56	(-50.38, 9.270)	1.472E-1

		P_2	19.86	(-30.86, 70.59)	3.853E-1
		P_3	-2.700	(-24.26, 18.85)	7.756E-1
	30°C	P_1	-12.06	(-48.01, 23.89)	4.535E-1
		P_2	4.393	(-57.27, 66.06)	8.710E-1
		P_3	4.271	(-22.14, 30.68)	7.135E-1
	45°C	P_1	-2.419	(-38.22, 33.38)	8.775E-1
		P_2	-12.93	(-74.97, 49.12)	6.373E-1
		P_3	11.93	(-14.91, 38.77)	3.282E-1
M35	15°C	P_1	0.014	(0.071, 0.135)	**1.310E-4**
		P_2	0.175	(-0.030, 0.799)	6.427E-2
		P_3	0.023	(0.857, 0.965)	**1.600E-**9
	30°C	P_1	0.106	(0.070, 0.143)	**2.420E-4**
		P_2	0.114	(-0.413, 0.640)	6.259E-1
		P_3	0.965	(0.934, 0.996)	**2.390E-11**
	45°C	P_1	0.112	(0.083, 0.140)	**3.500E-5**
		P_2	-0.320	(-0.823, 0.183)	1.763E-1
		P_3	1.003	(0.987, 1.018)	**1.250E-13**

* Bold numbers indicate that estimated parameters are insignificant



76x50mm (300 x 300 DPI)



75x48mm (300 x 300 DPI)