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STATISTICAL EVALUATION OF SOME FIVE PARAMETERS SORPTION ISOTHERMS MODELS

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Abstract: In the scientific literature various mathematical models are available for modelling on equilibrium moisture content data of food materials. The objective of the presented article was statistical evaluation of fifteen five parameters sorption isotherm models and to make comparison on their goodness of fit. The analysed sorption isotherm models were taken from the reference scientific literature and some of them were originally generated. The value on coefficient of determination and graphical evaluation of the residual randomness were the main assessment criterions for statistical evaluation of the sorption isotherm models. The statistical performances of those models were tested on the equilibrium moisture content data of quince. Based on the performed statistical analysis the model of Popovski & Mitrevski i.e. model with referent number M03 has the best statistical performances.
Keywords: five parameters models, statistical evaluation, moisture content data

1. INTRODUCTION

In the scientific literature numerous mathematical models for approximation of sorption isotherm data of agricultural and food materials are used. Depending on the number of parameters included in the model for approximation of moisture sorption data, the models may be one, two, three, four or more parametric [7]. In the last two decades an increasing number of articles were reported in this area. These articles includes the methods for determination of sorption or desorption isotherms [4,6], temperature dependence of sorption isotherms [8], determination of heat of sorption [2] and development of mathematical models for approximation of moisture sorption data [3,5]. In engineering calculations, the simplicity of a mathematical model, i.e. a model with a smaller number of parameters is of great importance. In the case where the sorption isotherm model is incorporated into the mathematical model for calculating the drying processes or used to predict the shelf–life of the packaged dried product, then the approximation of the experimental data on equilibrium moisture content has a greater significance in relation to the accuracy of the theory which is based on it [1]. The objectives of the presented article was statistical evaluation of fifteen five parameters sorption isotherm models for approximation of equilibrium moisture data of quince and to make comparison on their goodness of fit based on coefficient of determination and graphical evaluation of the residual randomness.

2. MATERIAL AND METHODS

The equilibrium moisture content of quince was determined at temperatures of 15, 30, 45 and 60°C using static gravimetric method [6,7]. 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 give defined constant equilibrium relative humidity in the glass jars from 0.110 to 0.920. Two dry samples of quince were placed on holder into each of the ten glass jars and exposed to atmospheres of various relative humidity. The glass sorption jars were placed and kept in the temperature controlled cabinet type SANYO MCO–15AC (SANYO Electric Co., Ltd. Refrigeration Products Division 1–1–1, Sakata Oizumi–Machi, Ora–Gun, Gunma 370–0596 Japan), maintained at temperatures 15, 30, 45 and 60°C with an accuracy of ±0.1°C. Three replications were made at each temperature and equilibrium relative humidity in the glass jars, using two samples per replication and the average values of equilibrium moisture content were calculated [6,7]. The change of samples mass was determined by electrical balance type KERN PLJ360–3M (Kern&Sohn GmbH, Ziegelei 1, 72336 Balingen, Germany), with precision of 0.001 g every 7 days. The equilibrium between samples and their environment was reached after 21 days when is achieved by the constant weight after two successive weighing of samples. The equilibrium moisture content of the quince samples was determined gravimetrically by drying in an oven at temperature of 105°C and atmospheric pressure for 24 h.

3. RESULTS AND DISCUSSIONS

The experimental values for the equilibrium moisture content, X_{eq} on the quince slices at each water activity, a_w for the four different temperatures were fitted with fifteen five–parameters sorption isotherm models M01–M15, Table 1.

The procedure for statistical evaluation of sorption isotherm model depends on the nature of the model. In scientific literature, for the goodness of fit of experimental sorption data and selection of the best isotherm model, following statistical criterions are used: 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 [3].

Table 1. Mathematical model for approximation sorption data of quince

Number of model	Name of model	Model	References
M01	D'Arcy–Watt	$X_{eq} = \frac{ABa_w}{1+Aa_w} + Ea_w + \frac{CDa_w}{1-Ca_w}$	[10]
M02	Popovski–Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{Ca_w}{1-Da_w})a_w + E$	[9]
M03	Popovski–Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{Ca_w}{1-Da_w})\frac{a_w}{1-a_w} + E$	[9]
M04	Popovski–Mitrevski	$X_{eq} = Aa_w^B + Ca_w^D + E$	[9]
M05	Popovski–Mitrevski	$X_{eq} = Ae^{Ba_w} + Ce^{Da_w} + E$	[9]
M06	Popovski–Mitrevski	$X_{eq} = A(\frac{a_w}{1-a_w})^B + C(\frac{a_w}{1-a_w})^D + E$	[9]
M07	Popovski–Mitrevski	$X_{eq} = Ae^{B\ln^2 a_w} + Ce^{D\ln^2 a_w} + E$	[9]
M08	Popovski–Mitrevski	$X_{eq} = \frac{A}{1-Ba_w} + \frac{C}{1-Da_w} + E$	[9]
M09	Popovski–Mitrevski	$X_{eq} = A(-\ln a_w)^B + C(-\ln a_w)^D + E$	[9]
M10	Popovski–Mitrevski	$X_{eq} = (\frac{A}{1-Ba_w} + \frac{C}{1-Da_w})(1+a_w)a_w + E$	[9]
M11	Popovski–Mitrevski	$X_{eq} = A[-\ln(1-a_w)]^B + C[-\ln(1-a_w)]^D + E$	[9]
M12	Popovski–Mitrevski	$X_{eq} = \frac{A}{B-\ln a_w} + \frac{C}{D-\ln a_w} + E$	[9]
M13	Popovski–Mitrevski	$X_{eq} = A(1-a_w)^B + C(1-a_w)^D + E$	[9]
M14	Popovski–Mitrevski	$X_{eq} = [\frac{A}{(1-Ba_w)^2} + \frac{C}{(1-Da_w)^2}]a_w + E$	[9]
M15	Popovski–Mitrevski	$X_{eq} = \frac{Aa_w}{1-Ba_w} + \frac{Ca_w^D}{1-a_w} + E$	[9]

Plotting of the residuals against independent variable is a measure of distribution errors. If the sorption model is correct, then the residual should be only random independent errors with a zero mean, constant variance and arranged in a normal distribution. If the residual plots indicate a clear pattern, the model should not be accepted [3]. In this study the value on coefficient of determination, R^2 and graphical evaluation of the residual randomness were the main statistical indicators for selection of the best five parameters sorption isotherm model.

Because the regression methods (indirect nonlinear or direct nonlinear), 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, a large number of numerical experiments were performed [4]. The method of indirect non–linear regression analysis 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 software Statistica (Statsoft Inc., Tulsa, OK, http://www.statsoft.com), were used to approximate the experimental equilibrium moisture content data of quince. On the basis of experimental data, and each mathematical model from Table 1, the values of coefficient of determination, R^2, was calculated. After that, the models were ranked on the basis of values of the coefficient of determination (Table 2).

Table 2. Ranking of the models

Model	R^2	Rank	Model	R^2	Rank
M01	0.9913	3	M09	0.9901	7
M02	0.9913	3	M10	0.9913	3
M03	0.9916	1	M11	0.9911	4
M04	0.9915	2	M12	0.9913	3
M05	0.9915	2	M13	0.9910	5
M06	0.9907	6	M14	0.9913	3
M07	0.9910	5	M15	0.9913	3
M08	0.9911	4	–	–	–

From Table 2 it is evident that the model of Popovski & Mitrevski with referent number M03, has the highest value of coefficient of determination, $R^2 = 0.9916$ (rank 1). So, this model correlates the experimental values of sorption data of quince better than other models. Similar, highest value of coefficient of determination was obtained when two–parameters sorption isotherm models were used for approximation of sorption data of quince [7]. From all models, the model with referent number M09, has the smallest value of coefficient of determination, $R^2 = 0.9901$ (rank 7). So, this model exhibited the worst statistical performance when is used to correlate the experimental values of equilibrium moisture content data of quince. The values of model parameters, A, B, C, D, E for the model M03, were estimated by fitting the models to experimental equilibrium moisture content data of quince using estimation methods which minimizes the sum squares errors. The estimated values of parameters are given in Table 3.

Table 3. Estimated values of parameters for model M03

Model	A	B	C	D	E
XEQ = ((A/(1−B*AW))+(C/(1−D*AW)))*(AW/(1−AW))+E	0.1372	−0.5734	−0.0005	1.0601	−0.0052

XEQ – equilibrium moisture content, AW– water activity, A, B, C, D, E – parameters

The experimental and predicted values for equilibrium moisture content for quince at four temperatures are shown on Figure 1a to Figure 1b.

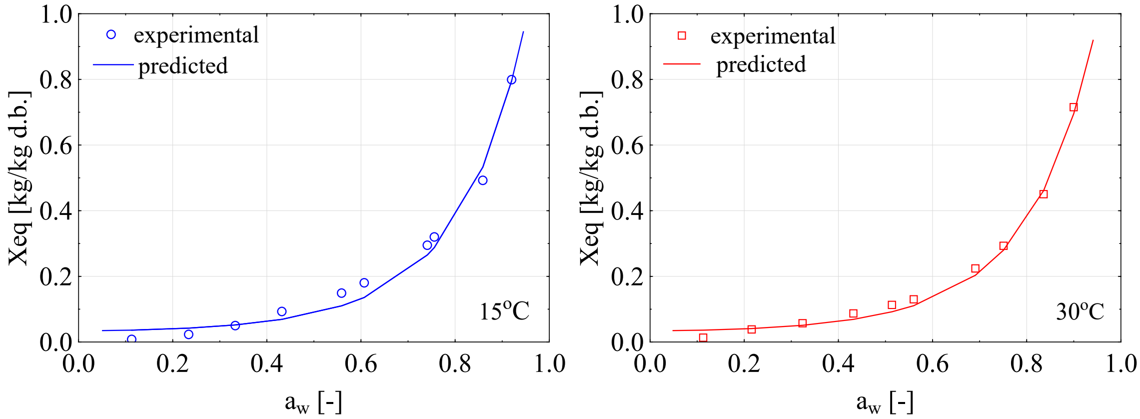

Figure 1a. Experimental and predicted sorption isotherms for quince at 15 and 30°C – Model M03

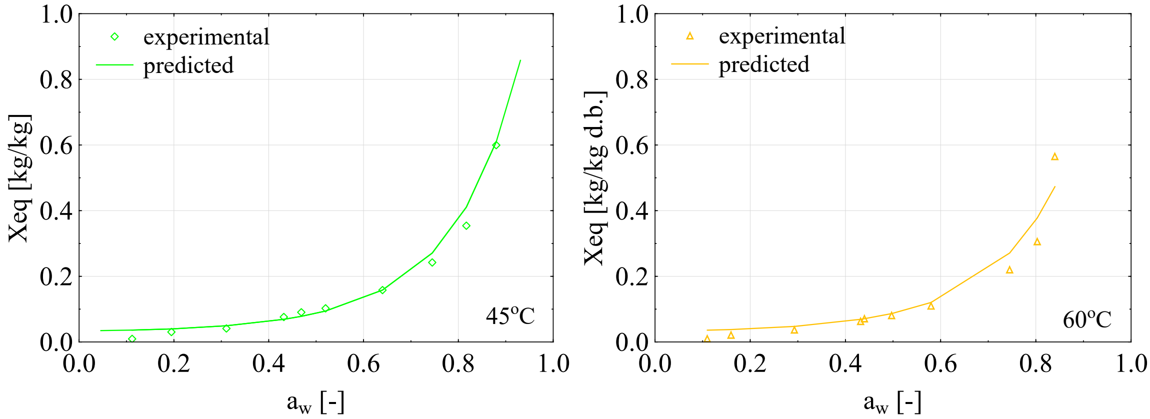

Figure 1b. Experimental and predicted sorption isotherms for quince at 45 and 60°C – Model M03

From figure 1a to figure 1.b is evident that has a good agreement between the experimental and predicted values of equilibrium moisture data of quince. Analyzing the residues on regression analysis for the model M03, the plots of the residues against the predicted values did not indicate abnormal distribution. In figure 2 the plots of the residuals of non–linear estimation against the predicted values are presented.

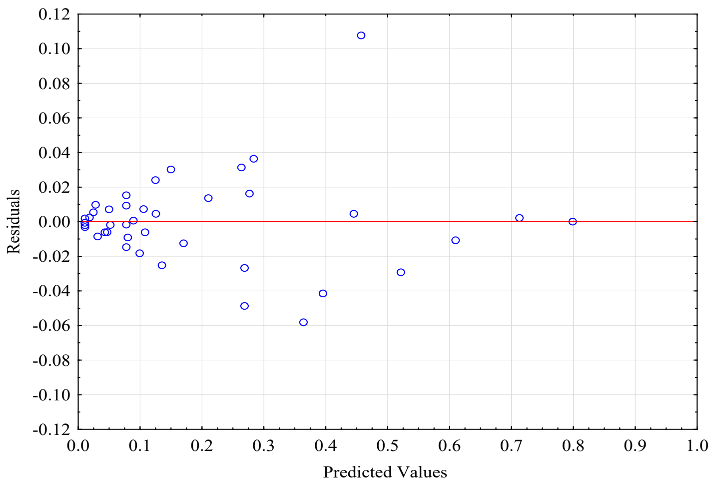

Figure 2. Residuals plot of sorption data versus predicted values for quince –Model M03

4. CONCLUSION

In this study statistical performance on fifteen five parameters sorption models were studied. The statistical performances of those models were tested on the equilibrium moisture content data of quince. The value on coefficient of determination and graphical evaluation of the residual randomness were the main assessment criterions for statistical evaluation of the sorption isotherm models. In accordance with these statistical criterions it was concluded that the models of Popovski & Mitrevski i.e. model with referent number M03 has a better statistical fit on experimental equilibrium moisture data of quince in whole range of water activity than other five parameters models.

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