STATISTICAL EVALUATION OF TWO-PARAMETER SORPTION ISOTHERM MODELS

STATISTIČKA OCENA DVOPARAMETARSKIH MODELA SORPCIONIH IZOTERMI

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ABSTRACT

Numerous mathematical models for approximating the water sorption data of food materials are available in the scientific literature. Depending on the number of parameters included, such models are referred to as one-parameter, two-parameter, three-parameter, or multi-parameter models. The objective of this study was to evaluate a total of sixty two-parameter sorption isotherm models for approximating the equilibrium moisture content data of quince and to compare the goodness of fit between the models examined. On the basis of the statistical analyses performed, it can be concluded that the Popovski&Mitrevski model has the best statistical performance of all the models examined. The coefficient of determination was the main criterion for assessing the model performance, totalling $R^2 = 0.9913$ for the best model performance.

Key words: sorption isotherms, two-parameter model, statistical evaluation

INTRODUCTION

Moisture sorption isotherms describe the relationship between the equilibrium moisture content and the water activity at constant temperatures and pressures. With regard to food materials, sorption isotherms are of great importance to modelling the drying process, designing and optimising the drying equipment, predicting the shelf-life stability, calculating changes in the moisture content during storage, and selecting the appropriate packaging material (Gal, 1987). Over the last two decades, an increasing number of studies have been reported in the scientific and engineering literature addressing the following issues: methods for determining sorption or desorption isotherms (Mitrevski et al., 2015; Mitrevski et al., 2018), temperature dependence between sorption isotherms (Popovski&Mitrevski, 2004), determination of sorption heat (Kaymak-Ertekin and Gedik, 2004), and mathematical models for approximating the moisture sorption of food materials (Mitrevski et al., 2012; Mitrevski et al., 2015a). Depending on the number of parameters included, models for approximating the moisture sorption data of materials are referred to as one-parameter, two-parameter, three-parameter, or multi-parameter models. In engineering calculations, the simplicity of a mathematical model, i.e. a model with a smaller number of parameters, is of great importance. When the sorption isotherm model is incorporated into the mathematical model for calculating the drying process or predicting the shelf-life of the packaged dried product, the approximation of the experimental data on the equilibrium moisture content is of particular significance (Boquet et al., 1978). The objective of the present study was to evaluate a total of sixty two-parameter sorption isotherm models for approximating the equilibrium moisture content data of quince and to compare the goodness of fit between the models examined on the basis of the coefficient of determination. The results obtained argue that the Popovski&Mitrevski model, i.e. the model M52 (Popovski&Mitrevski, 2007), has the best statistical performance.

MATERIAL AND METHOD

Quince samples for the determination of sorption isotherms were predried to the final moisture content in a convective dryer at an air drying temperature of 60 °C and an air drying velocity...
of 1 m/s for a period of 7 hours. The equilibrium moisture contents of the quince samples were determined at temperatures of 15, 30, 45 and 60 °C, using the static gravimetric method (Mitrevski et al., 2018). Ten saturated salt solutions, LC1, CH3COOK, MgCl2, K2CO3, NaNO3, NaBr, SrCl2, NaCl, KCl and BaCl2 were utilized to obtain the constant equilibrium relative humidity in the glass jars ranging from 0.110 to 0.920. Two dry samples were placed on holders in 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 SANYO MCO-15AC cabinet (SANYO Electric Co., Ltd. Refrigeration Products Division 1-1-1, Sakata Oizumi-machi, Ora-Gun, Gunma 370-0596, Japan), and maintained at temperatures of 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 the equilibrium moisture content were calculated (Mitrevski et al., 2018). Changes in the sample masses were recorded every 7 days using the electrical balance KERN PLJ360-3M with a precision of 0.001 g (Kern&Sohn GmbH, Ziegelei 1, 72336 Balingen, Germany). The equilibrium between the samples and their environments was reached after 21 days as evidenced by the constant weight of the samples after two successive measurements. The equilibrium moisture content of the samples was determined gravimetrically by drying in an oven at a temperature of 105°C and atmospheric pressure for 24 h.

RESULTS AND DISCUSSION

The equilibrium moisture content values (Xeq) of quince slices (Table 1), obtained at different water activity values (aw) and four different temperatures (Mitrevski et al., 2018), were fitted with sixty two-parameter sorption isotherm models M01-M60 (Table 2). In the scientific literature, the following statistical criteria are used for the goodness of fit of a sorption isotherm model, i.e. the selection of the best sorption isotherm model: the coefficient of determination (R²), the root mean squared error (RMSE), and the mean relative deviation (MRD). In this study, the coefficient of determination (R²) was used as a guide for selecting the best two-parameter sorption isotherm model. Furthermore, a large number of numerical experiments were conducted because the accuracy of the estimated parameter values is greatly affected by the regression methods (indirect non-linear or direct non-linear), the estimation method, the initial step size, the initial parameter values, the convergence criteria, and the function form. The method of indirect non-linear regression and the estimation methods of quasi-Newton, Simplex, Simplex 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 (Statsoft Inc., Tulsa, OK, http://www.statsoft.com) were used to approximate the data obtained on the experimental equilibrium moisture content of quince. On the basis of the experimental data and each mathematical model in Table 2, the values of the coefficient of determination (R²) were calculated. Subsequently, the models were ranked on the basis of the R² values obtained (Table 3).

Table 1. Equilibrium moisture contents of the quince samples

| Temperature | aw | 15°C | 30°C | 45°C | 60°C |
|-------------|----|------|------|------|------|
|             |    |      |      |      |      |
|             |     | Xeq  |      |      |      |
|             |     | aw   |      |      |      |
| 15°C        | 0.113 | 0.008±0.000 | 0.113 | 0.013±0.001 |
|             | 0.234 | 0.023±0.000 | 0.216 | 0.038±0.001 |
|             | 0.333 | 0.050±0.001 | 0.324 | 0.057±0.003 |
|             | 0.432 | 0.093±0.001 | 0.432 | 0.087±0.002 |
|             | 0.559 | 0.149±0.000 | 0.514 | 0.113±0.002 |
|             | 0.607 | 0.180±0.002 | 0.560 | 0.130±0.000 |
|             | 0.741 | 0.295±0.001 | 0.691 | 0.224±0.002 |
|             | 0.756 | 0.320±0.002 | 0.751 | 0.293±0.003 |
|             | 0.859 | 0.492±0.001 | 0.836 | 0.450±0.001 |
|             | 0.920 | 0.799±0.003 | 0.900 | 0.715±0.002 |
| 30°C        | 0.112 | 0.009±0.002 | 0.110 | 0.010±0.003 |
|             | 0.195 | 0.030±0.002 | 0.160 | 0.021±0.001 |
|             | 0.311 | 0.041±0.003 | 0.293 | 0.037±0.001 |
|             | 0.432 | 0.076±0.002 | 0.432 | 0.063±0.003 |
|             | 0.469 | 0.090±0.002 | 0.440 | 0.071±0.002 |
|             | 0.520 | 0.102±0.002 | 0.497 | 0.081±0.001 |
|             | 0.640 | 0.158±0.002 | 0.580 | 0.110±0.001 |
|             | 0.745 | 0.242±0.003 | 0.745 | 0.220±0.001 |
|             | 0.817 | 0.354±0.001 | 0.803 | 0.306±0.001 |
|             | 0.880 | 0.599±0.002 | 0.840 | 0.565±0.003 |

*mean and standard deviations were based on N = 3 replications.
\[
\begin{align*}
&X_n = A + \frac{Ba_n}{1-a_n} \quad \text{(Iglesias-Chirife, 1981)} \\
&X_n = \exp[\ln\left(\frac{A}{1-a_n}\right) + B] \quad \text{(Isse et al., 1993)} \\
&X_n = A + B \ln a_n \quad \text{(Kühn, 1964)} \\
&X_n = \frac{Aa_n}{1-Ba_n} \quad \text{(Langumir, 1918)} \\
&X_n = A + Ba_n \quad \text{(Castillo et al., 2003)} \\
&X_n = Aa_n \quad \text{(McGavack and Partric, 1920)} \\
&X_n = \exp[a_n(A + B)] \quad \text{(Lykov, 1958)} \\
&X_n = A \ln(1-a_n) + B \quad \text{(Pierce and Inst, 1929)} \\
&X_n = A \ln\left[\ln\left(\frac{1}{1-a_n}\right)\right] + B \quad \text{(Popovski and Mitrevski, 2003)} \\
&X_n = A \sin a_n \frac{\sin(1-a_n)}{1-a_n} + B \quad \text{(Popovski and Mitrevski, 2006)} \\
&X_n = A \sin a_n \frac{\sin(1-a_n)}{1-a_n} + B \quad \text{(Popovski and Mitrevski, 2007)} \\
&X_n = A \sin a_n \frac{\sin(1-a_n)}{1-a_n} + B \quad \text{(Popovski and Mitrevski, 2007)} \\
&X_n = \frac{Aa_n}{1-Ba_n} \quad \text{(Posnow, 1958)} \\
&X_n = A \ln(1-a_n) + B \quad \text{(Smith, 1947)} \\
&X_n = A \sin(1-a_n) + B \quad \text{(Thompson et al., 1968)} \\
&X_n = A + \frac{Ba_n}{1-a_n} \quad \text{(White and Eyring, 1947)}
\end{align*}
\]

| Model | \( R^2 \) | Rank |
|-------|-----------|------|
| M01   | 0.9897    | 8    |
| M02   | 0.9270    | 50   |
| M03   | 0.9867    | 18   |
| M04   | 0.9855    | 22   |
| M05   | 0.9278    | 51   |
| M06   | 0.9397    | 52   |
| M07   | 0.7251    | 60   |
| M08   | 0.8121    | 58   |
| M09   | 0.9740    | 34   |
| M10   | 0.9749    | 35   |
| M11   | 0.9853    | 25   |
| M12   | 0.9088    | 54   |
| M13   | 0.9375    | 48   |
| M14   | 0.9897    | 9    |
| M15   | 0.9280    | 49   |
| M16   | 0.9907    | 5    |
| M17   | 0.9853    | 26   |
| M18   | 0.9844    | 27   |
| M19   | 0.9762    | 49   |
| M20   | 0.9876    | 18   |
| M21   | 0.9769    | 33   |
| M22   | 0.9879    | 5    |
| M23   | 0.9820    | 49   |
| M24   | 0.9878    | 9    |
| M25   | 0.9907    | 5    |
| M26   | 0.9844    | 29   |
| M27   | 0.9894    | 13   |
| M28   | 0.9642    | 44   |
| M29   | 0.9702    | 39   |
| M30   | 0.9897    | 10   |

Table 3. Statistical summary of the regression analysis
As can be seen in Table 3, the highest coefficient of determination value ($R^2 = 0.9913$; rank 1) was recorded in the instance of the Popovski&Mitrevski model (M52) (Popovski&Mitrevski, 2007). Consequently, this model correlates the experimental values of quince sorption better than other models. Of all the models examined, the model of Chung and Pfost (M07) (Chung and Pfost, 1967) had the lowest value of the coefficient of determination ($R^2 = 0.7251$; rank 60), i.e. the worst statistical performance.

The parameter values $A$ and $B$ for the Popovski&Mitrevski model (M52) were estimated by fitting the model to experimental data obtained on the equilibrium moisture content of quince using the quasi-Newton estimation method, which minimizes the sum squares errors. The estimated values of the parameters $A$ and $B$ are shown in Table 4.

Table 4. Estimated values of the parameters $A$ and $B$

| Model  | $A$  | $B$  |
|--------|------|------|
| $X_{EQ} = 1/(A/ARCTAN(AW) + B)$ | 11.12 | -13.72 |

$X_{EQ}$ - equilibrium moisture content, $AW$ - water activity

The experimental and predicted values of the quince equilibrium moisture content at four temperatures are shown in Figure 1.

As can be seen in Figures 1a-1d, the model M52 exhibits a good agreement between the experimental and predicted values of the equilibrium moisture content of quince.

CONCLUSION

The experimental data obtained on the equilibrium moisture content of quince were fitted with sixty two-parameter sorption isotherm models. On the basis of the statistical criteria proposed in the present study, it can be concluded that the Popovski&Mitrevski model (M52) exhibits the best agreement between the experimental and predicted values of the equilibrium moisture content of quince throughout the entire range of water activity observed.

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