ABSTRACT
Moisture equilibrium data (adsorption and desorption) of walnut flour were determined using the static gravimetric method of saturated salt solutions at three temperatures 10, 25, and 40 °C. The range of water activities for each temperature was between 0.11 to 0.85. Equilibrium moisture content decreased with the increase in storage temperature at any given water activity. The experimental data were fitted to four mathematical models (modified Oswin, modified Halsey, modified Chung-Pfost and modified Henderson). The monolayer moisture content was estimated from sorption data using the Brunauer-Emmett-Teller (BET) equation. The isosteric heats of sorption were evaluated using Clausius-Clapeyron equation.

Introduction
Sorption properties of foods (equilibrium moisture content, monolayer moisture, heat of sorption) are essential for the design and optimization of many processes such as drying, packaging and storage (2). The water activity of the flour as a hygroscopic material exerts a strong influence on its quality and technological properties (1,12,14,16).

With recent consumer interest in functional food, walnut flour is increasingly being used as an ingredient and a functional modifier in many foods (7,10,15). A number of models have been suggested in the literature for the dependence between the equilibrium moisture content (EMC) and the water activity (aw) (17). The modified Chung-Pfost, modified Henderson, modified Halsey and modified Oswin equations which incorporate the temperature effect have been adopted as standard equations by the ASAE for the description of sorption isotherms (4).

The objectives of this work are: 1. to obtain experimental equilibrium sorption isotherms of walnut flour at 10, 25, and 40 °C; 2. to find out the suitable model describing the isotherms; 3. to calculate the monolayer moisture content; 4. to calculate the heat of sorption of the flour.

Materials and Methods
Material. Commercial semi-defatted walnut flour produced in Bulgaria was used in this study. AOAC standard procedures (3) were used for the determination of the proximate chemical composition (in wet basis): moisture – 8.98%, crude fat – 9.99 %, protein – 45.20 %, carbohydrate – 29.86 %, ash – 5.97 %.

Procedure. The EMC of the walnut flour was determined at 10, 25, and 40 °C. The static gravimetric method was applied (5,18). For the adsorption process, flour was dehydrated in a desiccator with P2O5 at a room temperature for 20 days prior to the beginning of the experiment. The desorption isotherms were determined on samples hydrated in a glass jar over distilled water
at a room temperature to approximately 30 % dry basis (d.b.) moisture content. Samples of 1±0.02 g were weighed in weighing bottles. The weighing bottles were then put in hygrostats with seven saturated salt solutions (LiCl, MgCl2, CH3COOK, K2CO3, NaBr, NaCl, KCl), used to obtain constant water activities environments (5). All used salts were of reagent grade. At high water activities (aw > 0.70) crystalline thymol was placed in the hygrostats to prevent the microbial spoilage of the flour. The hygrostats were kept in thermostats at 10, 25, and 40 ±0.2 ºC. Samples were weighed (balance, sensitivity ±0.0001 g) every three days. Equilibrium was acknowledged when three consecutive weight measurements showed a difference less than 0.001 g. The moisture content of each sample was determined by the oven method (105 ºC for 24 h) by means of triplicate measurements.

Analysis of data. The description of the sorption isotherms was verified according to the following four models:

Modified Chung-Pfost

\[
a_w = \exp\left(-\frac{A}{t + B} \exp(-CM)\right)
\]  

(1)

Modified Halsey

\[
a_w = \exp\left(-\frac{\exp(A + Bt)}{M^c}\right)
\]  

(2)

Modified Oswin

\[M = (A + Bt)\left(\frac{a_w}{1-a_w}\right)^C\]

(3)

Modified Henderson

\[1 - a_w = \exp\left(-A(t + B)M^C\right)\]

(4)

where \(M\) is the moisture content, % d.b.; \(a_W\) is the water activity, decimal; \(A, B\) and \(C\) are coefficients; \(t\) is the temperature, ºC.

A nonlinear, lest squares regression program was used to fit the four models to the experimental data (all replications). The suitability of the equations was evaluated and compared using the mean relative error (\(P, \%\)) and standard error of moisture (\(SEM\)) (8):

\[P = \frac{100}{N} \sum \frac{|M_i - \hat{M}_i|}{M_i}\]

(5)

\[SEM = \sqrt{\frac{\sum (M_i - \hat{M}_i)^2}{df}}\]

(6)

where \(M_i\) and \(\hat{M}_i\) are experimentally observed and predicted by the model value of the EMC, respectively, \(N\) is the number of data points, and \(df\) is the degree of freedom (number of data points minus number of constants in the model).

The monolayer moisture contents (MMC) for each temperature were calculated using the Brunauer-Emmett-Teller (BET) equation (6) and the experimental data for water activities up to 0.45 (5):

\[M = \frac{M_cCa_W}{(1-a_W)(1-a_W + Ca_W)}\]

(7)

The values of heat of sorption were calculated using the Clausius-Clapeyron equation from the slope of the plot between the values of \(\ln a_w\) and \(1/T\) at constant moisture (11):

\[\ln a_w = -\left(\frac{Q_a}{R}\right)\frac{1}{T} + \text{constant}\]

(8)

where \(Q_a\) is isosteric heat of sorption, kJ/mol; \(T\) is the absolute temperature, K; \(R\) is the universal gas constant, kJmol⁻¹K⁻¹.

Using eq. 2, the values of \(a_w\) were determined at the three temperatures and constant moisture contents 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, and 26 % d.b.

Results and Discussion

The obtained mean values of EMC based on the triplicate measurements for the respective water activity and temperature are presented in Fig. 1 for adsorption and in Fig. 2 for desorption. The sorption isotherms have an S-shape profile. The EMC values decreased with an increase in the temperature at constant \(a_W\). Similar trends
for many foods have been reported in the literature (2,9). Fig. 3 gives the experimental data obtained after adsorption and desorption at 25 °C. The hysteresis effect was not distinctly expressed.

The coefficients for the three-parameter models, $P$ and $SEM$ values are presented in Table 1 for adsorption and Table 2 for desorption. For adsorption and desorption the $P$ and $SEM$ values obtained by the modified Halsey equations were lower. Therefore we recommend the modified Halsey model for description of the walnut flour equilibrium isotherms.

The calculated values of MMC at the three temperatures are presented in Table 3. The MMC decreased with the increase in temperature. A similar effect has been reported for many foods (13).

The net isosteric heats of sorption as a
Fig 3. Comparison of isotherms at 25 ºC: desorption (●); adsorption (○).

Table 1
Model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for adsorption

<table>
<thead>
<tr>
<th>Model</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>P</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Chung-Pfost</td>
<td>283.5092</td>
<td>0.185916</td>
<td>42.07744</td>
<td>15.94</td>
<td>9.98</td>
</tr>
<tr>
<td>Modified Oswin</td>
<td>11.4714</td>
<td>-0.072297</td>
<td>0.533903</td>
<td>16.54</td>
<td>7.11</td>
</tr>
<tr>
<td>Modified Halsey</td>
<td>4.120304</td>
<td>-0.01924</td>
<td>1.810959</td>
<td>7.84</td>
<td>5.76</td>
</tr>
<tr>
<td>Modified Henderson</td>
<td>0.000193</td>
<td>-0.890059</td>
<td>2.31178</td>
<td>18.01</td>
<td>12.96</td>
</tr>
</tbody>
</table>

Table 2
Model coefficients (A, B, C), mean relative error (P, %) and standard error of moisture (SEM) for desorption

<table>
<thead>
<tr>
<th>Model</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>P</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Chung-Pfost</td>
<td>267.7466</td>
<td>0.167416</td>
<td>40.21068</td>
<td>16.02</td>
<td>9.90</td>
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<td>Modified Oswin</td>
<td>12.67664</td>
<td>-0.087521</td>
<td>0.50738</td>
<td>15.28</td>
<td>7.21</td>
</tr>
<tr>
<td>Modified Halsey</td>
<td>4.172518</td>
<td>-0.019654</td>
<td>1.76198</td>
<td>9.53</td>
<td>6.07</td>
</tr>
<tr>
<td>Modified Henderson</td>
<td>0.000202</td>
<td>-0.290928</td>
<td>2.173388</td>
<td>18.80</td>
<td>13.17</td>
</tr>
</tbody>
</table>

Table 3
BET monolayer moisture content (%d.b.) of walnut flour at several temperatures

<table>
<thead>
<tr>
<th>t (ºC)</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.54</td>
<td>6.40</td>
</tr>
<tr>
<td>25</td>
<td>4.48</td>
<td>5.47</td>
</tr>
<tr>
<td>40</td>
<td>3.73</td>
<td>3.73</td>
</tr>
</tbody>
</table>

The heats of sorption decrease continually with increasing moisture content. A power function was used to describe the relationship between isosteric heat of sorption and EMC (11):
Fig 4. Net isosteric heat of sorption of walnut flour: desorption (-●-); adsorption (-○-).

Adsorption:

\[ Q_{st} = 548.26M^{-1.8109}; \quad r^2 = 1 \]  

(9)

Desorption:

\[ Q_{st} = 584.41M^{-1.762}; \quad r^2 = 1 \]  

(10)

The high coefficient of determination values shows that the power function can be used to calculate the heat of sorption of walnut flour for varying moisture content.

Conclusions

The sorption capacity and monolayer moisture content of walnut flour decreased with an increase in temperature at constant water activity.

The modified Halsey model is suitable for describing the relationship between the equilibrium moisture content, the water activity, and the temperature for the walnut flour.

The power function described the relationship between the heat of sorption and the moisture content of the flour.

Acknowledgements

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REFERENCES