Moisture sorption and the applicability of the Brunauer-Emmett-Teller (BET) equation for blanched and unblanched mushrooms

F. Sahbaz, T. K. Palazoglu* and D. Uzman

Moisture sorption isotherms of blanched and unblanched mushrooms over 0.11–0.75 \(a_w\) were determined at 27 °C and 37 °C by using the static gravimetric method. Adsorption and desorption behaviors of blanched and unblanched mushrooms were compared. The unblanched material adsorbed more water than that of the blanched. In desorption isotherms, the equilibrium moisture contents of the unblanched material were found to be higher than those of the blanched throughout the entire \(a_w\) range. The BET equation was tested to fit the experimental moisture sorption data over the 0.11–0.43 \(a_w\), 0.11–0.55 \(a_w\), 0.11–0.64 \(a_w\), and 0.11–0.75 \(a_w\). Nonlinear regression analysis was used for the determination of the parameters in the equation. The quality of the fit of the BET model over each \(a_w\) range was judged from the value of the relative percent root mean square (% RMS). The moisture sorption behavior over 0.11–0.43 \(a_w\) of mushrooms has indicated that the BET equation is applicable generally up to 0.43 \(a_w\). Monolayer moisture contents and \(C\) constants in the BET equation obtained for each \(a_w\) interval were reported. The water activities corresponding to the monolayer values have been determined and discussed related to mushroom storage.

The net isosteric heats of adsorption and desorption were estimated from equilibrium sorption data, using the integrated form of the Claisius-Clapeyron equation. The heats of adsorption/desorption decreased with increase in moisture content and approached to a constant value. It was concluded that moisture adsorption/desorption occurred by physical mechanisms at high moisture contents, but at low moisture contents, besides physical adsorption, chemisorption was also observed.

1 Introduction

Food moisture sorption isotherms describe the mathematical relationship between the equilibrium moisture content and water activity. A knowledge of this equilibrium relationship is of great importance for the design of various industrial processes such as drying, packaging and storage.

Mushroom, being a perishable food product, must be either consumed or processed within 4–5 days after harvesting. Air drying is a commonly used method for preservation of mushrooms due to its low cost. Optimization of drying processes and prediction of shelf life stability requires the prediction of sorption isotherms and the evaluation of monolayer moisture content. The sorption behavior of native and blanched mushrooms were studied by many researchers in the past. Blanching is necessary to avoid the bitter taste characteristic of fresh mushrooms. The previous studies have shown that blanching changed the sorption behavior of the material, and also the temperature dependence of the water sorption was remarkable [1–4].

In literature, there are many mathematical equations (empirical or theoretical) used to describe the relationship between water activity and the equilibrium moisture content of foods. The most relevant ones have been reported by Iglesias and Chirife [5]. Many of these equations are of limited value as they are applicable over a narrow range of water activity. The equations of Brunauer-Emmett-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) appear to be the most popular food isotherm equations [6]. Since these equations provide the monolayer moisture content, both can be considered to be the most useful ones for determining the optimum moisture conditions for good storage stability, especially for dehydrated foods. The estimate of such a critical moisture content is of practical interest as it coincides with the maximum physical and chemical stability of the dry foods. The BET monolayer value for a certain food can be determined easily if data for the low-moisture content end of the sorption isotherm are available. Although the BET equation is known to hold for \(a_w\) values up to 0.5, it is still the common and widely used equation for the determination of the monolayer value, and many of the monolayer values reported have been computed by this equation.

The objectives of this study were: (1) to determine the moisture sorption isotherms of blanched and unblanched cultivated mushrooms at two ambient temperatures (27 °C and 37 °C), (2) to demonstrate and discuss the applicability of the BET equation to the experimental data over different \(a_w\) intervals, (3) to compute the monolayer water contents and the corresponding \(a_w\) values and discuss from the point of view of storage stability, and (4) to calculate the net isosteric heat of sorption by using the integrated form of the Claisius-Clapeyron equation.

2 Materials and Methods

2.1 Materials

The fresh cultivated mushrooms (Agaricus bisporus, Türktür) used in this study were supplied from Ankara Market. At the start of each experiment, fresh mushrooms were washed and cut into thin slices. When working with blanched samples, slices were scalded at 97 °C for 5 min. This blanching time was determined by the peroxidase test [7].

2.2 Sorption experiments

For desorption studies, samples (app. 1 g) prepared as explained above were placed in sample dishes brought to constant weight. The \(a_w\) values of both unblanched and blanched samples at the start of the experiment were determined to be equal to 1.0. The average moisture contents were 92.2 % for unblanched and 93.3 % for blanched ones.
For adsorption measurement, the samples were dried at ambient temperature in a desiccator with P\textsubscript{2}O\textsubscript{5} to an a\textsubscript{w} value of 0.15 for blanched and 0.05 for unblanched mushrooms. It took 10 days to reach these a\textsubscript{w} values. Then the dried samples were ground to powder in a stamp mortar and again dried in a desiccator with P\textsubscript{2}O\textsubscript{5}. The terminal a\textsubscript{w} values were 0.056 and 0.025 for unblanched samples. This required an extra 10 days period. The moisture contents of the samples were determined to be 2.4% for blanched and 2.2% for unblanched ones. Then samples of about 100 mg were weighed. The analytical balance used was a Shimadzu Libror AEG-220 with the accuracy of ±0.0001 g.

The gravimetric method proposed by Gal [8] was adopted for this study. Nine reagent salts (Reagent grade, Merck or Riedel de Haen) plus distilled water (a\textsubscript{w} = 1.0) were used. The salts were dissolved in boiling water and cooled to each temperature to form crystals. The salts were LiCl, CH\textsubscript{3}COOK, MgCl\textsubscript{2}, K\textsubscript{2}CO\textsubscript{3}, Mg(NO\textsubscript{3})\textsubscript{2}, NaNO\textsubscript{2}, NaCl, KCl and KNO\textsubscript{3} to obtain a\textsubscript{w} in the range 0.11 to 0.94. Duplicate mushroom samples were placed in 1 liter glass jars containing saturated salt solutions. Then ten jars were held either at 27 or 37 \degree C in an oven (Memmert-ULM 400; temperature sensitivity = ±0.01 \degree C). The equilibration time was judged to have been attained when the difference between two consecutive sample weighing was less than 1 mg/g solids (18–20 days), as suggested by Labaza et al. [9]. Then the dry weights of the samples were determined by the oven method (105 \degree C, 24 h). The equilibrium moisture content of samples (X) was expressed as g of moisture per 100 g of dry solids.

An AquaLab Model CX2 (reading accuracy = ±0.003) was used for water activity measurements of the salt solutions. At the start of each measurement, the equipment was calibrated according to the instructions given by the manufacturer [10]. Since there is no temperature control of this AquaLab model, the water activity measurements were recorded between 22 and 28 \degree C, depending on the ambient temperature.

Although the water activity range of the solutions used was between 0.11 and 1.0, the samples in the jars with a\textsubscript{w} values above 0.75 were not taken into consideration due to the mold growth in those jars within the first weeks.

3 Results and discussion

Sorption isotherms of both blanched and unblanched mushrooms, determined at 27 and 37 \degree C, are presented in Figures 1 and 2. All curves display the typical sigmoid shape to type II according to BET classification. Hysteresis can be seen in all isotherms.

![Figure 1](image1.png)  
**Figure 1.** Sorption isotherms of blanched and unblanched mushroom at 27 \degree C.

![Figure 2](image2.png)  
**Figure 2.** Sorption isotherms of blanched and unblanched mushroom at 37 \degree C.

The adsorption of blanched material at 27 \degree C was lower than that of the native material at all a\textsubscript{w} values. At 37 \degree C, the adsorption of blanched and unblanched materials was nearly the same until about 0.3 a\textsubscript{w} and at a\textsubscript{w} values higher than 0.3, unblanched material adsorbed more water than blanched. In desorption isotherms at both temperatures, the equilibrium moisture contents of the unblanched material were higher than those of the blanched throughout the whole a\textsubscript{w} range.

Blanching changes the adsorption and desorption properties of the material. During blanching, loss of water and some solids occur. This is due to the changes in the physical properties of the tissue, such as the destruction of the cell membranes and dissolution of some water soluble compounds like the soluble sugars. The dry matter of the mushroom contains about 60% carbohydrates and glucose is the main soluble sugar [11]. As explained in “Materials and methods” section, the native mushroom contains 7.8% dry matter on the average and the blanched one 6.7%. This means that a 14% decrease in the dry matter of mushrooms is caused by the blanching. High sugar foods sorb relatively small amounts of water at low water activities and large amounts of water at high water activities [12, 13]. Thus the dissolution of sugars during blanching may partly account for the higher adsorptive capacity of the native mushrooms observed at higher a\textsubscript{w} values. The chitin is the main insoluble carbohydrate polymer in mushrooms. In addition, blanching changes the structure of chitin due to the physical transition of the polymer. This in turn affects the moisture sorption characteristics [14, 15]. Moreover, the decrease in the adsorption of blanched material can be explained by the decreased sorptive surface caused by blanching.

The sorption model that has received the greatest application to food systems is that of Brunauer-Emmet-Teller [6], the usual mathematical form of which is given as the following:

\[
X = \frac{C \, a_\infty}{(1-a_\infty)(1-a_\infty + C \, a_\infty)}
\]

where: X is the equilibrium moisture content [g/100 g dry solids], X\textsubscript{m} is the monolayer value [g/100 g dry solids], a\textsubscript{w} is the water activity and C is the BET constant related to heats of adsorption.

The BET equation has two constants, both of which are temperature dependent [16, 17]. Experimental data were obtained...
at 27 and 37°C. These ambient temperatures were selected in order to achieve accuracy in obtaining the sorption isotherms because temperatures far from the ambient lead to difficulties in the evaluation of the results.

Food products are very complex, allowing many types of errors. Among them is the ability of these products to change with time, mainly during rather long period necessary to reach the sorption equilibrium. Thus the final value is no longer representative of the initial product, but is related to the transformed product due to the biological and biochemical changes. At higher temperatures, these reactions take place faster and lead to a modification of the composition of the product. Moreover, the constant alteration of the dry portion makes the constant weight very difficult to ascertain. If \( X_m \) and \( C \) are determined experimentally at two ambient temperatures, then equilibrium moisture content at any temperature and \( a_w \) value can be computed by using Equation 1.

The applicability of the BET equation over four different \( a_w \) regions of isotherms was studied, analysing the sorption data by nonlinear regression program (SPSS for Windows 5.0.1 Release). The \( X_m \) and \( C \) values thus obtained for each \( a_w \) range were presented in Table 1. The quality of the fit of the BET model was judged from the value of the relative percent root mean square (% RMS). RMS value shows the deviation between the observed (experimental) and predicted values and is defined by the following equation [18]:

\[
\% \text{ RMS} = 100 \times \sqrt{\frac{\sum (X_{oi}-X_{pi})^2}{n}}
\]

where: \( X_{oi} \) is the observed equilibrium moisture content, \( X_{pi} \) is the predicted equilibrium moisture content, \( n \) is the number of experimental points.

% RMS values obtained over each \( a_w \) range were given in Figures 3 and 4 for native and blanched mushrooms, respectively. The isotherm equation with a % RMS value of less than or equal to 10 was considered to be a good fit [18]. Data showed fairly significant variations in % RMS values and the BET equation generally fitted the sorption data in the \( a_w \) range of 0.11 – 0.43 (Figs. 3 and 4). Moreover the BET equation showed a good fit to the desorption data of blanched mushrooms at 27 and 37°C for all the water activity ranges (% RMS <10). Only exceptions to this was the data at 27°C for 0.11 – 0.75 \( a_w \) (Fig. 4).

**Table 1.** Summarized BET parameters of native and blanched mushrooms.

<table>
<thead>
<tr>
<th>( a_w = 0.11–0.75 )</th>
<th>( a_w = 0.11–0.64 )</th>
<th>( a_w = 0.11–0.55 )</th>
<th>( a_w = 0.11–0.43 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_m ) (C)</td>
<td>( X_m ) (C)</td>
<td>( X_m ) (C)</td>
<td>( X_m ) (C)</td>
</tr>
<tr>
<td>NA (27°C)</td>
<td>8.8</td>
<td>7.5</td>
<td>6.8</td>
</tr>
<tr>
<td>ND (27°C)</td>
<td>11.2</td>
<td>7.0</td>
<td>4.3</td>
</tr>
<tr>
<td>BA (27°C)</td>
<td>9.9</td>
<td>11.7</td>
<td>13.9</td>
</tr>
<tr>
<td>ND (37°C)</td>
<td>9.2</td>
<td>10.4</td>
<td>7.1</td>
</tr>
<tr>
<td>BA (37°C)</td>
<td>4.6</td>
<td>5.1</td>
<td>4.5</td>
</tr>
<tr>
<td>ND (27°C)</td>
<td>3.4</td>
<td>3.1</td>
<td>3.0</td>
</tr>
<tr>
<td>BD (27°C)</td>
<td>4.5</td>
<td>5.3</td>
<td>5.8</td>
</tr>
<tr>
<td>BD (37°C)</td>
<td>3.6</td>
<td>3.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>

NA: Native mushroom adsorption isotherm; ND: Native mushroom desorption isotherm; BA: Blanched mushroom adsorption isotherm; BD: Blanched mushroom desorption isotherm.
employs the monolayer concept in which the molecule is tightly bound on a homogenous surface. Water in the monolayer region is held by strong hydrogenic bonds on polar sites in the food. In the second region, called the multimolecular region, water is more loosely held by hydrogen bonds. The least firmly bound water occurs when the a_w is above 0.5. In this region, condensed water is entrapped within the void spaces of the food. Thus adsorbed water can be classified as the monolayer, multilayer and condensed capillary water.

The BET equation is based on adsorption on free surface without capillary condensation and therefore is applicable to adsorption for the mono and multilayer regions of the isotherm. In the derivation of the BET isotherm, it was assumed that the heat of sorption for the first layer to be constant and for all layers above the monolayer be equal to the heat of vaporization. In other words, the BET equation assumes energetically homogenous surfaces. Mushroom on the other hand, is heterogeneous but the adsorbing surface in mushroom could be constructed as practically homogenous up to a certain a_w. Low % RMS values (Figs. 3 and 4) indicated that the BET equation could be applicable over 0.11–0.43 a_w. This is in accordance with the reports of Labuza [20] who stated that the applicability of the BET equation is generally restricted to a_w values below 0.5 because of the assumptions used in the derivation of the equation [20]. In the sorption isotherms of blanched and unblanched mushrooms (Figs. 1 and 2), on the other hand, it was noticed that in all cases, the plot was made up of two different portions with an inflection point at about 0.55 a_w. Above this water activity value, the slope of the curves increased, indicating that more water was entrapped in the void spaces of mushrooms due to the capillary condensation. Although the low % RMS values obtained showed a good fit to the BET equation over the 0.11–0.43 a_w, the observation from graphical data indicated that the a_w value marking the end of monolayer region was 0.55. Therefore it may be concluded that at a_w values lower than 0.55, most of the water was absorbed as the monolayer or mostly in multilayers.

BET equation is used to explain the type II isotherms and is suitable for the range of values of a_w = 0.05 to 0.5. But still this equation gives sufficient data for the monolayer coverage of water. For unblanched mushrooms, the monolayer moisture contents varied between 4.3–9.0 g/100 g solids, and for blanched one, it varied between 2.5–5.9 g/100 g solids (Table 1, fourth column). When the monolayer coverage values of blanched and unblanched mushrooms were compared, it was found that the ones for blanched were always higher than those for blanched. Differences between these values showed that blanching changed the capacity for binding water and also for availability of free water. The reported monolayer values for mushrooms were 3.4–5.4 g/100 g solids [1, 5, 21]. Only the X_m values obtained for the blanched samples seem to be in accordance with those reported in literature. In this research, higher X_m values were obtained for the native mushrooms, they varied between 0.32 and 0.36, and for blanched between 0.15 and 0.40. The maximum a_w that can be tolerated in dry materials ranges from 0.35–0.50 depending on the product [23]. Thus our results were in good agreement with those reported in literature.

### 3.1 Effect of temperature

Food isotherms at different temperatures show a decrease in the amount sorbed with an increase in temperature at constant a_w. Temperature affects the mobility of water molecules and the equilibrium between the vapour and adsorbed phases. Thus an increase in temperature, at constant water activity, causes a decrease in the amount of adsorbed water. This means that the foods become less hygroscopic with an increase of temperature. From the well-known thermodynamic relationship,

\[ \Delta G = \Delta H - T \Delta S \]

where \( \Delta H \) is the net isosteric heat of sorption (adsorption or desorption), \( E_l \) is the heat of adsorption of the first layer and \( E_L \) is the heat of normal condensation of water (\( E_L = 43.9 \text{ kJ/mol at 25°C} \) [16], R is the universal gas constant (8.314 kJ/kg * mol * K), T is the absolute temperature [K].

The heats of adsorption were determined to be 2.9–3.8 kJ/mol for unblanched and 2.1–9.2 kJ/mol for blanched mushrooms. Thus high C values for the samples showed that water is strongly bound to the matrix if blanching is applied. Chirife et al. [22] calculated the heats of sorption for various foods using equation (3) and the values reported ranged between 4.6–10.9 kJ/mol. C values obtained for the native mushroom decreased with increasing temperature closely following the behavior indicated by the equation. But the blanched samples did not follow this behavior. In this case C increased rather than decreased with increasing temperature. This may be due to the known weakness of the BET theory to describe the energetics of water sorption in foods [20].

The moisture level considered to be safest with reference to good storage stability of foods is the monolayer value. When drying to low moisture levels, especially below X_m values, it becomes necessary to supply large amounts of extra heat in addition to the heat of evaporation. Hence, it is preferable to have initial moisture content at or slightly above the X_m value for extending the shelf life with minimal deterioration. The a_w values corresponding to X_m values can be found by solving equation (1). When the BET equation is solved for the monolayer moisture content (X = X_m and X/X_m = 1), the a_w at which the monolayer forms is as follows:

\[ a_w = \frac{1 + \sqrt{C}}{1 - C} \]

Equation (4) was solved for each X_m and the corresponding a_w values for good storage were given in Table 1. If the a_w values in the fourth column are taken into consideration for native mushrooms, they varied between 0.32 and 0.36, and for unblanched between 0.15 and 0.40. The maximum a_w that can be tolerated in dry materials ranges from 0.35–0.50 depending on the product [23]. Thus our results were in good agreement with those reported in literature.
Usually sorption phenomena in foods obey the Clausius-Clapeyron relationship. The temperature dependence of the isotherm may be expressed as \[ \ln\left(\frac{a_{w_2}}{a_{w_1}}\right) = \frac{Q_i}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \] where \(Q_i\) is the net isosteric heat of sorption and is defined as difference between the total molar enthalpy change and the molar enthalpy of vaporization. Clausius-Clapeyron equation provides useful information on the binding energy of water molecules. For the Clausius-Clapeyron equation to be valid, the process must be invariant. This means that the equation can be applied only for constant moisture content and also provided that no biological, chemical or other changes occur during sorption. If adsorption equilibrium data are available at two different temperatures, \(Q_i\) can be calculated by using the integrated form of Clausius-Clapeyron equation \[ \frac{d\ln(a_{w})}{dT} = -\frac{Q_i}{R} \] (6)

where \(a_{w1}\) and \(a_{w2}\) are the water activities at a given moisture content at temperatures \(T_1\) and \(T_2\), respectively. \(R\) is the universal gas constant (8.314 kJ/kg·mol·K).

In this work, the net isosteric heat of sorption at different moisture contents were calculated by using the sorption curves in Figs. 1 and 2 and the integrated form of Clausius-Clapeyron equation. The net isosteric heat of sorption in both cases decreased with increase in moisture content and nearly approached to a constant value. For the blanched mushrooms, the net isosteric heat of sorption was evaluated for the moisture range of 6.0 to 12 g/100 g dry solids. Within this moisture interval for adsorption, the heat of sorption varied between 26.4 to 11.3 kJ/mol and for desorption it was between 39.8 and 26.4 kJ/mol. For the unblanched mushrooms, the heat of sorption was evaluated between the moisture content of 6.0 to 20 g/100 g dry solids. For desorption, the heat of sorption changed from 30.5 to 5.4 kJ/mol and for desorption between 22.2 and 11.7 kJ/mol. The heat evolved during physical adsorption was reported to be 2.1 to 20.9 kJ/mol. For chemisorption, this value was 20.9 to 418.4 kJ/mol [24]. Thus it was concluded that the moisture adsorption occurred by means of physical mechanisms at high moisture contents. At low moisture contents, besides physical adsorption, chemisorption was also observed.

4 Conclusions

The following conclusions can be derived from this research:
1. Adsorption and desorption behaviors of blanched and unblanched mushrooms were determined to be different. The equilibrium moisture contents of unblanched mushrooms were found to be higher than those of the blanched.
2. The applicability of the BET equation over four different \(a_w\) regions of the isotherms was studied. Low % RMS values indicated that the BET equation can be applicable over 0.11–0.43 \(a_w\) for all samples. Also the monolayer and C values were reported.
3. The BET equation was solved for the monolayer moisture content and the \(a_w\) at which the monolayer forms was calculated for each sample. Thus the monolayer and the corresponding \(a_w\) values for good storage were presented.

References