The equilibrium moisture contents (EMC) of barley-pearl millet-milk based complementary food were determined using the static gravimetric method at 28, 37 and 45°C in the water activity (a_w) range of 0.11-0.92. The adsorption isotherms obtained were of sigmoid shape resembles type II curve in BET classification. EMC at a given (a_w) decreased as the temperature increased and inversion point was obtained at 37°C at higher water activity. BET and GAB models described the EMC/a_w relationship well by giving a closest fit to the experimental sorption data. The suitability of the models was determined by multiple statistical criterion viz. the coefficient of determination (R^2), mean relative per cent deviation modulus (P), Root Mean Square Deviation error (RMS %) and Chi-square (χ^2). The monolayer moisture content obtained by BET and GAB models are almost similar.

Keywords: Barley, pearl millet, milk, complementary food, adsorption isotherm, BET, GAB.

Introduction

Complementary foods are supplementary to mother's milk to complete the nutritional requirements of early age children (from 6 months to 2 ½ years). From the past many decades the development of novel complementary food formulations has been hot topic in scientific research with an aim towards utilizing diversified food sources for producing nutrient dense and low-cost food formulations. The cereals-milk based composite complementary foods are considered as complete food as they contain all the essential nutrients required for children to combat malnutrition and hidden hunger. Generally complementary foods are rich in carbohydrates which makes them highly hygroscopic and hence care has to be taken to avoid moisture related problems (Malleshi et al., 1989; Ghavidel and Prakash, 2010). The moisture adsorption behaviour of these solids can be ascertained by determination of sorption isotherms. Sorption isotherms describe the relationship between equilibrium moisture content and water activity at a constant temperature. It gives clear information on monolayer moisture content, energy required to remove the moisture, critical relative humidity where adsorption of moisture is high, etc. Such information would be useful in food industries in assessing drying and packaging requirements, temperature and humidity conditions for storage, etc. Several researchers studied sorption isotherms of complementary or weaning foods such as pearl millet based fortified nutrimix (Sharma et al., 2014; Lal et al., 2013), cereals, legumes and vegetables based composite weaning mixes (Ghavidel and Prakash, 2010), malted ragi and green gram based weaning food (Malleshi et al., 1989), cereals and legumes based nutritious supplementary foods (Baskaran et al., 2000) and spray dried infant food (Kumar and Venugopal, 1991). However, there is no information on the moisture sorption pattern of milk-cereal-based composite mineral fortified complementary food. Hence, the present study was undertaken to obtain sorption related information with a view to better understand the storage behaviour and packaging material requirements of novel barley-pearl millet-milk based complementary food.

Materials and Methods

Preparation of complementary food

The complementary food composed of barley, pearl millet (from local market, Karnal, India), skim milk powder (M/s Modern
Dairies LTD., Karnal, India), sugar (Trust™-sulphurless sugar, manufactured and packed by M/s Simbhaoli Sugars LTD., Ghaziabad, U.P.), flavouring agent and iron and zinc salts. Composite complementary food, nutrimix was prepared by following the method described by Zaheeruddin (2011) and Shuddodhan (2012). Pearl millet was subjected to treatments like germination, drying, derooting and dehulling, while barley was subjected to all treatments except germination. Barley (59%) and pearl millet (20%) grits were extruded through a single-screw extruder (M/s G.L. Extrusion, New Delhi) separately, milled and sieved (the sieve number BSS 60) before blending with fresh skim milk powder (21.3%), grounded sugar (12%) and minerals (ferric ammonium citrate and zinc sulphate ). The fresh product was kept in a desiccator containing phosphorous pentoxide to reduce moisture content near to zero or dry bone condition.

Sorption studies

The sorption isotherms were determined by using static gravimetric method (Rao et al., 2006). Saturated salt solutions with water activity (aw) ranging from 0.11-0.92 were prepared because at higher aw there will be a chance of mold growth and placed at the bottom of the sorbostat, consisting of glass jars of wide mouth closed by air tight lids, with sufficient quantity to maintain the large ratio of sorbate to sample. The sorbostats were transferred to the thermostatically operated incubators maintained at three different temperatures viz. 28, 37 and 45°C for 3 days to achieve equilibration. Potassium sorbate (0.5% w/w) was mixed with the sample to prevent mold growth during equilibration, especially at higher humidity levels. Beaker of 50 mL capacity containing trivets was placed into sorbostat and the sample of 1±0.001 g weighed accurately in the 10 mL beaker allowed to stand on the trivets. The sorbostats containing samples were placed in incubators for equilibration. The change in weight of the sample was measured after every 2 days. Equilibrium was considered to be achieved when the change in weight of three subsequent weighings was not more than 2 mg per gram of sample. The adsorbed moisture content was expressed on dry matter basis.

Analysis of data and fitting of mathematical model

The equilibrium moisture content (EMC) was estimated by using below formula.

\[
W = \frac{(W_2-W_1)+m_i}{(W_1-m_i)} \times 100
\]  
(1)

Where \( W \) is EMC (g of water / g of solids); \( W_1 \) is the initial weight of the sample (g); \( W_2 \) is the final weight of the sample (g); and \( m_i \) is the initial moisture content of the sample (g).

The Brunauer-Emmet-Teller (BET) and Guggenheim-Anderson-de Boer (GAB) models are the universally accepted models for describing sorption behaviour of most food products. BET model (Eq. 2) best describes data in the \( \alpha_w \) range of 0.1-0.5 while GAB model (Eq. 3) best describes in the range of 0.1-0.9. Fitting of models to experimental data has done using OriginTM pro software ver. 8.0.

\[
\frac{a_w}{(1-a_w)M} = \frac{1}{M_0C_b} + \frac{(C_b-1)}{M_0C_b}a_w
\]  
(2)

\[
M = \frac{M_0KC_{aw}}{(1-Ka_w)(1+(C-1)Ka_w)}
\]  
(3)

The goodness of fit was checked by four statistical parameters such as coefficient of determination (R2), Root Mean Square error (RMS %), percent mean deviation modulus (P) and Chi-square (\( \chi^2 \)) as shown below using Microsoft excel. Any given sorption model is said to best fit if the RMS %is less than 10%, P less than 5%, R2 near to one and 2 less than 0.5.

\[
RMS\% = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{P_{obs}-P_{pred}}{P_{obs}} \right)^2}
\]  
(4)

\[
R^2 = 1 - \frac{SS_{res}}{SS_{tot}}
\]  
(5)

\[
\chi^2 = \sum \frac{(O_i-E_i)^2}{E_i}
\]  
(6)

\[
P = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{M_i - M_{i,exp}}{M_{i,exp}} \right|
\]  
(7)

Results and Discussion

Moisture adsorption isotherms

The moisture adsorption isotherms of complementary food were generated at the three different temperatures viz 28, 37 and 45°C in the aw range of 0.11-0.92. The EMCs were plotted against a w to obtain an adsorption isotherm at the three temperatures (Figure 1). The isotherms resembled type II according to BET classification. The EMC was found to decrease with increase in temperature at a particular aw. Baskaran et al. (2000) observed moisture adsorption isotherms of four different formulations (FS1, FS2, FS3, FS4) of nutritious supplementary foods made up of cereals (popped wheat, ragi, bajra, sorghum) and legumes (Bengal gram flour) at 27°C and found that the sorption curves resembled type-II or sigmoid curve. The EMCs were reported to be in the range of 2.5 to 21.4, 3.4 to 18.6, 3.9 to 17.2 and 2.5 to 15.7 for the formulations FS1, FS2, FS3 and FS4, respectively. Ghavidel and Prakash (2010) studied the adsorption isotherms of composite weaning food made up of cereals, legumes and vegetables at 25°C and reported that the isotherm curves resembled the type-II or sigmoid shape. Recently, Sharma et al. (2014) evaluated the
moisture sorption characteristics of iron and zinc fortified milk-pearl millet based nutrimix at 15, 25, 35 and 45ºC and reported that the sorption curves resembled type II or sigmoid shape. The EMCs of the adsorption isotherms were reported to be in the range of 5.92 to 56.35, 5.79 to 55.50, 5.32 to 54.99 and 5.01 to 54.78 g/100 g solids at 15, 25, 35 and 45ºC, respectively. Generally, most of the foods exhibit sigmoid shape of adsorption isotherm and it indicates change in their adsorption behaviour with change in relative humidity and also temperature. We can observe (Figure 1) that steep increase in moisture adsorption after the a_w reached above 0.65. This behaviour may lead to adverse biochemical reactions and lose the native characteristics of the products.

**Table 1** BET and GAB model parameters and their statistical criteria

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>28°C</th>
<th>37°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET (a_w=0.10-0.44)</strong></td>
<td>Mo</td>
<td>4.05</td>
<td>3.86</td>
<td>3.09</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>21.86</td>
<td>29.12</td>
<td>26.24</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.985</td>
<td>0.981</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.12</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>RMS%</td>
<td>4.24</td>
<td>5.08</td>
<td>2.01</td>
</tr>
<tr>
<td><strong>GAB (a_w=0.10-0.92)</strong></td>
<td>P</td>
<td>4.29</td>
<td>5.59</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.97</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>0.98</td>
<td>33.74</td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td>Mo</td>
<td>4.15</td>
<td>3.81</td>
<td>3.91</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.996</td>
<td>0.998</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.49</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>RMS%</td>
<td>5.18</td>
<td>5.73</td>
<td>9.34</td>
</tr>
</tbody>
</table>

Temperature dependence of the sorption isotherms

The isotherms revealed decrease in EMC with increase in temperature. However, at higher a_w at 37ºC inversion point
was observed. It may be due to the dissolution of the sugars and other low molecular weight components (Kapsalis, 1987). EMCs at 45°C were found to be lower compared to the EMCs at 37 and 28°C which could be attributed to the loss of the hydrogen bonds at higher temperature or to breakaway of some water molecules from their sorption sites due to activation to higher energy levels at elevated temperatures (Palipane and Driscoll, 1992). Since the published information regarding the temperature effect on moisture adsorption of the complementary foods is very scanty, closely related foods are taken into consideration for discussing the temperature dependency of adsorption of barley-milk based complementary food. Recently, Lal et al. (2013) reported that the pearl millet based mineral fortified complementary food showed decreasing trend of moisture adsorption with increase in temperature. Brett et al. (2009) generated moisture sorption isotherms of oat flour and rice flour at 5, 23, and 45°C using a gravimetric technique in aw range of 0.08-0.98. It was reported that for aw values lower than 0.75, in both the flours, the sorption capacity decreased with increasing temperature, while the opposite behaviour was observed at aw greater than this value. Durakova and Menkov (2005) studied moisture adsorption isotherms of chickpea flour using the static gravimetric method of saturated salt solutions (0.11 to 0.85) at four storage temperatures viz. 10, 20, 30 and 40°C and reported that EMCs decreased with the increase in storage temperature at any given water activity. Palou et al. (1997) evaluated the moisture sorption isotherms of three cookies and two corn snacks at 25, 35 and 45°C and found that the isotherm for each product was different and significantly affected by temperature. In present investigation, the Barley-Pearl millet-milk based complementary food showed moisture

![Figure 2 Actual and predicted sorption isotherms by GAB model along with their residuals](image-url)
adsorption rate decreased with increase in temperature (28-45°C) shows the general behaviour of the non-hygroscopic food product either during storage or during drying. Whereas, undesirable increase in moisture adsorption at 37°C compare to 28°C indicates hygroscopic nature of the product because this kind of behaviour has been hypothesized to dissolution of low molecular weight solids.

Mathematical description of the adsorption isotherms

Table 1 shows the BET and GAB equation parameters of barley-pearl millet-milk micronutrient fortified complementary food. Since, R² alone is not a reliable statistical criterion for evaluation of the EMCs (Rao et al., 2006), in the present study we have chosen multiple criterion. GAB model was found to be the best fit over entire range of aw studied and BET model was found to be the best in the range of 0.10-0.44 as indicated by highest R² values and lowest RMS%, P and 2 values. Figure 2 illustrates the differences between actual and predicted adsorption isotherms for GAB model. GAB model performed well in fitting the sorption data of starch-rich foods like tapioca flour (Chiste et al., 2012), wheat and soya flour (Riganakos et al., 1994), oat and rice flour (Brett et al., 2009) and corn meal flour (Labuza et al., 1985). Recently, Lal et al. (2013) and Sharma et al. (2014) reported that among the several empirical models, GAB model was found to best represent the experimental data for pearl millet based iron fortified complementary food. In the present study, the monolayer moisture content (Mo) exhibited by the BET equation was close to the GAB at all the temperatures i.e. 28, 37 and 45°C. The applicability of the BET and estimation of Mo from BET and GAB equations was also evaluated by several authors. Chiste et al., (2012) found that BET model applicability was better and estimated that the monolayer content of 4.92 percent. Durakova and Menkov, (2004) mentioned the significance of BET model in estimating Mo. Palou et al. (1997) reported that the estimated Mo using BET and GAB models was found to be significantly different. Utilization of mathematical models in prediction of adsorption isotherm data has numerous applications for example M0 content is considered as most stable and not available for biochemical reactions. Hence, keeping product at this moisture content could preserve it for long period and it could form basis for extent of drying of foods.

Conclusions

The moisture sorption isotherms of barley-pearl millet-milk based micronutrient fortified complementary food presented a sigmoid shape and resembled type II of BET classification. The moisture sorption of the product increased steeply above 0.65 aw indicating the critical aw for the complementary food. GAB and BET proved to fit the experimental sorption data well as indicated by multiple statistical criterion. The estimated monolayer moisture content was almost similar in both the models. The sorption isotherm study provided the critical relative humidity and moisture content which would be useful while designing the optimum storing and packaging conditions to keep product stable for long period.

References


