1. Introduction

Fuzzy Cottonseed is a cotton by-product obtained after removing the long fibres (lint) through ginning. It is made up of three main parts: linters or fuzz, short fibres clinging to the seed; hull, a tough protective coating for the kernel; and protein- and oil-rich kernel (Salunkhe et al., 1992). It does not flow freely as particles due to clumping caused by the highly entangling nature of the linters and cannot be handled by the traditional grain handling equipment.

Coating fuzzy cottonseed with a mild dose of gelatinized starch is an effective way to improve its flow characteristics (Laird et al., 1997). Gelatinized starch glues the linters to the hull to make an integral part of the hull, and whole seed gets a relatively smooth surface. The static and dynamic friction between seeds themselves and between seeds and handling surfaces decrease enormously, then cottonseed can flow freely as particles. Starch coating also provides increased bulk density, no clumping, and no dispersing of the loose linters in the air. Starch coated cottonseed is as at least nutritive as the fuzzy cottonseed. It has a nutritional and dry matter advantage over the fuzzy cottonseed due to the added starch. In addition to its technical advantages, starch-coating adds value to the fuzzy cottonseed used as ruminant feed. For the time being, one of key markets for the starch-coated cottonseed is dairy industry which utilises the cottonseed as feed because of its high nutritive and calorific value.

Moisture is the major factor controlling biological activity and quality of cottonseed (Columbus & Mangialardi, 1996). High-moisture cottonseeds respire more vigorously, develop free fatty acids more rapidly, and deteriorate to a greater extent upon storage than seeds of lower moisture content (Karon, 1947). Cottonseed, like other hygroscopic materials, eventually attains moisture content in equilibrium with that of the surrounding atmosphere. Understanding the nature of the water vapour adsorption phenomenon is important in determining state of cottonseed, and for employing good storing, planting, and processing operations.
Early studies on the water vapour adsorption behaviour of the fuzzy cottonseed were conducted at or around room temperature (Chapman, 1971; Karon & Adams, 1948; Simpson & Miller, 1944; Franco, 1943). In recent works, the temperature range was extended a little. Kradanangga (1994) investigated adsorption isotherms of the fuzzy cottonseed at 10, 20, 25, and 30°C between relative humidity (r.h.) of 22 and 92%. Henain (1992) studied adsorption of the fuzzy cottonseed at 10 and 30°C between r.h. of 22 and 92%.

Data on physical properties of the starch-coated cottonseed is very scarce since it is a new application. Pelletier et al. (2001) investigated mass and heat transfer properties of the starch-coated cottonseed during drying for designing a new dryer. Duffy and Puri (1999) studied flow characteristics of the starch-coated cottonseed. Turhan and Gunasekaran (1999) compared some thermal and physical properties of the fuzzy and starch-coated cottonseeds. Laird et al. (1997) investigated effect of starch coating on handling characteristics of the fuzzy cottonseed.

Comparative information on the physical properties of the fuzzy and starch-coated cottonseeds is needed to be able to fully evaluate and benefit from the starch-coated cottonseed. In this work, water vapour adsorption behaviour of the fuzzy and starch-coated cottonseeds is studied. The specific objectives are to determine: (1) the adsorption isotherms of the fuzzy and starch-coated cottonseeds over a wide range of values for r.h. (10–96%) and for temperature (5–45°C); (2) the suitability of the Guggenheim–Anderson–Boer (GAB) equation in describing the sorption isotherms; (3) the critical storage parameters such as monolayer moisture content and heat of adsorption; and (4) the effect of starch coating on the water adsorption.

### Notation

- \( a_w \): water activity
- \( C \) and \( C_0 \): constant in the BET and GAB equations, and constant related to \( C \), respectively.
- \( H_R \): relative humidity, %
- \( h_m \): heat of adsorption of monolayer water (first layer), kJ mol\(^{-1}\)
- \( h_n \): heat of adsorption of multilayer water (above first layer), kJ mol\(^{-1}\)
- \( h_L \): latent heat of condensation of water, kJ mol\(^{-1}\)
- \( j \): number of water layers
- \( k \) and \( k_0 \): GAB constant and constant related to \( k \), respectively
- \( M_e \): mean relative error, %
- \( N \): number of observations
- \( Q \): heat of adsorption, kJ mol\(^{-1}\)
- \( Q_S \): net heat of adsorption, kJ mol\(^{-1}\)
- \( q_c \): heat related to \( h_m \), kJ mol\(^{-1}\)
- \( q_k \): heat related to \( h_m \), kJ mol\(^{-1}\)
- \( q_m \): constant related to \( X_m \), kJ mol\(^{-1}\)
- \( R \): universal gas constant, 8.31 J mol\(^{-1}\) K\(^{-1}\)
- \( R_e \): relative error, %
- \( T \): temperature, K or °C
- \( X \): equilibrium moisture content, % d.b.
- \( X_m \): monolayer moisture content, % d.b.
- \( X_i \) and \( X_{ip} \): experimental and predicted equilibrium moisture content, respectively

### 2. Materials and methods

Fuzzy cottonseed (Mississippi variety) and its gelatinized starch-coated form were obtained from a commercial source. The producer had coated the fuzzy cottonseed with 5% gelatinised corn starch. Adsorption isotherms of the samples were determined at nine r.h. between 10 and 96% each at five temperatures (5, 15, 25, 35, and 45°C). r.h. were obtained using air tight 1 l glass jars containing saturated solutions of LiCl, KCl, KC\(_2\)H\(_3\)O\(_2\), MgCl\(_2\), K\(_2\)CO\(_3\), NaBr, NaNO\(_2\), NaCl, KCl, and K\(_2\)SO\(_4\). Saturated salt solutions were prepared by adding salts in the boiling tap water till initial salt precipitation was observed. Jars were kept at experimental temperatures for 24 h for thermal equilibration. Experiments were conducted in a temperature controlled cabinet (VWR Scientific, Low Temperature Incubator 2005, ±0.5°C). At each temperature, RH of the salt solutions were measured using a water activity meter (AquaLab, Model CX-2, ±0.003) equilibrated to the experimental temperature in the given temperature controlled cabinet.

Moisture content of the cottonseed samples were reduced to 2–3% d.b. by drying at 40°C overnight. Dried samples were conditioned in a desiccator containing CaCl\(_2\) at the experimental temperature overnight for thermal equilibration. Moisture content of the samples was determined by drying at 105°C for 24 h in a laboratory oven.

Approximately 2.0–2.5 g of cottonseeds (25 seeds) were placed in a single layer in stainless-steel wire-mesh baskets. The baskets were hung from the lids of the jars over the salt solutions. Mass of the baskets were quickly measured off-line (less than 15 s) using an analytical balance (Mettler Toledo, AG245, ± 0.0001), so as not to disturb the condition of the samples and the atmosphere in the jars. Change in the mass was...
attributed to the mass of the water adsorbed by the samples. Cottonseed samples were assumed to attain equilibrium moisture content when the difference between two successive weekly mass measurements was less than 0.0001 g.

Statistical analyses of the data were conducted using a statistical software package (SPSS for Windows 5.0.1).

3. Sorption model and application

Several empirical, semi-empirical, and theoretical isotherm models have been proposed for the correlation of equilibrium moisture content $X$ of food and agricultural materials with r.h. $H_R$ of the surrounding air (Rahman, 1995). Among them, theoretical Brunauer–Emmet–Teller (BET) equation [Eqn (1)] is one of the most popular models considering sorbed water molecules lay on each other in layers calling the water layer next to the sorption surface the first layer:

$$X = \frac{X_m Ca_w}{(1-a_w)(1-a_w + Ca_w)}$$

(1)

$$C = C_0 \exp \left[ \frac{q_c}{RT} \right]$$

(2)

$$q_c = h_m - h_n$$

(3)

where $X_m$ is the monolayer moisture context in % d.b.; $C$ is a constant; $a_w$ is the water activity given by $H_R/100$; $C_0$ is a constant; $h_m$ is the heat of sorption of monolayer water (up to first layer) in kJ mol$^{-1}$; $h_n$ is the heat of sorption of multilayer water (above first layer) in kJ mol$^{-1}$; $R$ is the universal gas constant in kJ mol$^{-1}$ K$^{-1}$; and $T$ is the temperature in K.

The BET isotherm with the two parameters $X_m$ and $C$ provides poor agreement with experimental data above r.h. of 50% (Labuza, 1968). The principal limitation to the BET equation comes from the assumption that water molecules above the first layer have free water evaporation-condensation properties (Aguerre et al., 1989a), e.g. $h_n$ is equal to the latent heat of condensation of water $h_L$.

The BET equation was modified by introducing a third parameter $k$ considering that till the ninth layer $h_n$ differs from $h_L$ by the same constant amount, and above the ninth layer it is equal to $h_L$. This form of the BET equation is known as the Guggenheim–Anderson–Boer (GAB) equation (Van Den Berg & Bruin, 1981):

$$X = \frac{X_m Cka_w}{(1-ka_w)(1-ka_w + Cka_w)}$$

(4)

$$k = k_0 \exp \left[ \frac{q_k}{RT} \right]$$

(5)

where $k_0$ is a constant.

The GAB model extended the application of the BET model up to a r.h. of 95% (Timmermann & Chirife, 1991). It has been reported to predict the equilibrium moisture content satisfactorily over the largest r.h. range among the known sorption models for a wide variety of food and agricultural materials. It is recommended as the standard method by the European project COST 90 on Physical Properties of Foods (Wolf et al., 1984) and the ASAE (2001).

Since the GAB equation is an extended form of the BET equation, the same notation is conventionally used in both equations. However, they do not necessarily have the same physical meaning and magnitude. Though $X_m$ has the same physical meaning in both equations, it is smaller in the BET equation than in the GAB equation under the same conditions. Physical meaning of $C$ is different in both equations due to the correction factor $k$ in the GAB equation and it is greater in the BET equation than in the GAB equation under the same conditions (Timmermann et al., 2001).

Aguerre et al. (1989a) established a general approach considering variation of $h_n$ with water content with respect to $h_L$, namely $h_n$ differs from $h_L$ as a function of the number of the water layers $j$ above the first layer:

$$h_n = h_L + RT \ln f(j)$$

(7)

where $f(j)$ is the function giving variation of $h_n$ with the number of the water layers $j$.

Using Eqn (7), Aguerre et al. (1989a) derived BET-like sorption equations for the following cases for $j > 1$: (1) $h_n > h_L$ and $h_n$ decreases toward $h_L$ with $f(j) = j/(j - 1)$; (2) $h_n < h_L$ and $h_n$ increases toward $h_L$ with $f(j) = (j - 1)/j$; (3) $h_n < h_L$ and $h_n$ is constant with $f(j) = k < 1$.

For case 3, if $k = 1$, the sorption equation becomes the BET equation [Eqn (1)], and if $k < 1$ it turns into the GAB equation [Eqn (4)].

Fitting performance of the GAB equation to sorption data depends on the regression method used. Schar and Ruegg (1985) tested fitting of the transformed GAB equation (second degree polynomial) and the ordinary GAB equation [Eqn (4)] on the same data sets. The tests resulted in larger mean relative errors for the former equation and the authors suggested the use of the latter equation.

Maroulis et al. (1988) compared direct and indirect non-linear regressions of the GAB equation for sorption of dried fruits at different temperatures. In the direct regression, five constants of the GAB equation $X_m$, $C_0$, $q_c$, $k_0$, and $q_k$ were estimated simultaneously by substituting Eqns (2) and (5) into Eqn (4). In the
indirect regression, three constants of the GAB equation $X_m$, $C$, and $k$ were first estimated at each temperature using Eqn (4), and they were used to estimate $C_0$, $q_C$, $k_0$, and $q_k$ through Eqs (2)–(5). Maroulis et al. (1988) did not recommend use of the indirect method since $X_m$, $C$, and $k$ are interrelated. Samaniego-Esguerra et al. (1991) conducted a similar work on dried fruits and vegetables, and corroborated Maroulis et al. (1988) adding that the indirect method seems adequate and simpler to use than the direct method if predictions would be made at temperatures where the GAB constants were estimated.

4. Results and discussions

4.1. Regression of the GAB equation

The fit of the GAB equation to the water vapour adsorption data of the fuzzy and starch-coated cottonseeds was studied using the direct regression method taking into account effect of temperature on $X_m$ (Samaniego-Esguerra et al., 1991; Weisser, 1985)

$$X_m = X_{m0} \exp \left( \frac{q_m}{RT} \right)$$

(8)

where $X_{m0}$ and $q_m$ are constants.

Average values of $X$ collected through experiments are listed in Table 1. Above r.h. of 90%, both fuzzy and starch-coated cottonseeds developed mould at all temperatures worked as observed by Kradangnga (1994) and Henain (1992) for the adsorption of the fuzzy cottonseed between 10 and 30°C. Hence, adsorption data obtained for r.h. over 90% were not used in the calculations. Estimated GAB constants along with the statistics are shown in Table 2. The regression gave coefficients of determination $R^2$ very close to 1.000 for both cottonseeds. The fit of a sorption model is considered good enough for practical purposes if mean relative error $M_e$ is less than 10% (Aguerre et al., 1989b)

$$M_e = \frac{\sum |R_e|}{N}$$

(9)

$$R_e = \frac{X_i - X_{ip}}{X_i} \times 100$$

(10)

where $R_e$ is the relative error in %; $N$ is the number of observations; and $X_i$ and $X_{ip}$ are the experimental and predicted $X$ in % d.b., respectively.

The values for $M_e$ obtained in the regression of the GAB equation was much smaller than 10% for the fuzzy and starch-coated cottonseeds (Table 2). The values for $R_e$ randomly scattered around zero for both samples (Fig. 1). Considering the values for $R^2$ and $M_e$, and the random scattering of $R_e$, the GAB equation may be considered satisfactory for fitting the adsorption of the fuzzy and starch-coated cottonseeds (Fig. 2). However, further investigation into the estimated GAB constants and comparison with the literature would help to reach a more confident conclusion on the applicability of the GAB equation on adsorption of the cottonseeds.

Maximum, minimum, and average values for $X_m$, $C$, and $k$ were calculated for the fuzzy and starch-coated cottonseeds using the estimated constants $X_{m0}$, $q_m$, $C_0$, $q_C$, $k_0$, and $q_k$ (Table 2). The values for $X_m$ and $C$ are within the reported limits for nuts and oil seeds (Maskan

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Fuzzy cottonseed</th>
<th>Starch-coated cottonseed</th>
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</thead>
<tbody>
<tr>
<td>Relative humidity, %</td>
<td>$X_i$% (d.b.)</td>
<td>Relative humidity, %</td>
</tr>
<tr>
<td>5</td>
<td>11.5</td>
<td>4.5</td>
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<td></td>
<td>21.4</td>
<td>5.1</td>
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<td></td>
<td>32.6</td>
<td>6.3</td>
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<tr>
<td></td>
<td>44.7</td>
<td>7.9</td>
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<tr>
<td></td>
<td>64.3</td>
<td>11.0</td>
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<td>13.1</td>
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<td></td>
<td>76.0</td>
<td>16.8</td>
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<td></td>
<td>88.4</td>
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<td></td>
<td>44.1</td>
<td>8.0</td>
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<td></td>
<td>61.1</td>
<td>10.8</td>
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<td>57.5</td>
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<td>11.1</td>
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<td>75.2</td>
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<td></td>
<td>84.2</td>
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<tr>
<td>35</td>
<td>11.4</td>
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<td></td>
<td>74.3</td>
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<td></td>
<td>82.3</td>
<td>15.2</td>
</tr>
</tbody>
</table>
& Karatas, 1997; Yanniotis & Zarmboutis, 1996; Lopez et al., 1995; Palipane & Driscoll, 1992; Lomauro et al., 1985), and values for \( k \) are smaller than 1 (Table 2) as dictated by the GAB equation (Chirife et al., 1992). The magnitude and sign of \( q_C \) is also in agreement with the literature (Samaniego-Esguerra et al., 1991; Maroulis et al., 1988; Tsami et al., 1990). Though the magnitude of \( q_k \) was within the reported values, its sign is in

### Table 2

<table>
<thead>
<tr>
<th>Coefficient of determination ( R^2 )</th>
<th>Fuzzy cottonseed</th>
<th>Starch-coated cottonseed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean relative error ( Me, % )</td>
<td>0.996</td>
<td>0.996</td>
</tr>
<tr>
<td>Constant ( X_{m0} ) in Eqn (8), % (db)</td>
<td>2.06</td>
<td>2.52</td>
</tr>
<tr>
<td>Constant ( q_m ) in Eqn (8), kJ mol(^{-1} )</td>
<td>1.85</td>
<td>1.48</td>
</tr>
</tbody>
</table>

**Monolayer moisture content \( X_m \), \% d.b.**

- Maximum (5\(^\circ\)C): 4.58
- Minimum (45\(^\circ\)C): 4.14
- Average: 4.35

- Constant \( C_0 \) in Eqn (2): \( 7.72 \times 10^{-5} \) \( 2.20 \times 10^{-4} \)

**Heat related to monolayer water \( q_c \), kJ mol\(^{-1} \)**

- Maximum (5\(^\circ\)C): 31.49
- Minimum (45\(^\circ\)C): 28.15

**Constant \( C \) in Eqn (4)**

- Maximum (5\(^\circ\)C): 64.2
- Minimum (45\(^\circ\)C): 11.6
- Average: 31.7

**Constant \( k \) in Eqn (4)**

- Maximum (5\(^\circ\)C): 0.61
- Minimum (45\(^\circ\)C): 0.70
- Average: 0.68

**Heat related to multilayer layer water \( q_k \), kJ mol\(^{-1} \)**

- Maximum (5\(^\circ\)C): 1.06
- Minimum (45\(^\circ\)C): 0.58
- Average: 0.88

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**Fig. 1.** Distribution of relative error over the relative humidity range; ○, fuzzy cottonseed; □, starch-coated cottonseed

**Fig. 2.** Fit of the GAB equation to the experimental data; ○, fuzzy cottonseed at 5\(^\circ\)C; □, fuzzy cottonseed at 45\(^\circ\)C; -----, estimated for the fuzzy cottonseed; ○, starch-coated cottonseed at 5\(^\circ\)C; □, starch-coated cottonseed at 45\(^\circ\)C; -----, estimated for the starch-coated cottonseed
agreement with only a limited number of works (Pulipane & Driscoll, 1992; Soekarto & Steinberg, 1981). In the majority of the previous works, the sign of \( q_k \) was reported as negative (Samaniego-Esguerra et al., 1991; Tsami et al., 1990; Maroulis et al., 1988) which means that the value for \( h_h \) is greater than that for \( h_L \). However, if the value for \( k \) thermodynamically needs to be smaller than 1 (Chirife et al., 1992), then the value for \( h_h \) must theoretically be smaller than that for \( h_L \) according to Anderson (1946) and Case (3) of Eqn (7) (Aguerre et al., 1989a).

The fit of the GAB equation was also tested on the adsorption data of the fuzzy cottonseed collected from the literature (Table 3). In all previous works, high values for \( R^2 \) (~1.000) and low values for \( M_d < 10\% \) assured good fit of the GAB equation. Comparing the estimated GAB constants from this work (Table 2) and from the literature (Table 3), the following can be stated: values for \( k \) and \( X_m \) are in good agreement; values for \( q_C \) and \( q_k \) are comparable except the sign of \( q_k \) as mentioned above; agreement between values for \( C \) is mixed.

The good fit of the GAB equation to the experimental data of this work, and the agreement of this work with the literature and/or the GAB equation demands show that the GAB equation can be used to study water vapour adsorption of the fuzzy and starch-coated cottonseeds over the given r.h. and temperature ranges.

4.2. Evaluation of the sorption isotherms

Sorption isotherms of the fuzzy and starch-coated cottonseeds displayed an S-shaped pattern, and did not cross each other at different temperatures within the given r.h. range that is typical for materials with low sugar content (Maroulis et al., 1988). The behaviour of the cottonseed isotherms is presented in Fig. 2 for the temperature extremes worked. At low and intermediate r.h., multilayer sorption region, \( X \) increased linearly with r.h. for both fuzzy and starch-coated cottonseeds at all temperatures worked. Chapman (1971), Karon and Adams (1948), and Simpson and Miller (1944) reported a similar behaviour up to r.h. of 60% at 25°C. At high r.h., capillary condensation region, \( X \) drastically increased with r.h. for both cottonseeds.

Fuzzy and starch-coated cottonseeds had almost the same values for \( X \) in the linear multilayer region (Fig. 2). The range of linear region was the same for both cottonseeds at the same temperature. The lower limit of the region started at r.h. of 11% and its upper limit extended with increasing temperature (Table 4). At the upper limit of the region, fuzzy and starch-coated cottonseeds had about the same \( X \) of 8% (db) at all temperatures (Fig. 2). Isotherms departed from each other in the capillary condensation region and the discrepancy got more pronounced with increasing r.h. and decreasing temperature. In the capillary region, the starch-coated cottonseeds always exhibited lower \( X \) values than the fuzzy cottonseeds under the same conditions.

Coating the fuzzy cottonseed with gelatinised starch forms a barrier on the hull against water vapour in the surrounding atmosphere. Water molecules are essentially adsorbed on the amorphous sites of the starch. High-temperature drying (\( \approx 160^\circ \)C) of the gelatinised starch after the coating (Laird et al., 1997) increases the number of the crystalline sites at the expense of the amorphous sites (Labuza, 1968). In the crystalline sites, the bonds between the polysaccharide chains are very strong and form steric hindrance against water mole-

### Table 3

<table>
<thead>
<tr>
<th>Relative humidity, %</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
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<td>25</td>
<td>25</td>
<td>25</td>
<td>10,30</td>
<td>10–30</td>
</tr>
<tr>
<td>Coefficient of determination ( R^2 )</td>
<td>0.995</td>
<td>0.997</td>
<td>0.986</td>
<td>0.991</td>
<td>0.988</td>
<td>0.996</td>
</tr>
<tr>
<td>Mean relative error ( M_r ), %</td>
<td>2.2</td>
<td>4.3</td>
<td>6.0</td>
<td>7.4</td>
<td>3.1</td>
<td>1.91</td>
</tr>
<tr>
<td>Monolayer moisture content ( X_m ), % d.b.</td>
<td>5.00</td>
<td>4.78</td>
<td>4.49</td>
<td>4.48</td>
<td>5.49*</td>
<td>5.43*</td>
</tr>
<tr>
<td>Heat related to monolayer water ( q_C ), kJ mol(^{-1})</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Constant ( C ) in Eqn (4)</td>
<td>42.1</td>
<td>30.7</td>
<td>92.8</td>
<td>1.33 ( \times ) 10(^8)</td>
<td>1.97 ( \times ) 10(^8)</td>
<td>6.59 ( \times ) 10(^8)</td>
</tr>
<tr>
<td>Heat related to multilayer water ( q_k ), kJ mol(^{-1})</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Constant ( k ) in Eqn (4)</td>
<td>0.85</td>
<td>0.88</td>
<td>0.88</td>
<td>0.95</td>
<td>0.81*</td>
<td>0.82*</td>
</tr>
</tbody>
</table>


*Average values.
The monolayer moisture content

4.3. The monolayer moisture content

The monolayer moisture content \( X_m \) is recognised as the moisture content affording the longest time period with minimum quality loss at a given temperature (Labuza, 1968). Below it, rate of deteriorative reactions, except oxidation of unsaturated fats, are minimal (Rahman, 1995). The rate of oxidation is minimum only at \( X_m \). Therefore, at a given temperature, the unique and safest r.h. for oil seeds such as cottonseed is the r.h. corresponding to \( X_m \). The safest r.h. values for the fuzzy and starch-coated cottonseeds were predicted using data in Table 2 and tabulated in Table 5. The starch-coated cottonseed had higher values for \( X_m \) and r.h. than the fuzzy cottonseed at all temperatures. This shows the more tolerance of the starch-coated cottonseed to higher r.h. than the fuzzy cottonseed at \( X_m \) and higher durability of the former.

4.4. Heat of adsorption

Adsorption of water vapour is one of the major factors for temperature rise in cottonseed during storage. Raising temperature increases rate of the deteriorative activities in cottonseed such as respiration, microorganism development, oxidation of free fatty acids, etc. Deteriorative activities do not only decrease the seed quality, but also facilitate further moisture gain and then further temperature increase. This vicious circle may go on till total quality loss of cottonseed for all uses if no precaution is taken. Particularly during long-term storage, aeration is inevitable to control temperature and moisture content (Mayfield et al., 1993), and quality of the cottonseed.

Basic understanding of the heat of sorption is one of the keys to the good management of the cottonseed handling. Clausius–Clapeyron equation [Eqn (11)] has been widely used for calculating net heat of sorption \( Q_S \) (Iglesias & Chirife, 1976) of food and agricultural materials during water vapor sorption processes

\[
\frac{d \ln(H_R/100)}{d \left[1/T\right]} = -\frac{Q_S}{R} \tag{11}
\]

From Eqn (11), \( Q_S \) for the fuzzy and starch-coated cottonseeds was obtained by plotting a logarithm of the decimal r.h. versus the reciprocal of temperature at some selected \( X \) values. The plots had values for \( R^2 \) greater than 0.999 for both cottonseeds. Variation of heat of

### Table 4

Upper limit of r.h. where the linearity of the water vapour adsorption isotherms of the fuzzy and starch-coated cottonseeds diminishes.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Upper limit of r.h., %</th>
<th>Coefficient of determination (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>45</td>
<td>0.994</td>
</tr>
<tr>
<td>15</td>
<td>48</td>
<td>0.996</td>
</tr>
<tr>
<td>25</td>
<td>51</td>
<td>0.996</td>
</tr>
<tr>
<td>35</td>
<td>54</td>
<td>0.996</td>
</tr>
<tr>
<td>45</td>
<td>57</td>
<td>0.996</td>
</tr>
</tbody>
</table>

The lower r.h. limit is 11% at all temperatures.

The upper limit was identified by the point beyond which values for \( R^2 \) for the linear model began to significantly decrease.

### Table 5

Monolayer moisture content \( X_m \) and corresponding r.h. for the fuzzy and starch-coated cottonseeds.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Fuzzy cottonseed</th>
<th>Starch-coated cottonseed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X_m ) % d.b.</td>
<td>( RH ), %</td>
</tr>
<tr>
<td>5</td>
<td>4-58</td>
<td>11-8</td>
</tr>
<tr>
<td>15</td>
<td>4-46</td>
<td>14-8</td>
</tr>
<tr>
<td>25</td>
<td>4-34</td>
<td>17-2</td>
</tr>
<tr>
<td>35</td>
<td>4-24</td>
<td>20-7</td>
</tr>
<tr>
<td>45</td>
<td>4-14</td>
<td>24-5</td>
</tr>
</tbody>
</table>

Estimated values for \( X_m \) and corresponding r.h. of the fuzzy and starch-coated cottonseeds (Table 5) were below the moisture content of 9–14% d.b. and r.h. of 33–75% reported safe for cottonseed storage (Columbus & Mangialardi, 1996; Chapman, 1971). They were also within the range of 4–9% d.b. which is the safest moisture content for seed storage (Harrington, 1960). The values for \( X_m \) of this work are also comparable with those estimated using the literature data (Table 3).
adsorption \( Q = Q_s + h_L \) with \( X \) are provided in Fig. 3 for both cottonseeds. It decreased from 78 and 74 kJ mol\(^{-1}\) for the fuzzy and starch-coated cottonseeds, respectively, with increasing \( X \) and approached to \( h_L \) (44 kJ mol\(^{-1}\)). The decrease in \( Q \) was drastic between \( X_m \) (4–5% d.b.) and \( X = 8\% \) d.b. The change of \( Q \) against \( X \) for the fuzzy and starch-coated cottonseed obeyed the similar empirical formulae:

\[
Q = 44 + 2.8 \times 10^{-4} X^{3.3} \exp(16.4 X) \tag{12}
\]

with a value for \( R^2 \) of 0.997 for fuzzy cottonseed and:

\[
Q = 44 + 12.9 \times 10^{-4} X^{2.9} \exp(10.3 X) \tag{13}
\]

with a value for \( R^2 \) of 0.996 for starch-water cottonseed.

The starch-coated cottonseed exhibited lower values for \( Q \) than the fuzzy cottonseed (Fig. 3) probably due to the weak affinity between the water molecules and the existing crystalline starch discussed previously. During adsorption, the heat liberated by the starch-coated cottonseed would be lower than that by the fuzzy cottonseed which means the less energy consumption for the cooling of the starch-coated cottonseed than the fuzzy cottonseed.

Using the Clasius–Clapeyron equation (Fig. 3) for the range of \( X = 0\% \) d.b. and \( X_m = 4–5\% \) d.b., average \( Q \) was calculated to be 74 and 70 kJ mol\(^{-1}\) for the fuzzy and starch coated cottonseeds, respectively. Using the GAB equation for the same range \((j \leq 1)\), \( h_m \) was estimated to be 75 and 72 kJ mol\(^{-1}\) for the fuzzy and starch-coated cottonseeds, respectively. For most foods, \( Q \) varies between 52 and 86 kJ mol\(^{-1}\) between \( X = 0 \) and \( X = X_m \) (Labuza, 1968). The small difference (2%) between the Clasius–Clapeyron and the GAB methods points to the good performance of the latter in estimating the cooling load for the cottonseed samples for \( X < X_m \).

At \( j = 1 \), e.g. at \( X_m = 4–5\% \) (d.b.), \( Q \) was estimated to be 67 and 64 kJ mol\(^{-1}\) for the fuzzy and starch-coated cottonseeds using the Clasius–Clapeyron equation (Fig. 3). For a vast number of food and agricultural materials at \( X = 4–5\% \) d.b., \( Q \) was reported to be smaller than 100 kJ mol\(^{-1}\) (Maroulis et al., 1988; Iglesias & Chirife, 1976). For example, it was 57 kJ mol\(^{-1}\) for in-shell macadamia nut (Palipane & Driscoll, 1992) and 94 kJ mol\(^{-1}\) for sultana raisin (Saravacos et al., 1986).

For the range of \( X > 5\% \) d.b. and \( X \approx 40\% \) d.b. average \( Q \) was calculated to be 47 and 46 kJ mol\(^{-1}\) for the fuzzy and starch-coated cottonseeds using the Clasius–Clapeyron equation, respectively. Using the GAB equation for the same range \((j > 1 \) and \( j = 9)\), \( h_n \) was determined to be 43 kJ mol\(^{-1}\) for both fuzzy and starch-coated cottonseeds. From Eqn (7) average \( h_n \) was estimated to be 44 kJ mol\(^{-1}\) for both cottonseeds. The good agreement between the given values indicates the comparability of Eqn (7) and the GAB equation to the commonly accepted the Clasius–Clapeyron equation, for determining the cooling load for the cottonseeds above \( X_m \).

The heat values obtained in this work for the fuzzy cottonseed were compared with those estimated using data of Kradangnga (1994) and Henain (1992) (Table 3). Clasius–Clapeyron equation gave enormously high values for \( Q (> 4000 \text{ KJ mol}^{-1}) \) for \( X < X_m \), and 61 and 79 kJ mol\(^{-1}\) above \( X_m \), for the samples of Kradangnga (1994) and Henain (1992), respectively. For both works, the values for \( h_m \) and \( h_n \) were calculated around 91 and 43 kJ mol\(^{-1}\) using the GAB equation, respectively, and average \( h_n \) was determined to be 43 kJ mol\(^{-1}\) using Eqn (7).

5. Conclusions

The GAB equation well described the water vapour adsorption in the fuzzy- and starch-coated cottonseeds. The starch-coating was not effective on the adsorption in the multilayer sorption region, but was effective in the capillary sorption region. The starch-coated cottonseed adsorbed less moisture than fuzzy cottonseed at the same relative humidity and temperature in the capillary sorption region and exhibited greater monolayer moisture content than the fuzzy cottonseed. The starch-coated cottonseed released less heat of adsorption than the fuzzy cottonseed at the same conditions. Considering comparability with the Clasius–Clapeyron equation, the GAB equation, modified as a function of the number
of water layers (Eqn 7), can be used for estimating the heat of adsorption of the fuzzy and starch-coated cottonseeds. The application of the starch coating on the cottonseed is advantageous from view point of water vapour adsorption.

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