Moisture-Sorption Study of Dried Date Fruits

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Abstract

The sorption properties of dried date fruits, Khalas and Handal varieties, were studied at 30°C over a range of water activity, 0.10-0.98. A static gravimetric method was adopted and five sorption models: Bradley, BET (Brunauer, Emmet and Teller), Oswin, Henderson, and GAB (Guggenheim, Anderson and de Boer) were used in the analysis. Both Bradley and Henderson models were suitable for the Khalas variety while Oswin and Bradley models better described the behavior of the Handal variety. Monolayer moisture contents (M_o) for the two date fruit varieties were calculated using both the BET and GAB equations and both varieties of date exhibited the BET type II pattern. The monolayer moisture contents for the two varieties were recommended as the least moisture required for stability of dried date fruits in storage.

Keywords: *Khalas, Handal, models, monolayer, storage stability, water activity***.**

Introduction

Dates have been recognized for a long time as an energy-rich food throughout many countries of the world. However, the production of dates in the world is confined to a limited number of countries, most of them being the Arab countries. The Sultanate of Oman has 35,500 ha of land under date palms, constituting 52% of cultivated area of about 68, 600 ha in the country. The total number of date palm trees amount to more than 8 million trees of various sizes and varieties. Dates are produced for both local consumption and export. Annual production is estimated at about 200,000 t (Ampratwum and Al-Siyabi 2005). In the Middle East and parts of Africa, there exists a large volume of date fruits and post drying stability is of paramount importance as the fruits form a substantial part of energy sources for the people. Mature dates with high moisture content, averaging about 50% wet basis at harvest in Oman, must be dried to preserve them unless they are to be consumed immediately after harvest or placed in low temperature storage.

A fundamental property of a biomaterial that influences dehydration, shelf life predictions and storage stability is its water sorption characteristics (Chukwu and Ajisegiri 2006). Sorption characteristics have been reported to be influenced by environmental conditions such as temperature and relative humidity. Because of the importance of sorption properties coupled with diverse environmental conditions, literature abounds with extensive information on adsorption-desorption phenomena of some food materials (Iglesias and Chirife 1982).

Information on moisture sorption regime is generally required for the storage and enhancement of stability of stored agricultural products, both in raw and processed forms. Moisture sorption isotherm is needed for the prediction and practice of drying and other thermo-related processing of dates. It is also required in the determination of critical values for processing such as equilibrium moisture content, critical moisture content and other moisture regimes. Moisture sorption study is important for the determination of the minimum moisture required for stability of processed dates and therefore necessary information during packaging and selection of packaging materials. However, observations have shown that there is comparatively little information about the sorption characteristics of dried date fruits and such information is worthwhile as aids to preservation techniques.

Several methods have been developed for moisture sorption prediction in food (Caurie 1981; Ajisegiri 1987). However, actual determination of moisture characteristics in some crops is required in order to find the best-fit model for the particular crop. In addition, the information is required to predict the fundamental behavior of the product during handling, processing and storage. The reasons for this study, therefore, are to generate sorption data for dried date fruits in Oman, present moisture isotherm curves for the fruits, interpret the data using established moisture sorption models and state the best predictive models for the fruits.

Materials and Methods

Materials

Dried date fruits of *Khalas* and *Handal* varieties obtained from Samail Dates Factory (SDF) in Oman were used. The fruits were treated with 0.25% sodium azide solution to control mould growth.

Determination of Equilibrium Moisture Content (EMC)

The moisture contents of the dried date fruits were 22 and 20% w.b. for *Khalas* and *Handal* varieties, respectively. Duplicate samples of 50 g each of *Khalas* and *Handal* were placed in polythene mesh basket, which were suspended in equilibrium chambers (transparent wide-mouth jars). Each jar contained a saturated salt solution selected to provide water activity (a_w) from 0.10 to 0.98 at a temperature of 30^{o}C (Iglesias and Chirife 1982). The samples were then conditioned to constant weight over either 96% concentrated sulphuric acid (drying) or 0.5% sodium chloride solution (wetting) in sealed desiccators before the EMC was determined. The static gravimetric method of determining the EMC as presented by Spiess and Wolf (1983) was used. The temperature of 30^{o}C was chosen to simulate the average storage temperature in the Middle East region. This process gave the adsorption mode. After this, the process was reversed to determine the desorption mode. The samples were weighed at intervals of 30 min throughout the experimental period of 15 hours, until equilibrium was reached when four consecutive measurements gave the same readings.

Sorption Equations

A number of equations have been published by various workers to describe the water sorption isotherms of agricultural products. In this study five such models were selected to analyze their suitability for predicting moisture sorption behaviour of dried date fruits. The linearized forms of the models are shown in Table 1. These models were chosen because of their suitability for high carbohydrate foods, application over a wide range of water activities, simplicity, and ease of evaluation. A program was written in BASIC language based on the linear regression equations in Mead and Curnow (1983) to fit the models, calculate the parameters and obtain the coefficients of determination and standard error (SE) of the estimate. All the models were analyzed using the EMC as the dependent variable.

Results and Discussion

The moisture characteristics of the *Khalas* and *Handal* date fruits produced in Oman are shown in Figs. 1 and 2 to emphasize adsorption-desorption patterns. The two graphs are sigmoid and are of type II according to the Brunauer, Emmet and Teller (BET) classification (Labuza 1968). For most biological materials, the adsorption–desorption curves are sigmoid (Labuza 1968) as confirmed by Ajisegiri and Chukwu (2004) and Chukwu and Ajisegiri (2006). The curves also show that the adsorptive and desorptive modes follow different paths. This observation is in agreement with reports in the literature (Iglesias and Chirife 1982; Onayemi and Oluwamukomi 1987).

Tables 2 and 3 summarize the regression analysis for *Khalas* and *Handal* varieties of date fruits, respectively, based on the five sorption models used to predict the adsorptive and desorptive EMC at 30°C. Both the coefficients of determination and SE of the estimates are shown. The coefficients range between 0.7118 ± 0.83–0.9276 ± 0.10 for adsorptive mode and 0.8659 ± 0.32 – 0.9429 ± 0.40 for desorptive mode for *Khalas* date fruits. For the *Handal* date fruits, the coefficients range between 0.9148 ± 0.41 – 0.9366 ± 0.80 and 0.8188 ± 0.62 – 0.9256 ± 0.10 for adsorptive and desorptive modes, respectively. Judging from the SE, the Bradley model gave the best fit. It can be observed that the Bradley and Oswin models gave better fits for the adsorptive mode than for the desorptive mode for the two varieties of dates studied, while the reverse was the case for the Henderson model for the two crops. It can also be observed that the BET and GAB models gave better fits for the desorptive mode than for the adsorptive mode in the case of *Khalas* variety, while the reverse was the case for the two models in the case of *Handal* variety. The reason for this is not immediately known.

It can be summarized from the foregoing that for *Khalas* variety of dates, Bradley model gave the highest coefficient of determination of r^2 = 0.9276 with an SE of the estimate of 1.5% for adsorption data.

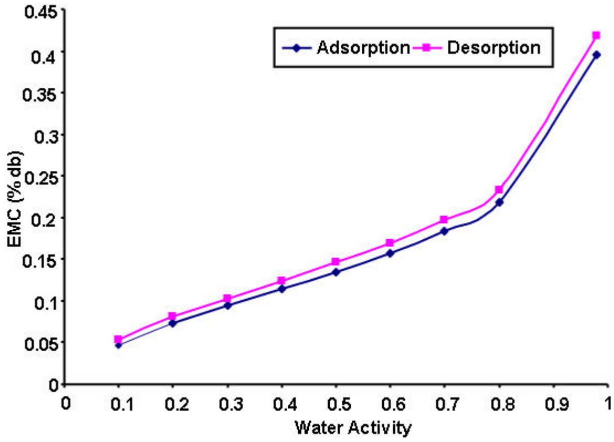

Fig. 1. Moisture-Sorption Isotherms for Khalas at 30°C.

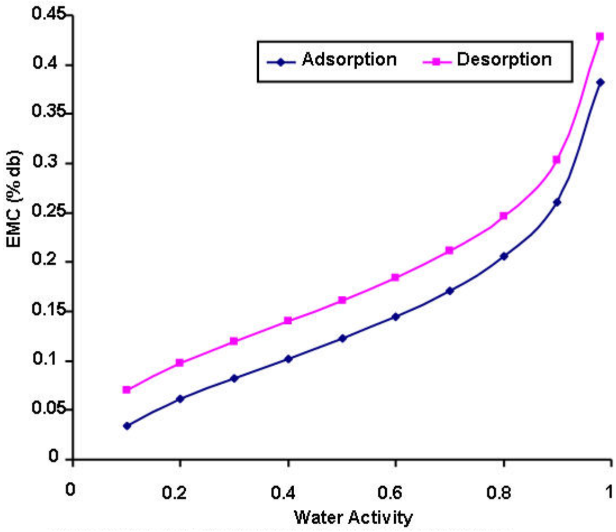

Fig. 2. Moisture-Sorption Isotherms for Handal at 30°C.

Table 1. Sorption models and their linear forms.

Author	Model	Linear Forms
Bradley (1936)	$\ln a_w = A(B)^M$	$\ln(-\ln a_w) = -\ln A - M \ln B$
BET (1938)	$M = \frac{M_O A a_w}{1-a_w} + \frac{M_O A}{(A-1)(1-a_w)}$	$\ln M = \ln(M_O A)(1 + a_w(A-1)) - \ln(A-1)(1-a_w)$
Oswin (1946)	$M = A - \ln(1-a_w)^B$	$M = A - B\ln(1-a_w)$
Henderson (1952)	$M = -\frac{1}{AT}\ln(1-a_w)^{\frac{1}{B}}$	$\ln M = \frac{1}{B}\ln(-\ln(1-a_w)) + \frac{1}{B}\ln\frac{1}{AT}$
GAB (1966)	$M = \frac{M_O A B a_w}{(1-Aa_w)(1-Aa_w+ABa_w)}$	$\ln M = \ln M_O A B a_w - \ln((1-Aa_w)(1-Aa_w+ABa_w))$

Note: *M*, equilibrium moisture content (decimal, dry basis); M_o, monolayer moisture content (decimal, dry basis); a_w = water activity (decimal); *A*, *B*, dimensionless parameters pertinent to each equation; *T*, absolute temperature (K). BET is an acronym formed from the surnames of the three authors that developed the model; GAB is an acronym formed from the surnames of the three authors that developed the model. The models are therefore referred to as BET or GAB model in literature.

Table 2. Suitability of selected sorption models for *Khalas* variety of date fruits at 30°C.

Parameter	Sorption Models Bradley BET Oswin Henderson GAB				
Adsorption					
r^2	0.9276 ± 0.10	0.9221 ± 0.25	0.8889 ± 0.81	0.9249 ± 0.21	0.7118 ± 0.83
SE (%)	1.5	45	21	31	52
A	0.223	15.29	0.0929	0.0564	3.01
B	6.36 x 10^5	-	0.441	1.54	3.19
M_o	-	5.62	-	-	3.45
Desorption					
r^2	0.9055 ± 0.40	0.9338 ± 0.32	0.8659 ± 0.51	0.9429 ± 0.40	0.9226 ± 0.80
SE (%)	1.5	42	19	4.5	11
A	0.281	11.53	0.01449	0.0861	5.65
B	3.92 x 10^5	-	0.289	1.79	1.94
M_o	-	9.51	-	-	10.36

Table 3. Suitability of selected sorption models for *Handal* variety of date fruits at 30°C.

Parameter	Sorption models Bradley BET Oswin Henderson GAB				
Adsorption					
r^2	0.9281 ± 0.10	0.9323 ± 0.84	0.9366 ± 0.80	0.9148 ± 0.41	0.9223 ± 0.91
SE (%)	1.5	47	10	17	25
A	0.227	28.78	0.089	0.0546	6.47
B	7.61 x 10^5	-	0.482	1.43	2.93
M_o	-	4.28	-	-	4.56
Desorption					
r^2	0.9256 ± 0.10	0.9225 ± 0.14	0.9017 ± 0.61	0.9227 ± 0.21	0.8188 ± 0.62
SE (%)	1.5	41	18	14	35
A	0.127	11.85	0.01258	0.0474	5.21
B	4.65x 10^5	-	0.349	1.45	2.82
M_o	-	6.96	-	-	6.24

However, the desorption coefficient was higher when the Henderson model was used for the same crop (r^2 = 0.9429) compared to Bradley model (r^2 = 0.9055) but with a higher SE of 4.5%, compared to 1.5% for Bradley model. Therefore, for prediction of moisture sorption characteristics of *Khalas* variety of date fruits grown in Oman, Bradley model is the best of the models considered for both adsorption and desorption with minimal SE of the estimate. For *Handal* variety, and based purely on the SE of the estimate, the Bradley model gave the best prediction for sorption characteristics (r^2 = 0.9281 adsorption; r^2 = 0.9256 desorption; SE = 1.5%). Therefore, for *Khalas* and *Handal* varieties of date palm grown in Oman, the Bradley equation was the most suitable for moisture characteristics prediction.

Furthermore, the parameters *A*, *B* and M_o under adsorptive mode are different from those under desorptive mode. This is possibly a result of hysteresis exhibited by most biological materials. The EMC curve obtained by drying a wet grain (desorption) is different from the curve obtained by rewetting the dried grain (adsorption or resorption). This phenomenon is known as moisture hysteresis. For a given relative humidity, the moisture content on resorption is always lower than the moisture content at desorption. The theory behind this phenomenon has been dealt with elsewhere (Labuza 1968; 1975). Hysteresis is a natural built-in protective mechanism against extreme cases of too much or too little moisture shock treatment. Therefore, hysteresis could be a manipulative tool to achieving a better storage stability of dried date fruits. The monolayer moisture content (M_o) as presented, represents the minimum (not optimum) moisture to prevent auto-oxidation and to enhance product stability during storage, depending on the method of equilibration of moisture used. At this level of moisture content, it is possible that some trace elements would have been exposed causing a browning effect.

The predictions for the two-parameter models are shown in Tables 4 and 5 for dried fruits of *Khalas* and *Handal* date varieties, respectively. The immediate use of these linear multiple regression equations is in predicting the EMC of dried *Khalas* and *Handal* date fruits at any desired level of a_w, because linearization is the ultimate in an equation. This provides a rapid result approach for estimating the EMC of dried date fruits for storage.

Conclusion

Moisture sorption isotherms were obtained for both *Khalas* and *Handal* varieties of date fruits produced in Oman. The Bradley, BET, Oswin, Henderson, and Guggenheim, Anderson and de Boer equilibrium moisture isotherm equations were used to assess the goodness of fit to experimental data. The Bradley model was found to give the best fit for moisture content prediction in the two varieties of date fruits commonly grown in Oman. This model could therefore be used to plan and evaluate storage conditions and moisture regime in the drying and handling of dates. This information is considered useful for processors and consumers of dates.

Table 4. Multiple regression equations for the two-parameter models for *Khalas* variety.

Adsorption	
Bradley	$\ln(-\ln a_w) = 1.5006 - 13.3630\, M$
BET	$\ln M = 1.7939 + \ln(1 + 14.29a_w) - \ln(1 - a_w)$
Oswin	$M = 0.0929 - 0.441\ln(1 - a_w)$
Henderson	$\ln M = -1.8431 + 0.6494 \ln(-\ln[1 - a_w])$
GAB	$\ln M = 3.5003 + \ln a_w - \ln([1 - 3.01a_w][1 + 6.5919a_w])$
Desorption	
Bradley	$\ln(-\ln a_w) = 1.2694 - 12.8790\, M$
BET	$\ln M = 2.3431 + \ln(1 + 10.53a_w) - \ln(1 - a_w)$
Oswin	$M = 0.0145 - 1.7900\ln(1 - a_w)$
Henderson	$\ln M = -1.8221 + 0.5587 \ln(-\ln[1 - a_w])$
GAB	$\ln M = 4.7323 + \ln a_w - \ln([1 - 5.65a_w][1 + 5.311a_w])$

Table 5. Multiple regression equations for the two-parameter models for *Handal* variety.

Adsorption	
Bradley	$\ln(-\ln a_w) = 1.4828 - 13.5424\, M$
BET	$\ln M = 1.4893 + \ln(1 + 27.78a_w) - \ln(1 - a_w)$
Oswin	$M = 0.0126 - 0.4820\ln(1 - a_w)$
Henderson	$\ln M = -1.9622 + 0.6993 \ln(-\ln[1 - a_w])$
GAB	$\ln M = 4.4595 + \ln a_w - \ln([1 - 6.47a_w][1 + 12.4871a_w])$
Desorption	
Bradley	$\ln(-\ln a_w) = 2.0636 - 13.0498\, M$
BET	$\ln M = 2.0283 + \ln(1 + 10.85a_w) - \ln(1 - a_w)$
Oswin	$M = 0.0126 - 0.3490\ln(1 - a_w)$
Henderson	$\ln M = -1.8377 + 0.6897 \ln(-\ln[1 - a_w])$
GAB	$\ln M = 4.5183 + \ln a_w - \ln([1 - 5.21a_w][1 + 9.4822a_w])$

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