WATER SORPTION ISOTHERMS OF LIBYAN DATE PASTE

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ABSTRACT

WATER SORPTION ISOTHERMS OF LIBYAN DATE PASTE

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Water sorption and desorption isotherms of destoned and ground saiadey jà ul type dates were obtained at 30°C, 40°C and 50°C,using the gravimetric method. Data were analyzed by applying the GAB, BET, Smith, Iglesias & Chirife, Halsey, Henderson and Oswin Models. Isosteric heat of sorption value was calculated using the Clausius-Clapeyron Equation and tried to be as a function of moisture content of dates. It was found that the experimental data fitted well to, Smith, Iglesias and Chirife, Halsey, Hendreson and Oswin equations, which are suitable for high sugar foods. In BET model, the constant C, which is related to the heat of sorption, was negative which is physically impossible. Isosteric heat of sorption for dates varied from 0.9 to – 1.84 KJ/mol as moisture content changed from 11.0 to 18.0 %.

Key words: Dates, Isotherms, Sorption, Water activity, GAB, BET

ÖZ

EZİLMİŞ LİBYA HURMASININ SU SOĞURMA EŞSICAKLIK EĞRİLERİ

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Çekirdekleri çıkartılıp parçalanarak öğütülmüş saiadey ja'ul türü hurmanın suyu yüzeye soğurma ve yüzden salma eşsicaklık eğrileri, 30°C, 40°C ve 50°C'de ağırlıksal yöntem kullanılarak elde edilmiştir. Veriler, GAB, BET, Smith, Iglesias & Chirife, Halsey, Henderson ve Oswin denklemleri uygulanarak incelenmiştir. Yüzeye soğurma değerinin eşbasınç ısısı, Clausius-Clapeyron denklemi kullanılarak hesaplanmış ve hurmaların su içeriğine bağlı olarak açıklanmaya çalışılmıştır. Deneysel verilerin , yüksek şekerli besinler için uygun olan Iglesias ve Chirife, Halsey, Handreson ve Oswin denkliklerine iyi bir uyum gösterdiği bulunmuştur. BET denkleminde ise, yüzeye soğurma ısısı ile bağlantılı olan C değişmezi, eksi bir değer olarak çıkmıştır ki bu fiziksel açıdan olanaksızdır. Hurma için yüzeye soğurmanın eşbasınç ısısı, su içeriği % 11.0 ' den %18.0' e çıkarken – 1.84 ile 0.9 KJ/mol değerleri arasında değişmiştir.

Anahtar Kelimeler: Hurma, Eşbasınç eğrileri, Yüzeye soğurma, Su aktivitesi GAB, BET

ACKNOWLEDGEMENTS

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NOMENCLATURE

a   constant of the material in the Chung & Pfost model, (cal g.mole^{-1})

A   constant in the Smith model, (cm^3)

b   dimensionless constant in the Chung & Pfost model

B   constant in the Smith model, (cm^3)

c   dimensionless constant of the BET model related to the enthalpy of sorption

C   dimensionless constant in the Kuhn model

D   dimensionless constant in the Kuhn model

H   equilibrium RH , P/P$^°$

K   constant in the GAB model related to temperature effect

k   characteristic constant for the material in the Henderson model

L   constant in the Karel model to modify the Henderson model

L_w Latent heat of vaporization of pure water (kJ/kg)

M   equilibrium moisture content(g.H$_z$O/g.dry solid)

M_m monolayer coverage (kg water / kg solid)

X_m GAB monolayer moisture, (kg water/kg drysolid)

M_o monolayer moisture content (g.H20/g.dry solid)

n   exponent, constant of the material in the Henderson model

N   Avogadro'snumber(6.023x10^{23}molecules/kgmolel)

P / P$_°$ Relative humidity

P (1)   monolayer of absorbed water

P (2) constant correcting of the multilayer molecules with respect to the bulk
liquid

Q   net isosteric heat of sorption (cal/g)

R   gas constant (8.32 J g.mole'deg K^{-1})

RH   relative humidity   ,

s   slope of the relation according to the Karel model

S   surface area (m^2/kg solid)

S_W contact surface area of a water molecule (10.6×10^{-20} m^2)

t   thickness of the water layer (m)

T   absolute temperature (K)

C   constant in the GAB model related to temperature

V   volume occupied in the gas phase by n_s moles of sorbate at temperature T and pressure P

V_{wt} volume of water adsorbed (m^3/kg solid)

Xw   Mass fraction (wet basis)

λ_W molecular weight of water (18 kg/kg mole)

Subscripts:

a Adsorption

d Desorption

o Mono-layer value

SUMMARY

The purpose of this study was to obtain sorption and desorption isotherms of macerated date saiady jà ul type (*phoenix dactylifera .L*) at different temperatures in order to use the control of deterioration during storage and drying processes. A sorption isotherm is a plot of equilibrium moisture content versus relative humidity at a given temperature for a material and sigmoid shape for food material. The typical water sorption isotherms are composed of three regions depending on the state of water present; unimolecular layer, multimolecular layer and moisture within the pores. In this study, sorption and desorption of dates pastes were obtained at 30 ˚C, 40˚C and 50˚C Only two of the three regions in the water sorption isotherms were obtained and for all temperatures hysterysis were observed.

In this study, the equilibrium moisture content of date pastes was expressed as a function of temperature and relative humidity of air as sorption isotherms and the relationship between the parameters were obtained. The GAB, BET, Smith, Iglesias & Chirife, Halsey, Henderson and Oswin Models were applied to the water sorption and desorption isotherms, and Smith, Iglesias & chirife, Halsey, Handerson and Oswin models were tested as the most useful moldels.An empirical equation to relate the heat of sorption as a function of moisture content of dates paste was also obtained.

CHAPTER I
INTRODUCTION

1. WATER SORPTION ISOTHERMS

There are lots of very important applications of water sorption isotherms in food science and technology. They are mainly used to control deterioration during food storage. Also, enthalpy of adsorption and desorption of water are used in drying operations.

Sorption isotherm is the plot of equilibrium moisture content of a material subjected to different relative humidities at a given temperature in closed environment. Depending on the direction of water transferred the process is named as adsorption or desorption.

An adsorption isotherm can be obtained by subjecting a relatively dry material to an atmosphere of constant relative humidity and measuring the weight gained at equilibrium due to water and repeating this procedure for different relative humidities. The desorption isotherm is found by placing the wet material into an atmosphere of lower relative humidity and then again determining its equilibrium moisture content (Labuza, 1968).

General types of sorption isotherms are shown in Figure 1 (Brunauer, et.al., 1940). The sorption isotherms of food materials are generally Type II, sigmoid shape with respect to relative humidity, depicting one inflection point, a linear portion and a reflection point. The sorption isotherms of food materials with high fat content are of Type III that behaves parabolically or exponentially.
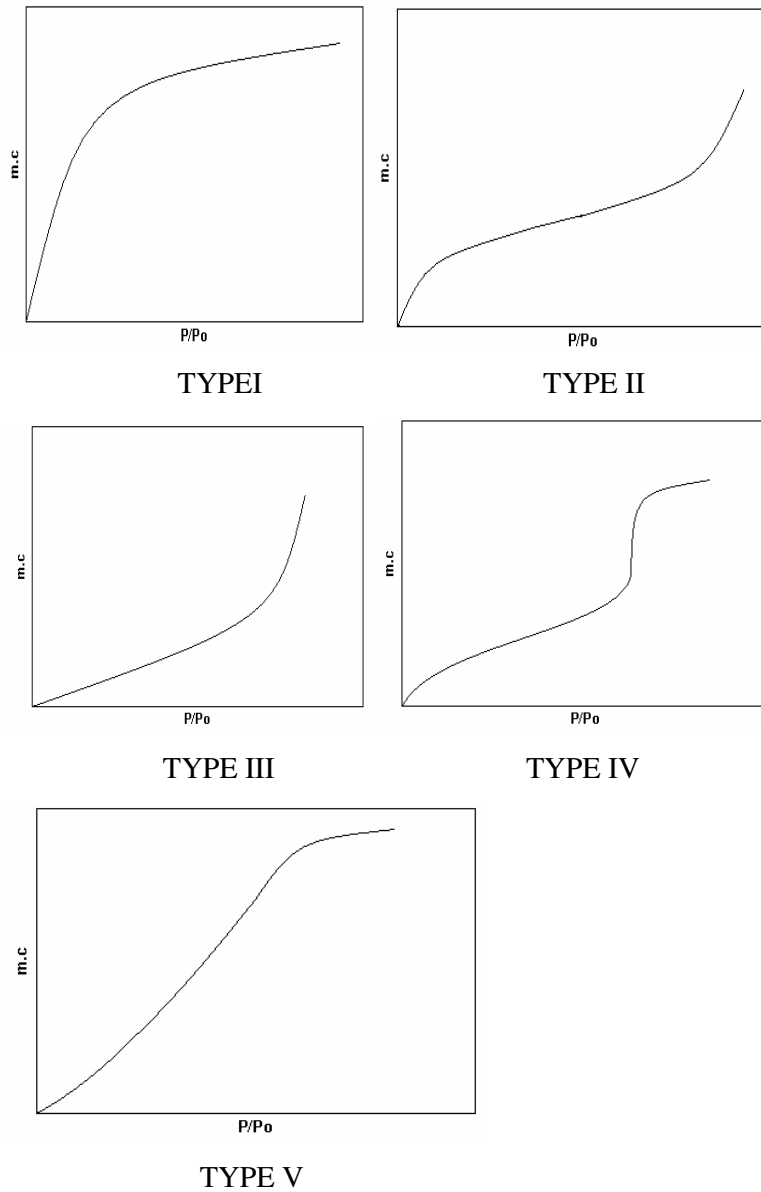
Figure 1.Types of Adsorption Isotherms

In Figure 2, the Type II sorption isotherm is shown in detail. The typical moisture sorption isotherm can be-divided into three regions depending on the state of water present. Since a biological material is a combination of many biological cells, three mechanisms are hypothesized by which water is held by the material.
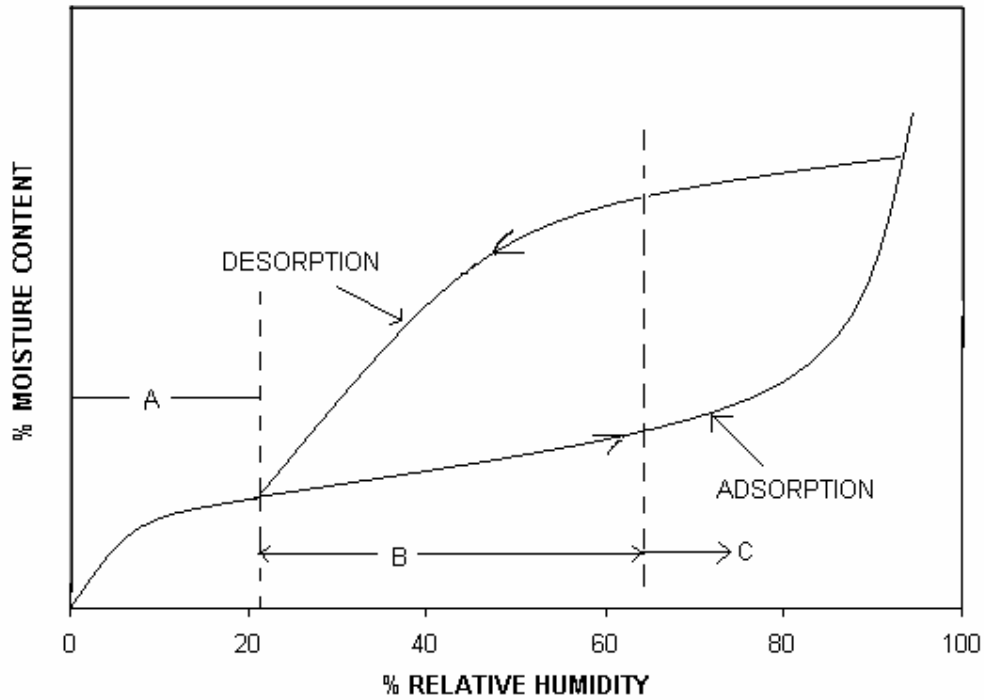
Figure 2. Typical Moisture Sorption Isotherm.

First, there can be a unimolecular layer of water molecules bound to the surface of the adsorbent. Second, there can be multimolecular layers of molecules stacked on top of the first layer. Third, there can be moisture within the capillaries.

Moisture held in the first two ways may correctly be called adsorbed moisture if adsorption is considered as the moisture held on the surface of the cells rather than the exterior surface of the material. However, the moisture within the cells cannot be called adsorbed moisture, because it has actually entered into the cell rather than adhering to the surface (Young and Nelson, 1967).

In Region A water molecules may be bound to an ionic group such as a carboxyl or an amino group or held by molecular forces. In Region B, adsorption of additional layers over this monolayer occurs and water binding is assumed to consist of water molecules bonded by hydrogen bonds to hydroxyl and amide

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groups. Region C corresponds to condensation of water in the pores of the material and is followed by dissolution of the soluble material present (Rockland, 1969).

The heat of adsorption of the water decreases as the moisture content increases. This may be explained by the following hypothesis: The first layer of water molecules is bound to the surface of the cells by forces in excess of those which would bind the water molecules to each other in normal condensation. The second and higher layers of moisture are condensed with a normal heat of condensation. When the moisture content of the material is very low, practically all of the adsorbed moisture will be in the first layer, and will thus have a high heat of adsorption. As the moisture content increases, more and more of the moisture adsorbed will be in the second or higher layers where the condensation is normal, and thus the average heat of adsorption will decrease. With this hypothesis in mind, the first two types of moisture held by the food may be called unimolecular bound moisture and normally condensed moisture, respectively.

1.1. Hysteresis in Sorption Isotherms

In foods, a variety of hysteresis loop shapes can be observed, depending on the type of food. Desorption isotherms usually give a higher water content than adsorption isotherms. In general the types of changes encountered upon adsorption and desorption will depend on the initial state of the sorbent (amorphous versus crystalline), the transitions taking place during adsorption, and the speed of desorption (Young, 1967).

Several theories have been formulated to explain the phenomenon of hysteresis and at present no theory has given a complete insight into the several mechanisms responsible and no quantitative prediction of hysteresis is available in the literature. Thus, the principal factors affecting hysteresis are composition of the product, its temperature, storage time, drying temperature and the number of successive adsorption and desorption. In general, at low moisture content the

heat of desorption was significantly higher than the heat of adsorption (Henderson, 1970).

The adsorption process is completely reversible so that the amount of adsorbed moisture in the food at equilibrium conditions would be the same, regardless of whether the equilibrium was reached in a drying or wetting environment. Then the hysteresis effect must be due to the adsorbed moisture. If a dry biological material is subjected to a wetting environment, moisture first adheres to the surface of the cells, primarily in a unimolecular layer. When a layer of molecules builds up on the surface, increasing diffusion forces tend to cause transfer of moisture into the cell. However, the surface molecules of the cell exert binding forces on the water molecules which prevent them from moving inward. As more and more molecules adhere to the surface, the diffusional forces exceed the binding forces and allow some moisture to move inside the cell. Then, upon a reduction of the vapor pressure of the environment, there is no force to pull the moisture out of the cell until all the moisture has been removed from the surface. At this time, diffusional forces caused by the concentration gradients cause the absorbed moisture to move out of the cell. Thus a hysteresis effect occurs between the sorption and desorption curves.

1.2. Food Composition

The effect of composition of a food on the shape of the isotherm has not been studied very much. In most cases, it can be assumed that the amount of water adsorbed at any relative humidity is derived by the weight percentage of each component times the amount it would adsorb alone.

Proteins and starches adsorb much more water at low relative humidities than do fatty materials or crystalline substances like sugars. Pre-treatment such as heating has little effect on proteins (Hubinger et. al., 1992).

With starch, on the other hand, such pre-treatment increases the amount of crystalline water-impenetrable starch at the expense of amorphous starch. The smaller surface area available for adsorption means that less water will be

adsorbed.

Sugars present a difficult problem because the change from an amorphous to a crystalline state occurs fairly rapidly at normal temperatures. This changeover releases water which will be picked up by other materials if the sugar is present in a mixture such as dried milk (Andrieu et.al., 1986).

1.3. Equilibrium Moisture Content

A knowledge of the equilibrium moisture content of a biological material is essential for the efficient design and operation of systems for drying, wetting, or storing the material. The equilibrium moisture content for a given environment may be defined as the moisture content which the material would approach if left in that environment for an infinite period of time (Young and Nelson, 1967).

Equilibrium moisture content is directly related to drying and storing of hygroscopic materials which are likely to be influenced from atmospheric water vapor. Equilibrium relative humidity of the air, in contact with the material, determines whether it will gain or lose moisture in a particular environment (Dinçer and Esin, 1995).

1.4 Methods for Determination of Sorption Isotherms

A variety of methods has been developed and used for determining sorption and desorption isotherms of food materials. There are two main methods for the derivation of these isotherms. The first method is based on the production of a range of samples of known moisture contents. The water activity of each of these samples is recorded and the isotherm plotted from the collected data. This technique can require water activity determinations of many samples. Furthermore, the determination of the desorption isotherm is almost impossible, and the method is thus considered impractical.

The second method entails exposure of a sample of known moisture content to a series of predetermined humidities. After a period of time at a particular

humidity, the sample will equilibrate and the weight gain represents the water adsorbed. The humidity is successively raised to the next higher setting, and each equilibration weight is recorded. The adsorption isotherm is then plotted. The desorption isotherm is determined in a like manner except that the humidity series is reversed and is slowly dehydrated by lowering the humidity of the immediate atmosphere. This technique works well but the time to equilibration can take long time.

Labuza (1975) have published the results of a survey of the 32 different methods for the determination of the adsorption or the desorption isotherms (Van Doore, 1985). This work showed that the most favored technique is the desiccator method in which a weighed sample is placed in a desiccator, maintained at a known relative humidity by saturated salt solutions, until a constant weight is obtained. The moisture content of the sample is then determined. This method suffers from extreme slowness in reaching equilibration.

An improvement to this technique came from Steinberg (1981) (Van Doore, 1985). His system used a small plastic chamber into the base of which was poured the saturated salt solution. The sample was suspended above this on a circle of filter paper. This modification drastically reduced the volume of the system, compared with the traditional desiccator, while at the same time it preserved a proven method.

The equilibrium methods outlined so far are tedious because the system comes to equilibrium mainly via molecular diffusion. An attempt was made to speed up this basic desiccator technique by the incorporation of a fan into the system. The instrument is called an isopiestic sorption apparatus. It uses a saturated salt solution in a center container to humidify the air, with a fan for circulation. This device has two major drawbacks. Firstly, the fan will always introduce a heating factor, thus possibly rendering the system thermally unstable. Secondly, to achieve rapid equilibration the sample sizes are limited to 10-100 mg.

It is obvious from the shortcomings of the static techniques, that a dynamic

system could be advantageous. The method involves repeated circulation of the same humid air over the sample in an enclosed system. After equilibration, the water in the air was removed by adsorption in concentrated sulfuric acid and the change in the volume of the air measured. This method is used in the confectionery industry. It is accurate but requires highly skilled operators to obtain reliable results.

The "sorption rate" technique is another dynamic system. This technique does not require the samples to reach equilibration. It is based on the calculation of the rate of loss or gain of moisture in a set of identical samples of the same weight and surface area. It depends on the vapor pressure difference between the sample and its environment when each sample is exposed to different relative humidities.

1.5. Temperature Shift of Isotherms

Temperature shift of isotherms are mainly due to the change in water binding, dissociation of water or increase the solubility of solute in water. The reliable data on the influence of temperature on sorption isotherms are relatively scarce. It is widely accepted that an increase in temperature results in decreased equilibrium moisture content. The curves for several temperatures intersect. While for relative humidity values higher than 70% there was inversion of the effect of temperature (i.e., equilibrium moisture content increased with temperature). This was due to an increase in solubility of sugars in water. The intersection (inversion) point depends on the composition of the food and the solubility of sugars. For products with protein or starch content, there is also no intersection point with the increase of temperature (Iglesias et.al., 1986).

Clausius-Clapeyron equation is often used to predict the temperature effect on relative humidity. The Clausius-Clapeyron equation can be written as:

$$\ln RH_2 / RH_1 = Q_s / R (1/T_1 - T_2) \tag{1}$$

The assumptions in the above equation are: (1) the heat of vaporization of pure water and excess heat of sorption (Q_s) do not change between T_1, and T_2, (2) the moisture content of the system remains constant (Chen, 1971).

$$Q_d/\lambda_w = 1+0.9386[\exp(-0.3249X_W)] \tag{2}$$

where, λ_w, latent heat of vaporization of pure water, X_w= mass fraction

$$Q_a=\xi \exp (-M/\eta) \text{ where } \xi \text{ and } \eta \text{ are constants} \tag{3}$$

2. MODELS OF ISOTHERMS

There are many equations for describing the sorption isotherm of different food products (Table 1). Some of them are entirely empirical in nature while others have a theoretical basis. Water sorption isotherms in foods are of special interest in many aspects of food storage, drying, preservation by dehydration, especially for the prediction of the shelf life of a dried product in a packaging material or the prediction of drying times of foodstuffs (Iglesias and Chirife, 1976).

2.1. GAB Model

The Guggenheim-Anderson-de Boer (GAB) model is a semi-theoretical multimolecular localized homogeneous adsorption model and has been considered the best fit model for many food materials over a wide range of relative humidity and can be written as;

$$M= (M_{gm}YK (RH))/ ((1-K (RH)) (1-K (RH) +Y (RH))) \tag{4}$$

where, M_{gm} is GAB monolayer moisture, Y and K are related to the temperature. The GAB isotherm equation is an extension of the two parameter BET model which takes into account the modified properties of

Table 1: Some Isotherm Equations

NAME	EQUATION	PRODUCTS	REFERENCES
GAB Equation	$M=(XmCK(RH))/((1-K(RH))(1-K(RH)+C(RH))$	Grains, dairy products,nuts,fruits	Bizot(1983)
Smith Equation	$M=A-B \ln(1-RH)$	Cerela,nut,starchy foods	Smith(1974)
BET Equation	$RH/(M(1-RH))= 1/Moc+((c-1)/Moc)RH$	Cereals ,fruits,vegetables,starchy foods	Brunauer,Emmet&Teller(1938)
Kuhn Equation	$M=C/\ln (1/(RH))+D$	Cereals ,nuts, spices ,starch foods	Kelvin(1871)
Henderson Equation	$1-RH =\exp-(KM^n)$	Spices ,starchy foods	Henderson (1952)
Karel Equation	$\mathrm{loglog} (1/1-RH)s\mathrm{log} (M) +L$	Starchy foods	Karel (1955)
Chung-Pfost Equation	$\ln(RH)=a/(RH) \exp(-bM)$	Starchy foods	Chung & Pfost(1967)
Halsey Equation	$RH=\exp(-P(1)/MP(2))$	Cereals ,fruits	Halsey (1948)
Harkins&Jura Equation	$\ln (RH)=E-F/V^2$	Cereals ,grains	Harkins &Jura (1944)
Iglesias&Chirife Equation	$\ln(M+(M^2+M0.5)^{1/2})=P(1)H+P(2)$	Cereals,vegetables,fruits	Iglesias &Chirife(1976)
Oswin Equation	$M=P(1)(H/(1-H))P(2)$	Meat, vegetables, starchy foods	Oswin (1946)

The sorbate in the multilayer region and bulk liquid properties through the introduction of a third parameter K. If K is less than unity, a lower sorption than that demanded by the BET model is predicted and allows the GAB isotherm to be successful up to relative humidities 0.90. When K=1 and if K>1 the sorption will become infinite at a value of relative humidity less than unity which is physically unsound. GAB model has been used for some varieties of dates by Alhamdan (1999) (Table 2).

2.2. Smith Model

Smith developed an empirical model to describe the final curved portion of water sorption isotherm of bio-polymers with high molecular weight. It has been found that this equation could be used between 0.5 to 0.95 relative humidity.

Smith equation was expressed as,

$$M=A-B \ln (1-RH) \tag{5}$$

where A and B are dimensionless constants for the material. The parameter represents moisture bound to the surface and the parameter B represents the moisture in a unimolecular layer of normally condensed moisture in Equation 5.

2.3. BET Isotherm

The isotherm model with the greatest popularity, in all fields of interest, is the BET Isotherm developed by Brunauer, Emmet and Teller in 1938. The BET equation gives a sigmoidal-type isotherm similar to the type observed experimentally for biological materials. However, for most biological materials the predicted equilibrium moisture content isotherms generally approach infinity too rapidly above relative humidities of approximately 50 percent (Young, 1962).

It is well known that despite the theoretical limitations of the BET

adsorption analysis, the BET monolayer concept is a reasonably correct guide with respect to various aspects of interest in dried foods (Chirife and Iglesias, 1984).

BET theory is based on the concept of a sorbed molecule which is not free to move over the surface and which exerts no lateral surfaces on molecules sorbed on adjacent sites. When a surface is in equilibrium with a gas phase at a particular concentration, in general the number of molecules on each part of the surface will not be the same, but the net amount of surface associated with non-molecular layer, with a bimolecular layer, and so on, will be constant.

The general form of the BET equation is;

$$RH/[M(1-RH)] = 1/M_oc + [(c-1)lM_oc]RU \qquad (6)$$

RH/ [M (1-RIT)] versus RH plot is simply named as the BET plot, where monolayer value and constant c are evaluated from the slope and the intercept of the line. Determination of the monolayer value from the BET plot is the most important aspect of the equation since the optimum stability of the food products is at its monolayer coverage value, i.e. moisture content of a product when the monolayer completed (Dinçer and Esin 1995).

2.4. Kuhn Model

Another equation suggested by Kuhn was expressed as;

$$M = C/ln(1/(RH)) + D$$

where C and D are constants $\qquad (7)$

2.5. Henderson Model

Henderson (1970) has developed an empirical equation to cover the whole Isotherm by using 18 different hygroscopic products. A widely used model

relating relative humidity and amount of sorbed water in food is,

$$1-RH = \exp(-kM^n) \tag{8}$$

This may be written as,

$$\ln[-\ln(1-RH)] = n\ln M + \ln k \tag{9}$$

2.6. Karel Model

Karel (1955) employed a great number of experimental data for evaluation of constants in Henderson' equation (1952) and eliminated the temperature term, since the constants deviated greatly with temperature. Then the equation becomes:

$$\log\log(1/1-RH) = n\log(M) + Y \tag{10}$$

where, $Y = \log(k) - \log(2.303)$

Rockland (1969) made sorption experiments on some food materials and introduced a new concept named as "localized isotherm". Plot of loglog (1/ (1-RH)) versus log (M) for the obtained data gave two or three intersecting lines rather than a single straight line. With these results, Rockland stated that the complete moisture sorption is composed of coupled independent localized isotherms each representing a limited relative humidity interval and each may represent a special type of water binding (Ferro et.al.,1982).

2.7. Chung & Phost Model

The equation developed by Chung and Phost (1967) usually fits to cereal products and was of the form:

$$\ln(RH) = a/(RT)\exp(-bM) \tag{11}$$

It may be expressed as;

$$M = [\ln A/(RT)\text{-In }[\text{-}\ln(RH)]]/B \qquad\qquad (12)$$

The Chung - Phost equation is based on directly upon an assumption about the way in which the free energy change for sorption or desorption is related to moisture content (Young, 1967).

2.8. Halsey Model

Halsey equation (1948) was expressed as;

$$RH = \exp(\text{-}P(1)/MP(2)) \qquad\qquad (13)$$

where P(1) and P(2) are constants.

Many authors, concerned with the drying of food products, have concentrated their efforts on the desorption isotherm. Brooker et.al. (1974) examined a number of equations using the desorption data obtained on major cereal grains. They concluded that the accuracy of an empirical equation was greater than that of a theoretical or semi-theoretical approach. Since the accuracy of the equation used in modeling and in grain drier design is important, empirical equations were therefore of more practical interest in such applications (Pixton, 1973).

There exists many models in literature but in this part only some of empirical equations will be introduced, which are useful for nuts and grains especially.

PREVIOUS STUDIES ON THE EQUILIBRIUM MOISTURE CONTENT OF DATES:

Table 2.Constants for the GAB Equation (Alhamdan, 1999)

Dates cultivars	Temp^{O}C	M_m	C	K
Ruziz	5	0.173	13.980	0.560
Ruziz	25	0.154	2.790	0.840
Ruziz	40	0.137	4.760	0.950
Khudari	5	0.148	7.220	0.690
Khudari	25	0.132	5.863	0.849
Khudari	40	0.063	5.863	1.324
Khlass	5	0.167	8.350	0.578
Khlass	25	0.143	7.530	0.781
Khlass	40	0.117	3.220	1.062

In 1999, Alhamdan has used Halsey Equation for some date cultivars

Table 3. Constants for the Halsey Equation (Alhamdan,1999)

$\ln M=(1/r)\ln c -(1/r)\ln[\ln(1/a_w)]$				
Dates cultivars	**Temp ^{O}C**	R	c	R^2
Ruziz	5	15.073	14.895	0.871
Ruziz	25	5.885	2.205	0.963
Ruziz	40	4.007	1.941	0.899
Khudari	5	12.083	7.163	0.942
Khudari	25	7.891	3.351	0.931
Khudari	40	3.864	1.850	0.924
Khlass	5	14.853	10.889	0.924
Khlass	25	9.175	4.129	0.898
Khlass	40	3.198	1.721	0.948

3.1 Dates

Considered as one of the most ancient cultivated plants, the date palm (Phoenix dactylifera.L) is mainly present in Mediterranean Africa, Middle East, and Asia. The world-wide production of dates is about 7 million tones, FAO (2004). In Libya, there are about 8.5 millions of date trees. Annual production is estimated as over 140.000 tons of more than 400 different date cultivars.

The date is a sugar-rich and low-moisture material (on the average, the sugar content is 0.8 g per g dry solid).The sugars are of reducing or non-reducing type. The biochemical composition of the fruit is of strong interest since it constitutes the main part of the ration for people in certain countries (Ahmed, Al-Gharibi, Daara & Kabir 1995; Reynes, Bouabidi, Piombo & Ristrucci, 1994; Booidj et al., 1992; Khalifa & Sidahmed, 1988; Magboul & Noura, 1985; Hussein, 1974; Munier, 1971; Dowson & Atten, 1963; Munier, 1961; Cook & Furr, 1953; Cavel, 1947).

Presently, considerable proportion of the dates exported by North-African countries does not fulfil FAO/OMS Codex Alimentarus - ONU-DF 08. The water content is variable, with differences as high as 25%. The biochemical and microbial stabilities of a food product such as the date, subjected to transportation and storage before marketing, need a control of the water content and water activity (a_w). which should be below 0.65. Water sorption isotherms are useful in predicting the interaction of the solid with the water vapor in the atmosphere, during storage and after packaging. Types of packaging used must also be considered. They are also a useful tool for understanding the water behavior during heat processing, such as drying (Rahman, Prera & Thebaud, 1997; Lewicki, 1997; Themelin, Aymard, Lebert & Guilbert, 1995; Chuzel & Zakhia, 1991; Ayranci, Ayranci & Dogantan, 1990; Saravacos & Tsiourvas, 1986; Multon, Bizot &Martin, 1981; Bolin, 1980).

There is enormous potential for fresh dates and date products with better quality attributes. Date processing industries are producing various date products like date-paste, date-syrup, date-dip, date-honey, date-jam, date-vinegar, etc. Date

is steamed, destoned, macerated, and converted to a semi-solid form known as paste. Paste is an intermediate moist food as it contains approximately 20–23% moisture content and the water activity lies below 0.6. Date paste has been utilized as a filler and also to substitute for sugar in many food formulations. The confectionary industry has utilized date paste as one of its major ingredients (Alhamdan & Hassan, 1999). Therefore, studies on date paste are relevant to generate physico-chemical parameters that would help the processing industries to design new food products.

Water activity (a_w) is an important tool to predict available water in foods and the physical state of solid foods (Roos, 1995). Water activity is defined as the ratio of the vapour pressure of water in a food to the vapour pressure of pure water at the same temperature. The relationship between moisture content and the corresponding water activity of a food over a wide range at constant temperature represents a graphical form known as the moisture sorption isotherm (MSI). These are indispensable tools of the food technologists (Karel, Fennema, & Lund, 1975; Labuza, 1984). The concept of water activity has been adopted by food regulatory agencies in defining safety regulations regarding growth of undesirable micro-organisms, definitions of food hazards, critical control points, standards for various preserved foods and packaging requirements (Fontana, 2000).

It is generally accepted that water activity (a_w) is more closely related to physical, chemical, and biological properties of foods and other natural products than to its total moisture content. Specific changes in color, aroma, flavor, texture, stability, and acceptability of raw and processed food have been associated with relatively narrow water activity ranges (Rockland, 1969). The sorption isotherms reveal information about sorption mechanisms and interaction of food biopolymers with water. They are very useful in design and optimization of unit operations such as preservation, drying, mixing, storing, and packaging (Van den Berg, 1984).

3.2 Previous Studies on The Equilibrium Moisture Content of Date Pastes

Studies on equilibrium moisture content of omani dates performed by (Robert ,1998) have shown that moisture sorption isotherms conducted at three temperatures displayed a crossing effect due to the dissolution of crystalline sugars at higher temperatures and moisture contents. Modeling with the GAB equation predicted monolayer moisture contents (X_m) of 13.9% for Fard and 14.4% for Khalas. Isosteric heat of sorption, for both varieties, varied from 9.4 to - 1.6 KJ/mo1 as the moisture content changed from 5.0 to 40.0%. Differences in moisture sorption behavior of the two varieties were attributed to compositional differences Robert M. Myhara, (1998).

Studies on water sorption isotherms of dates were performed by R.M.Myhara et.al. (1998). Water sorption isotherms at 15, 25 and 45°C were determined for two date varieties. Water sorption modeling was carried out using the five-parameter Guggenheim-Anderson-de Boer (GAB) equation, a modified-GAB equation and a novel artificial neural network (ANN) approach. Modeling using the GAB equations used physical data as input, while the ANN approach used both physical and chemical compositional data. The five-parameter GAB equation had a lower mean relative error (approximately 7%) than the modified-GAB equation (approximately 16%), in predicting equilibrium moisture content M. The effects of temperature on the water sorption isotherms were not evident with the five-parameter GAB equation. Although the temperature effects on water sorption isotherms were evident with the modified GAB equation, the overall error was very high. Neither GAB equation could predict the water sorption isotherm crossing, an effect observed in the experimental data. An ANN model, optimized by trial and error, was superior to both GAB equations. It could predict M with a mean relative error of 4.31% and standard error of moisture content of 1.36 g/kg. The correlation coefficients (r^2) of the relationships between the actual and predicted values of equilibrium moisture content and date varieties obtained by the ANN were 0.9978 and 0.9999 respectively. The ANN model was able to capture water sorption isotherm crossing due to temperature effects. Water

activity and chemical compositional data, however, had more impact upon the water sorption isotherms than temperature (R.M.Myhara, 1998).

The study which done by A.M.Alhamdan and his coworkers in 1999 indicated that the water sorption isotherms of pastes of three date cultivars (Ruziz, Khudari, and Khlass) were determined using the static method of saturated salt solutions at three storage temperatures: 5°C, 25°C and 40°C. The effect of temperature on sorption behavior was more pronounced than the effect of date cultivar. Equilibrium moisture content decreased with increasing temperature at water activities below 0.45-0.55. However, above 0.45-0.55, equilibrium moisture content increased with increase in temperature, mainly due to the additional dissolution of sugars at higher temperatures. The experimental data fitted well to GAB, Iglesias and Chirife, and Halsey equations, suitable for high sugar foods (Abdullah M.Alhamdan 1999).

In the study on desorption isotherms of Tunisia Deglet Nour dates at four temperatures (30, 40, 50, 60°C)(Nabil and Mohamed 2000) it was found that the desorption isotherms of Deglet Nour date gave the S-shaped characteristic curve, typical of many sorption isotherms of food.The Guggenheim Anderson and de Boer (GAB) equation is suitable for representing the relationship between water activity and equilibrium moisture content of date in the range of water activity 0-0.9 . Hence, it may be applied for processing and storage programming of these products. and the monolayer values were found to range between 0.026 and 0.153 Kg/Kg d.b, depending on temperature (Kechaou.et.al2000).

A.Belarbi et al,(2000) studied the water vapour desorption isotherms, at 25°C, of the eleven date varieties, from diferent locations, collected at full ripeness: Mech-Degla, Deglet-Nour and Haloua (Algeria), Barhi, Fardd, Khadrawi, Khalass,Madjol, Rizaz (Saudi Arabia), Madjhoul (Israel) and Kentichi (Tunisia). He used the static gravimetric method, according to the COST 90 recommendations. The overall shape of the curves describing the water content as function of the water activity was typical of sugar-rich materials. Experimental data were analysed using the (GAB) and the (BET) models, through direct non-linear regression without any transformation of data. Both models correctly

represented the whole set of data, in water activity range from 0.11 to 0.90, but the BET model was preferred since the values of its parameters were more realistic.

4.AIM OF THE RESEARCH

The objectives of this study were to determine the water sorption isotherms of dates pastes at different temperatures 30^0C ,40 ^{0}C and 50 ^{0}C and the correlate experimental sorption data with seven well-known high sugar foods sorption isotherms equations, namely BTE , GAB , Smith , Iglesias & Chirife , Halsey,Henderson and Oswin equations, and the most suitable equation was determined by comparing the data obtained with the various equations proposed in literature.

CHAPTER II

EXPERIMENTAL

1.   Apparatus

In this study, an experimental set-up was constructed on the basis of the gravimetric method with modified static system to measure the equilibrium moisture content of dates as a function of relative humidity and temperature. Set-up proposed by Bosin and Easthouse (1970) was modified to work at different temperature conditions (Dinçer and Esin, 1995).

A laboratory oven (NUVE,ES 400 , 0-125 ± 0.1°C, chamber dimensions 24.5x28.0x41.5cm) was used as the constant humidity chamber (Figure 3). A sample holder was suspended by a steel wire to a digital balance (100 ± 0.01 gr) placed on one of the two openings at the top of the oven. The relative humidity probe (10-96±%2,-30/+ 80°C) was inserted through the other opening. Constant relative humidity inside the oven was maintained by the saturated salt solutions placed in the plastic cuvette. The cuvette dimensions were 17x25x6 cm providing maximum contact of the solution with the confined air to have efficient evaporation. Further, homogeneity of the humidity of the chamber air was maintained by the electrically driven fan mounted on the back wall of the oven.   .

Dates used in the experiments were saiadey ja` ul type and have been brought from Benghazi Libya during the 2005 season. Average moisture content of the dates was 25% (w/w) when received. ,Than these were destined ,macerated and converted to a paste like semi-solid form which was dried in the air-oven at 80 ˚C for 48 h to the moisture content of 10.5 % .The resulting date paste was put in polyethylene bag and stored at $4^{°}$C in a refrigerator.

Figure 3 .The front view of the experimental set-up.

2. Procedure

In-the experiments, the moisture content determinations were done according to offical methods A.O.A.C(1990).Average moisture content of the date paste sample used was 10.5 %(w/w).

Equilibrium moisture content of the samples were measured at three temperatures 30, 40 and 50 °C and at least five or six relative humidity conditions in the range of 10-97%. Constant relative humidity was sustained by using saturated salt solutions (Spencer 1917, O'Brien 1948, Rockland 1969). The percent relative humidities observed for the saturated salt solutions are given in Table (4) at each operating temperature and for the set-up used.

For the adsorption experiments, date paste samples of about 3 g was used. The saturated salt solution, corresponding to the lowest relative humidity, was placed in the oven in the cuvette. Then, the desired temperature was adjusted and held for some time for the system to come up.Then the date paste sample was placed into the oven by attaching it to the balance. It was observed that constant relative humidity inside the chamber was maintained, at maximum, in 30 minutes. The sample was weighed intermittently until no change in weight was observed, as measured to the second decimal place (Zurith et.al., 1979). Usually, the time to reach equilibrium was about (75) hours. After the

equilibrium was attained, the weight of the sample was recorded and equilibrium moisture content was calculated on dry basis.

Upon recording the data, the dates paste sample was subjected to a higher relative humidity condition by using the next salt solution in the rank and allowed to reach equilibrium. To obtain sorption isotherm, equilibrium moisture content values of date paste were measured at the provided relative humidity conditions in increasing order. Finally, the sample was exposed to the highest relative humidity by placing pure water into the cuvette.

To obtain the desorption isotherm; the same saturated solutions were used for the same sample, but in this case in decreasing relative humidity order. After the desorption procedure was completed, sample was placed in an oven at 135℃ for 2 hours and the amount of dry solid present in the sample was determined .

Upon completing a set of adsorption and desorption data, the temperature was readjusted to another experimental value and the entire procedure, as explained above, was repeated for all of the temperatures.

Table 4.Percent relative humidities of the chamber according to the saturated salt solutions used in the experiments

Adsorption			
Temprature (˚C)			
Saturated Salt Solution	30	40	50
LiCl	20.0	17.0	14.0
K_2CO_3	44.0	36.0	24.0
$Mg(NO_3)_2.6H_2O$	51.0	48.0	38.0
NaCl	60.0	53.0	41.0
KNO_3	68.0	62.0	50.0
H_20	78.0	74.0	65.0
Desorption			
Temprature (˚C)			
Saturated Salt Solution	30	40	50
KNO_3	52.0	48.0	40.0
NaCl	49.0	42.0	35.0
$Mg(NO_3)_2.6H_2O$	37.0	41.0	33.0
K_2CO_3	33.0	29.0	22.0
LiCl	13.6	16.0	10.0

CHAPTER III

RESULTS AND DISCUSSION

Sorption isotherms of the dates paste were obtained at 30, 40 and 50°C. The data were treated with respect to the BET ,GAB ,Smith ,Iglesias and Chirife, Henderson ,Oswin equation and Halsey equations**.** Variation of the heat of sorption with equilibrium moisture content and temperture was also determined by using the Clausius-Clapeyron relation.Finally, modified BET equation was used and the monolayer values were calculated . Calculations were performed using sigma plot the package program**.**

3.1 Experimental Results

Experimental results, equilibrium moisture content and relative humidity values, at 30, 40 and 50 $^{\circ}$C are given in Appendix A. Data are plotted as equilibrium moisture content values, on dry basis, at different relative humidities for each temperature (Figures 4a-4b-4c).
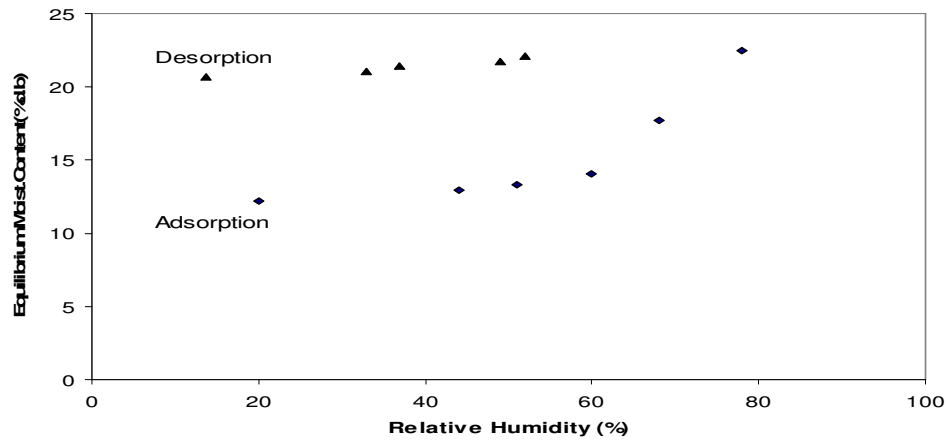
Figure 4.a. Desorption and adsorption Isotherms of the date paste at 30˚C

Figure 4.b. Desorption and adsorption isotherms of the date paste at 40˚C

The results indicated that the adsorption isothems of the date pastes exhibit about the Type II curved.

The sigmoid shapes of the sorption isotherms shown in Fig.4a-4b-4c indicate the characteristics of high sugar foods (Tsami et al.,1990). In the first segment (low relative humidity) of the so named S-shaped sorption isothem curves,the date

pastes sorbed relatively lower amounts of moisture due to the water sorption of biopolymers (high molecular weight components). However, large amount of moisture was absorbed at higher relative humidities (above 0.45-0.55 range) due to the dominant water sorption capacity of sugars.
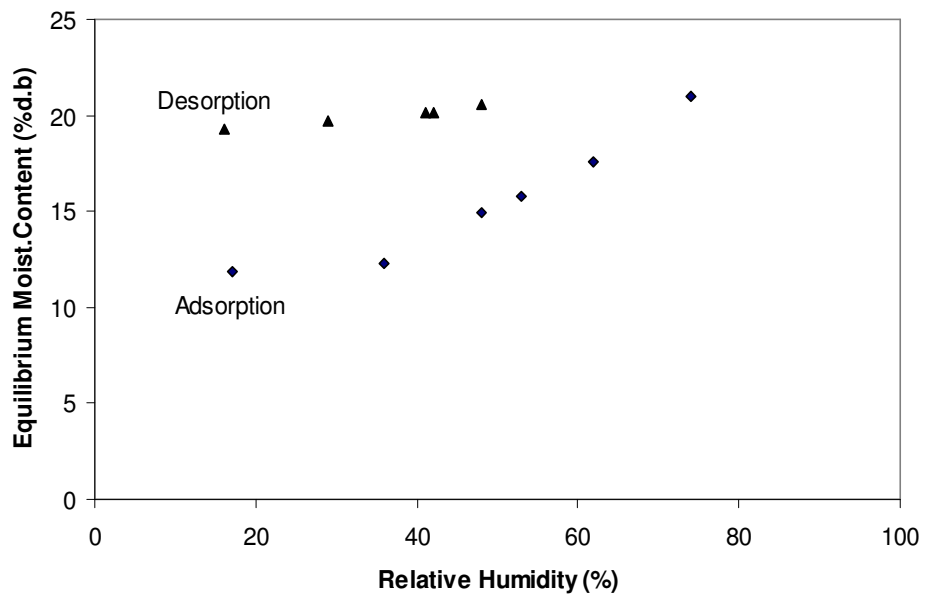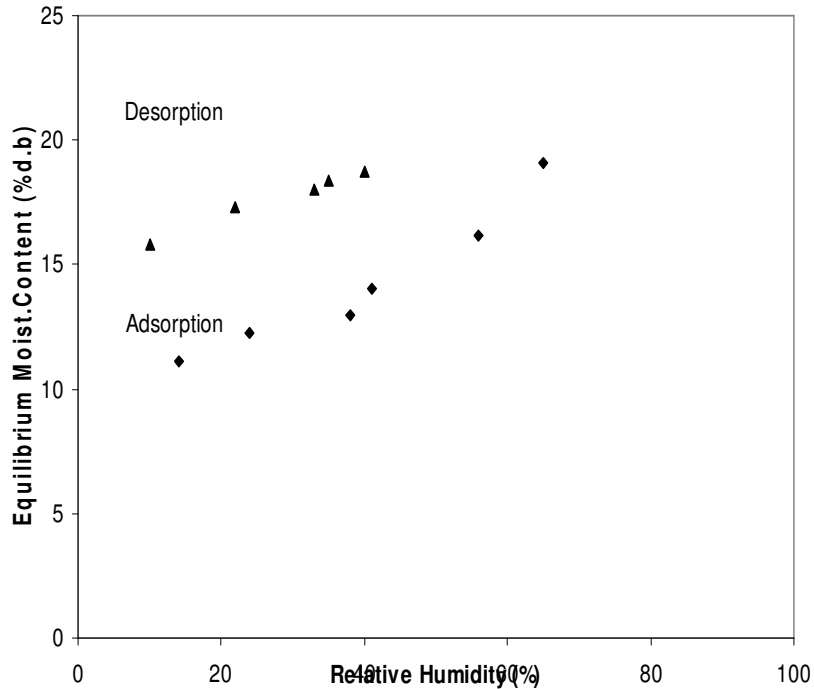

Figure 4.c. Desorption and adsorption isotherms of the date paste at 50˚C

Water is more strongly bound at lower temperatures with a concomitant increase in a_w as temperature increases. This trend, evident in this study at lower a_w levels,is due to water sorption onto primary sites of hydrophilic compounds present in the dates(Saravacos et al., 1986) . At higher a_w levels a reversal of this occurs where a_w levels are lower at constant M, as temperture increases. The result is a crossing of moisture sorption isotherms conducted at differing temperatures. Dates contain large quantities of fructose and glucose, which at low temperature and equilibrium moisture contents may at least partly be present in crystalline form.The crossing phenomenon described above is due to the incresed

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solubility of sugars as temperature is increased.The increased quantity of sugar in solution binds large amounts of water thus, decreasing water activity.Similar results have been obtained (Saravacos *et al*., 1986; Ayranci *et al* .,1990; Tsami *et al*.,1990;Robert M.Myhara. *et a*l., 1998).for other high sugar fruits. As glucose concentration increases , this crossing shall be expected to move down the curve to lower a_w values.

Lower relative humidities, below 10% ,could not be stuided as this necessitates the room air humidity be at least below 10 % from the treud of isotherms.Hence behaviour of the isotherms in the monolayer region could not be detected. Nevertheless it can be stated the monolayer is completed at relative humidities above of 10% and up to 20%.

There was a marked hystersis in the sorption isotherms for all temperatures .As expected, for most biological materials, hystersis decreased at low and high relative humediates and the maximum hysteresis was at the intermediate RH values.

The effect of temperature on adsorption and desorption isotherms are given in Figures 5a and 5b. For most food products it is widely accepted that an increase in temperature increases the water activity(Alhamdan,1999).This was valid for this study also but up to a water activity range of 0.45-0.55. In this range crossing of sorption isotherms curves of the different temperatures were observed. Above this range,it was found that increase in temperature resulted in a decrease of water activity. The crossing phenomenon of those curves was observed by several investigators (Saravacos et al.,1986; Tsami et al., 1990; Hassan 1991; Leiras & Iglesias,1991; Ayranci et al.,1990 Manuel & Sereno,1993) for high sugar foods. Saravacos et al.(1986) explained this trend by the dissolution of sugars resulting with an endothermic process.
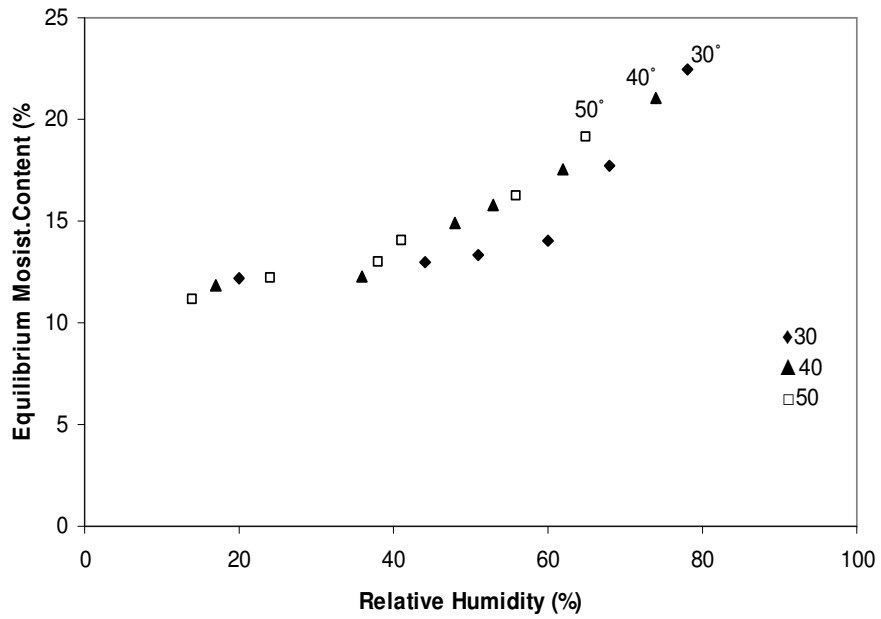
Figure 5.a The effect of temperature on Adsorption isotherms isotherms of the date paste .
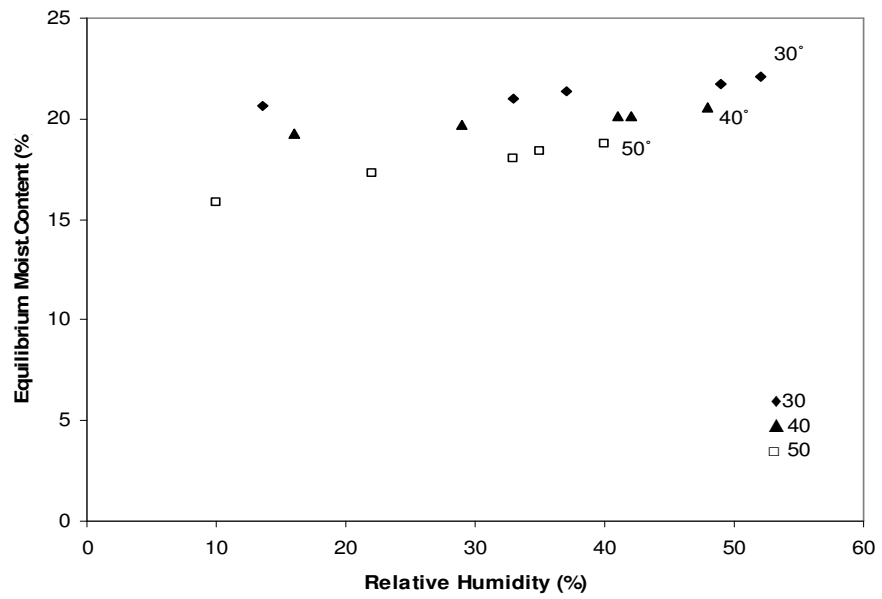
Figure 5.b The effect of temperature on Desorption isotherms isotherms of the date paste

3. 2 . Analysis with Respect to the Models.

The data obtained were treated according to BET, modified BET, GAB, Smith , Iglesias and Chirife , Halsey , Henderson and Oswin isotherm models. It was tried to correlate the data using a relevant model and to determine the physical and/or chemical parameters associated with the most acceptable one.

3. 2.1. The BET Model.

When the BET equation (Eqn. 6) was used to represent the entire data, the results displayed in Table 5. were obtained through regression analysis. However, for both adsorption and desorption, intercepts of the fits appeared to be negative. Simply this means that, the constant "c" in the BET equation is negative which is physically impossible, though the correlation coefficients were extremely high with full data analysis, In Figures 6.a to 6.c, BET plots for the date pastes at 30, 40, and 50 °C are given at different relative humidities.

Table 5. Results of Regression Analysis for Date pastes According to B.E.T Equation for all points.

Temperature ˚C	Adsorption	Desorption	mo	C
30	A= -0.0343 B=0.2334 R=0.9879	A= - 0.0094 B= 0.11076 R= 0.9870	5.022* 10.18**	-5.80* -10.45**
40	A=- 0.0246 B=0.1974 R=0.9738	A= - 0.0086 B= 0.1072 R= 0.9728	5.78* 10.14**	-7.02* -11.46**
50	A= - 0.0116 B= 0.1577 R= 0.9878	A= - 0.0033 B= 0.0943 R= 0.9962	6.84* 10.99**	-12.60* -27.57**

*Adsorption

** Desorption

Regression Model : y = A+ B X

$X=a_w$, $y = a_w / EMC(1-aw)$

R : correlation coefficient.

m_o= 1/ (intercept+ slope)
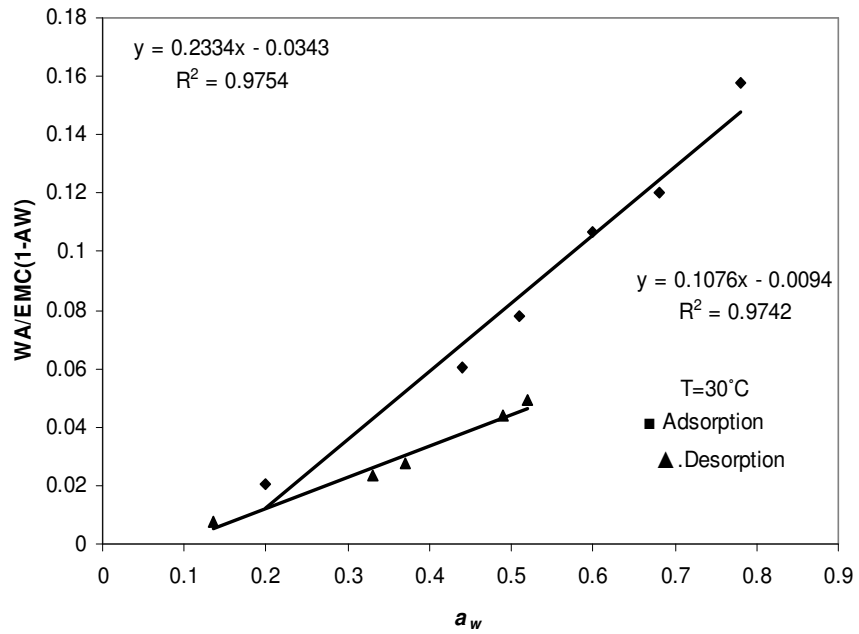
C = 1 / (intercept * m_o)

Figure 6.a. BET plot for Date pastes at 30 ˚C
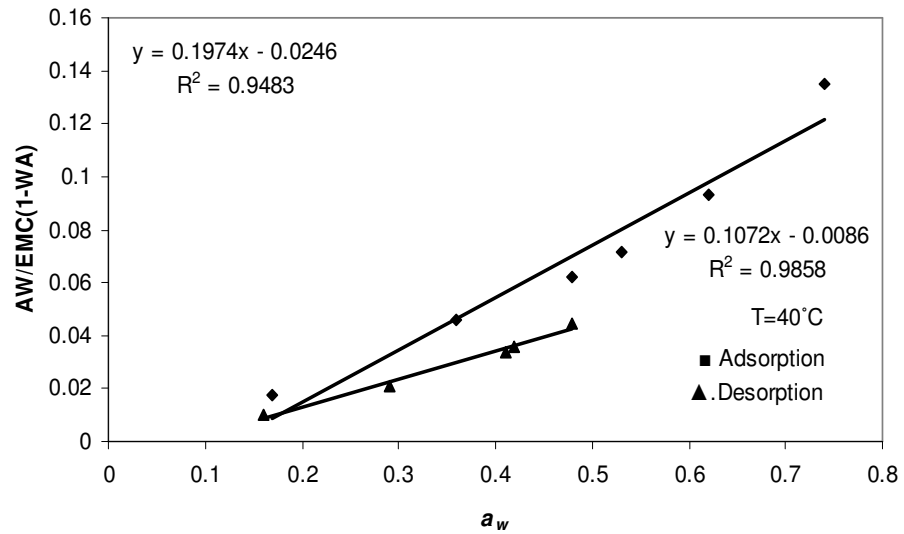
Figure 6.b. BET plot for Date pastes at 40 ˚C
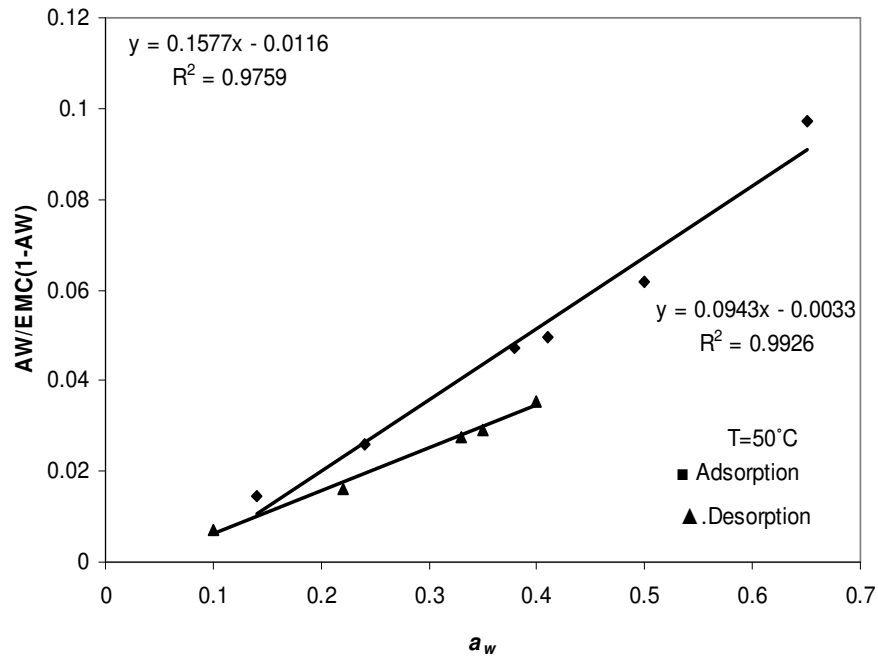
Figure 6.c. BET plot for Date pastes at 50 ˚C

Negative intercept values in the BET plot for n propyl alcohol vapor on iron have been reported by Loeser et.al. (1953) where similar observation has also been reported by Young and Crowell (1956) The position has been clarified by Emmet (1956) who has developed a more valid isotherm equation and have shown that the BET equation does not fit relative humidities higher than 0.2 for some materials. With regard to this claim,when the BET plot is constructed for relative humidities below 0.2 positive intercepts were obtained(Young and Crowell,1962).

In this study ,minimum relative humidity attained was 0.10 and only two points are present below 0.2 for some isotherms. so, it was not possible to check the validity of BET plot in suggested range with the obtained data results shown in Table 5 ;On the other hand they were obtained the BET model to describe the interaction between water vapour and the date paste. The values of the monolayer m_o were between 5.0 to 7.0 for adsorption and 10.0 to 11.0 for desorption which were close to the values that were reported by A.Belarbi at.,el.(2000) from his

study on water desorption isotherms for eleven varieties of dates.

3.2.2 The GAB model

In GAB equation, it is assumed that the number of molecular layers at   the saturation pressure is finite, possibly a small number. The constant "k" introduced measures the strength of attractive force field of the adsorbant. A small value of "k" implies a low attractive force field of the adsorbant and it is one of the reasons for the compensation in the BET theory caused by strong force field attributed to the adsorbant. The GAB model has been considered as versatile sorption model for various foods and earlier works on date products (Alhamdan & Hassan, 1999; Myhara et al., 1998) reported that the model described well the sorption data.

GAB equation was transformed into a quadratic form as:

$M = X_m C K a_w / (1-K a_w)(1-a_w+CKa_w)$

Since , M is the moisture content of the material on a dry basis(g/100 g dry basis), X_m the moisture content of monolayer of water adsorption (g/100 g dry basis), K the constant related to multilayer properties and C is a constant related to the heat of sorption and a_w water activity.   The constants of the model for date paste is shown in Table 6.

Table 6: GAB parameters(X_m,K and C) for Dates paste.

Adsorption	X_m	K	$Cx10^{-6}$	R^2
30°	8.416	0.7818	-215.7	0.97
40°	9.5523	0.7488	-2.556	0.99
50°	21.87	0.0047	0.00117	0.94
Desorption				
30°	20.0897	0.1635	-8.190	0.93
40°	18.6791	0.18	-1.919	0.99
50°	15.2989	0.47	-3.695	0.99

In Table 6 the results of the nonlinear fit using GAB model are displayed Monolayer moisture content, X_m, varied from a minimum 8.416 g water/100 g dry matter at 30˚ C and increased with temperature to 21.87 g water/100 g dry matter.where are close to those reported by A.Belarb *at.el* (2000). The values of *K* at 30˚C and 40˚C are close to 1.0.

3.2.3 The Smith Model

When Smith model was used to correlate the data of sorption and desorption isotherms, the correlation coefficients were between 0.86 to 0.98(Table 7) .Smith considered the sorbed water to be of two principal classes; that which is bound to the inner and outer surface of soildad sorbent and that which is normally condensed with the adsorbent.So only regions B and C of the isotherm were accounted for and thus is valid for sorption above monolayere region (Dincer and Esin,1990). In this study , a relatively low correlation coefficient at 30˚C resulted which was satisfactorILY high at the other temperatures.

The parameter A represents moisture bound to the surface and parameter B represents the moisture in a unimolecular layer of normally condensed moisture.

Table 7.ConstanTS of Smith Equation:

M=A-Bln (1-RH)

Temperature (˚C)	A	B	R^2
Desorption isotherms			
30	20.245	2.3814	0.9508
40	18.70	2.8172	0.9873
50	15.276	7.0276	0.9772
Sorption isotherms			
30	8.3899	8.2991	0.8674
40	9.2938	8.7941	0.9645
50	9.4646	9.0766	0.9732

There are not data about Smith parameters for dates in the literature.

3.2.4 The Iglesias and Chirife Equation:

Chirife and Iglesias (1984) proposed the following eqaution for high sugar foods:

$\ln[M +(M^2+M_{0.5})^{1/2}]= ba_w+p$

where M is the equilibrium moisture content (g water/g dry matter), a_w the water activity , $M_{0.5}$ the equlibrium moisture content at a_w=0.5 ,and b and p are constants. $M_{0.5}$ was directly determined from the experimental sorption isotherms by manually finding the values of M at a_w=0.5.Results of linear regression of the Iglesias and Chirife equation using experimental sorption data are shown in Table 8.

Table 8.Estimated parameters for Iglesias and Chirife for Dates pastes.

Temperature ˚C	Adsorption	Desorption
30	b=1.0068 P=2.8806 R^2=0.7545	b=0.1724 P=3.7057 R^2=0.9253
40	b=1.0092 P=2.9487 R^2=0.9284	b=0.1903 P=3.6335 R^2 =0.9764
50	b=1.0635 P=2.9487 R^2=0.9572	b=0.537 P=3.4252 R^2=.9849

The values of the constant *b* consistently increased with increasing temperature, while values of *p* consistently decreased with increasing temperature for the desorption data.The regression coefficient (R^2) was high for most of the samples at the three temperatures studied indicating a good fit of the experimental sorption data by the model as shown in Table 8. Iglesias and Chirife applied their model for sorption data of nine high suger foods which were mostly fresh fruits with sugar precent mainly in dissolved form (Ayranci et al.,1990).The date pastes are similar in sugar type since they contain predominantly reducing sugars (glucose and fructose) naturally in dissolved state.(Abdullah M. Alhamdan,1999).

3.2.5 The Halsey Equation

Halsey equation is also one of the widely used equation in modeling experimental sorption data of high sugar foods. The equation can be written as follows:

$$M = X_M(- \ln(a_w))^n$$

where *M* is the equilibrium moisture content (g water/g dry matter) ,a_w the water activity , X_M monolayer moisture content.

The values of the parameters are shown in Table 9. The values of the regresion coefficient(R^2) indicate a good fit of the equation by the experimental data. According to the fit, values of X_M , monolayer moisture content are increasing with temperature for the adsorption .while decreased with temperature for the desorption data. The values of n are negative .which are similar to which were found by Jasim Ahmed et.,al (2005)

Table 9.Estimated parameters for Halsey equation for Dates pastes:

Temperature ˚C	Adsorption	Desorption
30	X_M =12.66 n= -0.3 R^2=0.85	X_M =21.43 n= -0.0604 R^2=0.91
40	X_M =13.54 n = -0.35 R^2=0.93	X_M =20.047 P=-0.0684 R^2 =0.97
50	X_M =13.75 n = -0.36 R^2=0.95	X_M =18.485 n= -0.1808 R^2=0.99

3.2.6 The Henderson Equation:

Henderson equation is also one of the widley used equation in modeling experiments sorption data of high sugar foods. The equation is in this form:

$$M = X_M(- \ln(1 - a_w))^n$$

where M is the equilibrium moisture content (g water/g dry matter) , a_w the water activity , X_M monolayer moisture content.

The values of the parameters are shown in Table 10. The values of the regresion coefficient(R^2) indicate an acceptable fit of the equation to the experimental data . Again as in the other models,the values of X_M monolayer moisture content are increasing with temperature for adsorption .while

decreasing with temperature for the desorption . The results and values are similar to which were found by Jasim Ahmed et.,al 2005.

Table 10.Estimated parameters for Henderson equation for the date pastes:

Temperature	Absorption	Desorption
30	$X_{m=}16.14$ n=0.2732 R^2=0.849	$X_{m=}22.09$ n=0.0374 R^2=0.918
40	$X_{m=}17.647$ n=0.2912 R^2=0.9148	$X_{m=}20.82$ n=0.0461 R^2=0.971
50	$X_{m=}17.478$ n=0.2704 R^2=0.940	$X_{m=}20.015$ n=0.1046 R^2=0.998

3.2.7. The Oswin Equation

The Oswin equation is also one of the widley used equation in modeling experimental sorption data of high sugar foods. The equation can be attered to logarthmic form which is more suitable regresion analysis.

$$M = X_M(a_w/1-a_w)^n$$

$$\ln M = \ln X_M + n.\ln(a_w/1-a_w)$$

Here M is the equilibrium moisture content (g water/g dry matter) ,a_w the water activity , X_M monolayer moisture content. The values of the parameters are shown in Table 11. The values of the correlation coefficient(R^2) indicate a good fit of the equation to the experimental data. Here again values of X_M increased with of temperature for the adsorption.while X_M decreased with increase temperature for the desorption data. The results are similar to those reported by Jasim Ahmed et.,al 2005.

Table 11.Estimated parameters for Oswin equation for Dates pastes

Temperature	Absorption	Desorption
30	$X_{m=}14.37$ n=0.265 R^2=0.890	$X_{m=}21.86$ n=0.0333 R^2=0.93
40	$X_{m=}15.67$ n=0.2303 R^2=0.941	$X_{m=}20.50$ n=0.0391 R^2=0.977
50	$X_{m=}15.788$ n=0.2214 R^2=0.958	$X_{m=}19.408$ n=0.0925 R^2=0.998

3.3. Isosteric moisture sorption.

The relationship between a_w and temperature (at constant equilibrium moisture content) is described by a moisture sorptin isostere. The isosteric heat of sorption(Q_{st}), is a measure of interaction between absorbate and absorbent, which can be determined from the integrated form of the Clasius-Clapeyron equation (Ayranci et al.,1990).

$$\ln(a_{w\ 1}/\ a_{w\ 2}) = -\Delta\ Q_{st}/R\ (1/T_1 - 1/T_2)$$

At constant equilibrium moisture content. a_{w1} and a_{w2} are water activities at temperatures T_1 and T_2.

As moisture content increased for the date paste(Fig.6), Q_{st} decreased from 0.90KJ/mol at 11.0% moisture, to -1.84 KJ/mol at 18.0 % moisture. These trends, similar to those of date variety Fard and Khalas(Robert M.Myhara *el al*.,1998) indicate weaker interactions between date soilds and water, as well as the endothermic dissolution of sugars at higher equilibrium moisture contents.
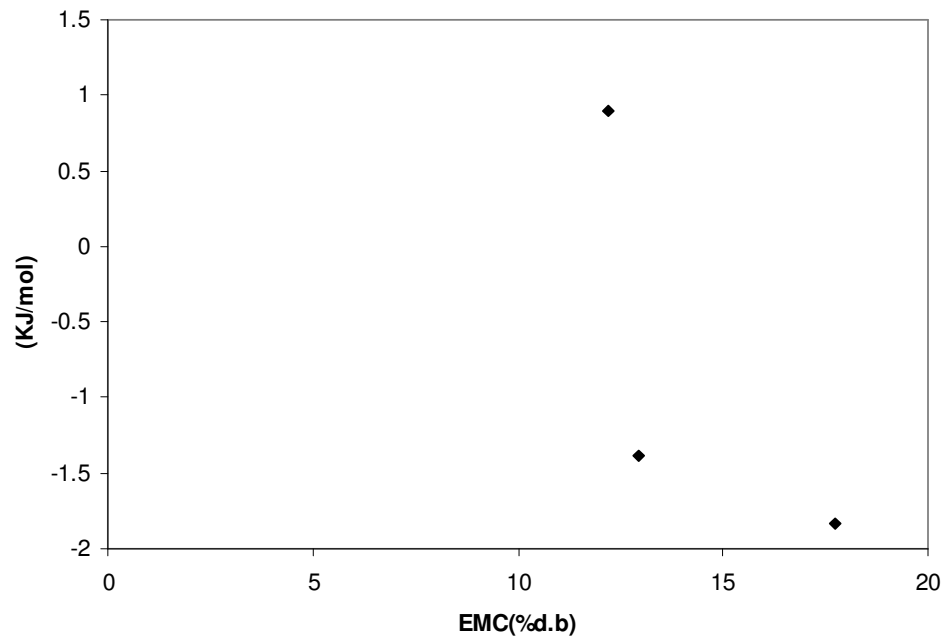
Figure 7.Isosteric heat of sorption for date paste.

CHAPTER IV

CONCLUSION

On the basic of sorption isotherms obtained experimentally for the date paste prepared from saiad ja `ul variety and related discusion it is possible to draw the following conclusions the Type II trends which is quite common for most foods. Isothers of the dates indicate that the well-known general shape of high sugar content materials could be observed only for the two of the three regions present in Type II isotherms namely multilayer adsorption and capillary condensation regions,where only partially wıth the monolayer zone.

Sorption isotherms exhibit lower moisture contents and approach each other with increasing temperature but the decrease in the heat of sorption varies non-linearly with temperature.

Considering the simplicity of the equation as well as its ability to fit experimental equilibrium moisture isotherms in specified of relative humidity, the Smith, Iglesias & Chirife, Halsey, Henderson and Oswin models proved to be more useful for describing equilibrium moisture isotherms of the date paste.

Monolayer moisture content, Xm, values were between 8.0 to 22.0 for adsorption and between 15.0 to 22.0 for desorption. An empirical equation to relate the heat of desorption as a function of moisture content is possible.

For future research, it can be recommended that chemical composition of dates, crystalline sugar dissolution and transitions between the amorphous state and other factors can be studied to obtain a truly universal moisture content model.

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APPENDIX A

Table A. 1. Relative Humidity and Equilibrium Moisture Content Values of Dates at 30 C.

(Dry Solid = 2.72 g)

Relative Humidity (%)	Sample Weight (g)	Equilibrium Moisture Content (%db)
Adsorption		
20.0	3.06	12.22
44.0	3.08	12.95
51.0	3.09	13.32
60.0	3.11	14.05
68.0	3.21	17.72
78.0	3.34	22.50
Desorption		
52.0	3.33	22.12
49.0	3.32	21.76
37.0	3.31	21.40
33.0	3.30	21.02
13.6	3.29	20.66

Table A. 2. Relative Humidity and Equilibrium Moisture Content Values of Dates at 40 C.

(Dry Solid = 2.29 g)

Relative Humidity (%)	Sample Weight (g)	Equilibrium Moisture Content (%db)
Adsorption		
17.0	2.56	11.85
36.0	2.57	12.30
48.0	2.63	14.91
53.0	2.65	15.79
62.0	2.69	17.54
74.0	2.77	21.03
Desorption		
48.0	2.76	20.60
42.0	2.75	20.16
41.0	2.75	20.16
29.0	2.74	19.72
16.0	2.73	19.28

Table A. 3. Relative Humidity and Equilibrium Moisture Content Values of Dates at 50 C.

(Dry Solid = 2.76 g)

Relative Humidity (%)	Sample Weight (g)	Equilibrium Moisture Content (%db)
Adsorption		
14.0	3.07	11.13
24.2	3.10	12.22
38.0	3.12	12.94
41.0	3.15	14.03
50.0	3.21	16.20
65.0	3.29	19.10
Desorption		
40.0	3.28	18.73
35.0	3.27	18.37
33.0	3.26	18.08
22.0	3.24	17.28
10.0	3.20	15.84