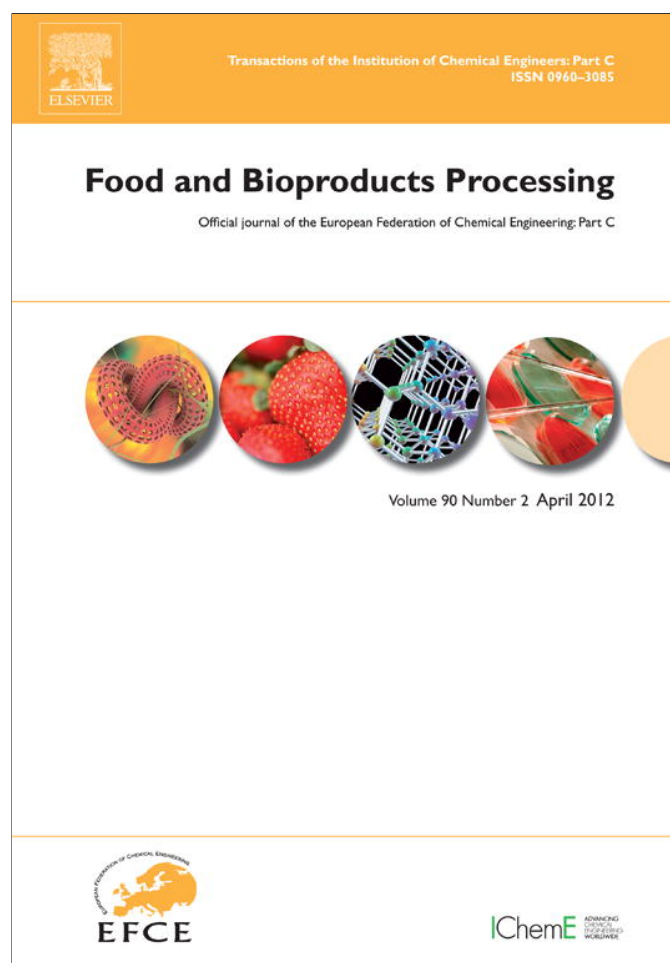


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Effect of osmosis and ultrasound pretreatment on the moisture adsorption isotherms of quince

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A B S T R A C T

The effect of pretreatment osmotic–ultrasonic dehydration on the sorption isotherms of quince was determined by static gravimetric method at temperatures of 30 °C, 45 °C, and 60 °C. The curves obtained can be considered as type II according to the Brunauer–Emmett–Teller (BET) classification. Adsorption data were fitted into seven isotherm models. The best fit of the experimental data was obtained with Peleg for both fresh- and pretreated dried quince slices.

Thermodynamic properties such as net isosteric heat, differential entropy, enthalpy–entropy compensation, and spreading pressure were determined from moisture adsorption isotherm data of quince. The net isosteric heat of sorption and differential entropy decreased with increasing moisture contents in an exponential function. A plot of differential heat versus entropy satisfied the enthalpy–entropy compensation theory. The spreading pressure increased with increasing water activity, and decreased with increasing temperature. The value of net isosteric heat, differential entropy and spreading pressure of untreated samples is higher than that of pretreated samples of quince.

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Keywords: Adsorption isotherms; Mathematical models; Osmotic–ultrasonic dehydration; Quince; Thermodynamic

1. Introduction

Quince (*Cydonia oblonga* Mill) is a member of pome fruit family. The mean of the last 10 year (1998–2008) world production of quince is estimated to be 510,000 t (FAO, 2010). It is used to make jam, marmalade and jelly, as well as quince pudding. Dried quince can also be used as ingredients of traditional Iranian food. Air-drying the fruit can cause serious decreases of nutritive and sensorial values, damaging mainly the flavor, color, and nutrients of the product (Lenart, 1996; Lin et al., 1998). Thus, there is a need to modify the air-drying method to limit its adverse influence, especially on flavor, color, nutrients and fruit texture. One possible solution is to apply osmotic dehydration, which involves the immersion of fruit in osmotic solution resulting in the removal of water from tissue, and replacing it with soluble solids (Fernandes et al., 2008; Azoubel et al., 2009). Among emergent new technologies, ultrasonic is an encouraging process, which is commonly regarded as a non-thermal process. Such processes are favorable because of reduction in food degradation. No liquid phase change will occur in this process for

water removal (Povey and Mason, 1998; Fernandes et al., 2008; Fernandes and Rodrigues, 2007). Complementary treatments such as hot air or vacuum drying may be applied to previously osmotic–ultrasonic fruit or vegetable to produce an intermediate moisture food product. Intermediate moisture fruit products are developed to preserve the quality characteristics such as color, flavor, appearance, and texture as close as possible to their fresh counterparts. Moreover, intermediate moisture foods are expected to be stable under storage and marketing. Thus, it is important to derive adequate information in this regard. The water sorption isotherm represents the equilibrium relationship between moisture content of the food sample and water activity at constant temperature and pressure. Further analyses of the sorption phenomena can be undertaken in terms of thermodynamic functions. Thermodynamic approach relates to the understanding of water equilibrium with its surroundings at certain relative humidity and temperature; energy requirements associate with the sorption behaviour. Thermodynamic properties are readily calculated from sorption isotherms. Some thermodynamic functions, used in analyzing sorption behaviour of

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biological systems, include total heat of sorption, differential heat of sorption, differential entropy, enthalpy–entropy compensation, and spreading pressure.

The net isosteric heat (q_{st}) is defined as the difference of the total heat of sorption and heat of vaporization at the system temperature. The heat of adsorption is a measure of the energy released on sorption, and the heat of desorption is the energy required to break the intermolecular forces between the molecules of water vapor and the surface of adsorbent. Thus, the heat of sorption is considered as indicative of the intermolecular attractive forces between the sorption sites and water vapor (Al-Muhtaseb et al., 2004b). The differential entropy of a material is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996). Enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as sorption reaction. The theory states that it is necessary to minimize free energy changes due to these phenomena, compensation arises from the nature of the interaction between the solute and solvent causing the reaction and that the relationship between the enthalpy and entropy for a specific reaction is linear (Fasina, 2006). The spreading pressure, or surface potential, represents the surface excess free energy, and provides an indication of the increase in surface tension of bare sorption sites due to sorbed molecules (McMinn and Magee, 2003). The objectives of the present work are to (i) determine the effect of osmotic–ultrasonic pretreatment on the adsorption isotherms of quince and to improve general knowledge on sorption phenomena; (ii) model the sorption isotherm using selected equations; (iii) determine the thermodynamic properties; and (iv) evaluate the application of the enthalpy–entropy compensation theory to the sorption phenomena.

2. Materials and methods

Fresh quinces (*varieties of Nishabur*) were purchased at local market in Mashhad, Iran. The quince was peeled and cut into slabs of about 4 mm using a thin blade.

2.1. Ultrasonic pre-treatment

An experimental set of four quince samples was immersed in distilled water and submitted to ultrasonic waves for 0–30 min. The experiments with ultrasonic treatment were carried out in separate 250 ml Erlenmeyer flasks to avoid interference between the samples and runs. The experiments were carried out under ambient temperature (30 °C) in an ultrasonic bath (Schaper model Unique USC 25 kHz) without mechanical agitation. The ultrasonic frequency was 25 kHz and the intensity was 500 kW. The temperature increase of water during the experiments was measured using a mercury thermometer and was lower than 2 °C after 30 min of ultrasonic treatment. To determine the effect of ultrasonic treatment, the same experimental procedure was carried out without applying the ultrasonic treatment. After removal from the distilled water, the samples from each group were drained and blotted with absorbent paper to remove the excess water. Weight and moisture content were measured individually. At the end, samples were transferred to osmotic solution.

2.1.1. Light microscopic analysis

After the end of ultrasonic pre-treatment, the samples were carefully cut into cubes of 5 mm average side. The sample cubes were fixed with 4% solution of paraformaldehyde in

0.1 M phosphate buffer, pH 7.2 and 1% glutaraldehyde for 24 h at ambient temperature. The material was then dehydrated in a graded ethanol series and embedded in Histo-resin embedding kit (Jung). The tissue blocks were sectioned at 8 μ m. The Periodic Acid-Schiff (PAS) reagent cytochemical reaction was employed for polysaccharide detection (Fernandes et al., 2009). Photomicrographs of the cell structure were taken using an Olympus BX41 (Olympus, Japan) light microscope with digital image capture system.

2.2. Osmotic dehydration

Each experimental group consisting of three quince slabs was immersed in the osmotic solution for 1, 1.5 or 2 h. The osmotic solution used in each experiment was prepared by mixing food grade sucrose with distilled water to give a concentration of 40–60° Brix. The osmotic solution to fruit ratio was maintained at 20:1 (weight basis). Osmotic dehydration was performed under the same magnetic agitation to maintain uniform temperature and concentration throughout the experiment. After removal from the solution, the dehydrated samples from each group were drained and blotted with absorbent paper to remove the excess solution. Weight and moisture content were measured individually.

The empirical models were generated from response surface methodology (RSM) to predict osmotic–ultrasonic conditions considered in this research. As a consideration of the osmotic–ultrasonic pretreatment, it was considered appropriate to maximize water loss (WL) and weight reduction and minimize solid gain (SG). The results of the optimum conditions for quinces were found to be 27.25 min for ultrasonic time, 120 min for osmose time and 50.52% for sucrose concentration. Details are discussed by Noshad et al. (2011).

2.3. Air drying

Hot air drying was performed in a laboratory drier (Soroush Medical Company) operating with air velocity of 1.5 m/s. Before each drying experiment the drier was run without sample for about 0.5 h to set desired conditions. The quince samples, fresh and pretreated with optimized osmotic–ultrasonic dehydration condition, were subjected to air drying at 70 °C for 24 h.

2.4. Determination of sorption isotherms

The equilibrium moisture contents of dried quince were determined by a gravimetric technique, which is based on the use of saturated salt solutions to maintain constant water activity at determined values of the samples when equilibrium is reached between atmosphere and food sample. Nine saturated salt solutions selected to give different relative humidities in the range of 0.11–0.90 were used. The salt solutions used and their corresponding relative humidities at different temperatures were taken from data reported by Greenspan (1977) and Kiranoudis et al. (1993) and given in Table 1. Three replications of the same experiment were carried out. The glass sorption jars were placed in a temperature-controlled cabinet, with an accuracy of ± 1 °C at the selected temperatures 30 °C, 45 °C and 60 °C. Equilibrium was reached when the sample weight difference between two successive measurements was less than the balance accuracy 0.001 g. The time required for equilibrium was 3 weeks or more depending on relative humidity and temperature of the sam-

Table 1 – Water activity values of the saturated salt solutions at three temperatures used in the experiment.

	Temperature (°C)			Reference
	30 °C	45 °C	60 °C	
LiCl	0.113	0.112	0.11	Greenspan (1977)
CH ₃ COOK	0.216	0.195	0.16	Kiranoudis et al. (1993)
MgCl ₂	0.324	0.311	0.293	Greenspan (1977)
K ₂ CO ₃	0.432	0.432	0.432	Kiranoudis et al. (1993)
Mg(NO ₃) ₂	0.514	0.469	0.44	Kiranoudis et al. (1993)
NaNO ₂	0.645	0.614	0.59	Greenspan (1977)
NaCl	0.751	0.745	0.745	Greenspan (1977)
KCl	0.836	0.817	0.803	Greenspan (1977)
BaCl ₂	0.9	0.88	0.84	Kiranoudis et al. (1993)

ples. The moisture contents of the sample were determined by oven method at 105 °C for 24 h (Munde, 2000). In order to inhibit microbial growth a small quantity of thymol was also placed in the glass flasks in which water activity was greater than 0.5.

2.5. Data analysis

2.5.1. Modeling adsorption isotherms

The experimental adsorption data of quince at three different temperatures were fitted to seven sorption equations shown in Table 2. These mathematical models were reported to be suitable for dehydrated foods, and even high sugar foods (Falade and Aworh, 2004). The parameters of the sorption models were calculated using nonlinear least square regression analysis. Two criteria that were the mean relative deviation modulus (P) and the standard error of estimate (SE) were used to evaluate the well fitting of sorption models to experimental adsorption data:

$$P = \frac{100}{N} \sum_{i=1}^N \frac{|X_{ei} - X_{pi}|}{X_{ei}} \tag{1}$$

$$SE = \sqrt{\frac{\sum_{i=1}^N (X_{ei} - X_{pi})^2}{N - n}} \tag{2}$$

where X_{ei} and X_{pi} are the experimental and predicted moisture content values, respectively; N and n are the number observation and the number of constants in each model, respectively. A model is considered acceptable if it has a P value less than 10% (Lomauro et al., 1985). The model with lowest SE and P and highest regression coefficient (r^2) was selected.

Table 2 – Equations describing the sorption equilibrium isotherms.

Name of the equation	Equation
Peleg (Peleg, 1993)	$M = m_1 a_w^{n_1} + m_2 a_w^{n_2}$
GAB (Van den Berg and Bruin, 1981)	$M = M_0 C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$
Halsey (Halsey, 1948)	$M = [(-a) / \ln a_w]^{1/r}$
Caurie (Caurie, 1970)	$M = \exp(A + B a_w)$
Henderson (Henderson, 1952)	$M = [-\ln(1 - a_w) / A]^{1/B}$
Chen (Chen, 1971)	$a_w = \exp[k - c \exp(-bM)]$
BET (Brunauer, Emmett and Teller, 1938)	$M = M_0 C a_w / [(1 - a_w) + (C - 1)(1 - a_w) a_w]$

2.5.2. Isosteric heat of sorption and entropy of sorption

The heat of adsorption is the energy released in the process of adsorption of water molecules on a surface of the adsorbent, which is also an indicator of the state of water absorbed by the solid material. The net isosteric heat of sorption (q_{st}) is the amount of energy above the heat of vaporization of water (H_L) associated with the sorption process, and is calculated from the experimental data using the Clausius–Clapeyron equation (Tsami, 1991; Tolaba et al., 2004):

$$q_{st} = -R \left[\frac{d \ln(a_w)}{d(1/T)} \right]_x \tag{3}$$

$$Q_{st} = q_{st} + H_L \tag{4}$$

The net isosteric heat of sorption is calculated from Eq. (3) by plotting the sorption isotherm as the natural logarithm of water activity versus $1/T$, for specific moisture content, the slope of the regression line provides a measure of the net isosteric with the heat of sorption Q_{st} being obtained by applying Eq. (4). The application of method requires the measurement of sorption isotherms at more than two temperatures. Sorption entropy is proportional to the number of available sorption sites at a specific energy level. For a thermodynamic system, the relationship between the net isosteric heat (q_{st}) and the differential entropy of sorption (S_d) is given by (Polatoglu et al., 2010):

$$(\ln a_w)_x = -\frac{q_{st}}{RT} + \frac{S_d}{R} \tag{5}$$

Sorption entropy for given moisture content is calculated from the intercept of the line of $\ln a_w$ versus $1/T$ (Aguerre et al., 1986).

2.5.3. Enthalpy–entropy compensation theory

Enthalpy–entropy compensation theory or isokinetic relationship is used to evaluate physical and chemical phenomena that prevail in the sorption processes. This theory proposes a linear relationship between Q_{st} and S_d , Eq. (6) (Leffler and Grunwald, 1963):

$$Q_{st} = T_1 S_d + G \tag{6}$$

Plotting Q_{st} against S_d , isokinetic temperature (T_1) and the free energy (G) at T_1 can be calculated using linear regression. T_1 represents the temperature at which all reactions in the sorption series proceed at the same rate. Krug et al. (1976) recommended a test for the compensation theory, which involves the evaluation of the isokinetic temperature with respect to the harmonic mean temperature T_{hm} , which is defined as

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T)} \tag{7}$$

where n is the number of isotherms.

The compensation theory only can be applied if $T_1 \neq T_{hm}$. If $T_1 > T_{hm}$ the process is enthalpy driven, while if the opposite condition is observed, the process is considered to be entropy controlled.

2.5.4. Spreading pressure

The spreading pressure is the force applied in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading. This parameter

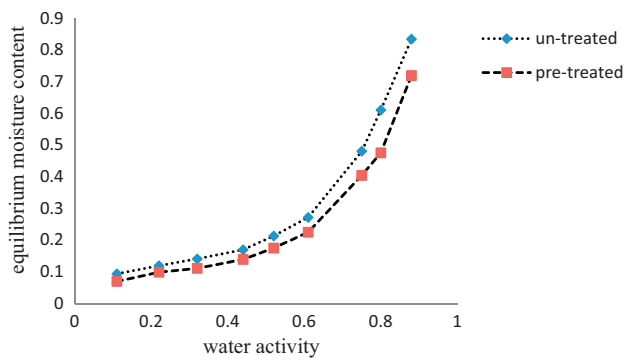


Fig. 1 – Moisture adsorption isotherms of quince at 30 °C.

is not subject to direct experimental measurement; it can be estimated using an analytical procedure when to be used the empirical relationship between moisture content and water activity (Smith et al., 2001). Halsey equation was used to obtain the parameters a and r , which are used in the following equation that defines the spreading pressure:

$$\phi = \frac{K_B T}{A_m} a^{1/r} \left[\frac{1}{((1/r) - 1)(-\ln(a_w))^{(1/r)-1}} \right]_{0.05}^{a_w} \quad (8)$$

where ϕ , spreading pressure (J/m²); A_m , area of a water molecule (1.06 × 10⁻¹⁹ m²); K_B , Boltzmann's constant (1.38 × 10⁻²³ J/K), a and r , Halsey parameters; a_w water activity; T absolute temperature (K).

3. Results and discussion

Fig. 1 shows the effect of pretreatment on adsorption isotherms of quince. The microscopic image analysis of the fresh fruit showed typical thin-walled cells with normal morphology and no visible intercellular spaces (Fig. 2A). After

ultrasonic treatment, the cells became more distorted and microscopic channels began to form (Fig. 2B). In the process of osmosis, sugar may have entered into the micro-channel, saturating the channel. Generally, equilibrium moisture contents decreased with increasing solids in quince slices. Lazarides et al. (1995), Singh (2001), and Singh and Mehta (2008) reported that the osmotic pretreatment of fruits in sucrose solution resulted in the decrease of equilibrium moisture content, and thus made the product less hygroscopic. Both fresh- and pre-treated dried quince slices sorbed low moisture in the low and intermediate a_w range, but sorbed more moisture at higher a_w (Fig. 1). Adsorption isotherms followed the type II classification of BET (Brunauer et al., 1938). The characteristic shape of moisture isotherms depends upon the variety and total amount of hygroscopic materials present in the particular heterogeneous mixture of hydrophilic substances (Bolin, 1980). The inherent sugars in the quince and sucrose infused during osmotic dehydration accounted for the shape of isotherms. At low water activities, water can be adsorbed only to the surface –OH sites of crystalline sugars. Weisser (1985) reported that at low water activities there was a local dissolution of sugar, a swelling of the biopolymer, and appearance of new active sites. At high water activities, dissolution of sugar occurs and crystalline sugar is converted into amorphous sugar (Saltmarch and Labuza, 1980). The amount of water to be absorbed increases greatly after this transition because of the increase in the number of adsorption sites upon breakage of the crystalline structure of sugar (Ayrançlı et al., 1990).

3.1. Effect of temperature on adsorption isotherm of fresh and pretreated dried quince slices

In general, moisture content is expected to decrease with increasing temperature at a constant water activity (Hill and

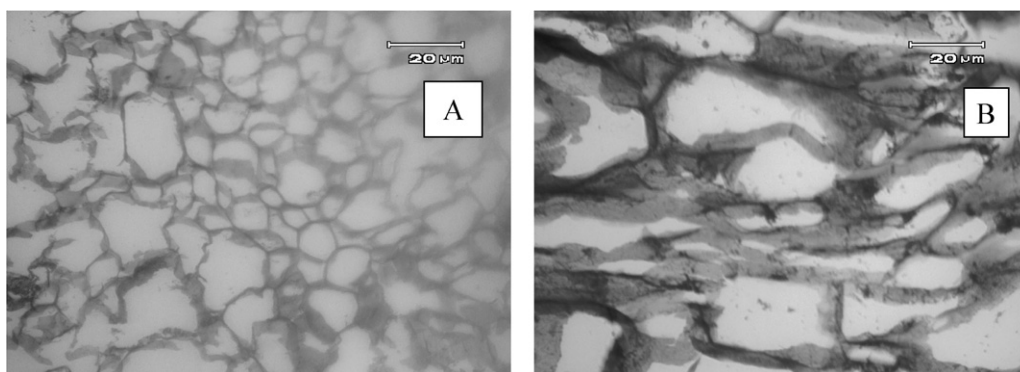


Fig. 2 – Photomicrographs of quince cubes before processing (raw fruit) (A) and after ultrasonic pretreatment (B).

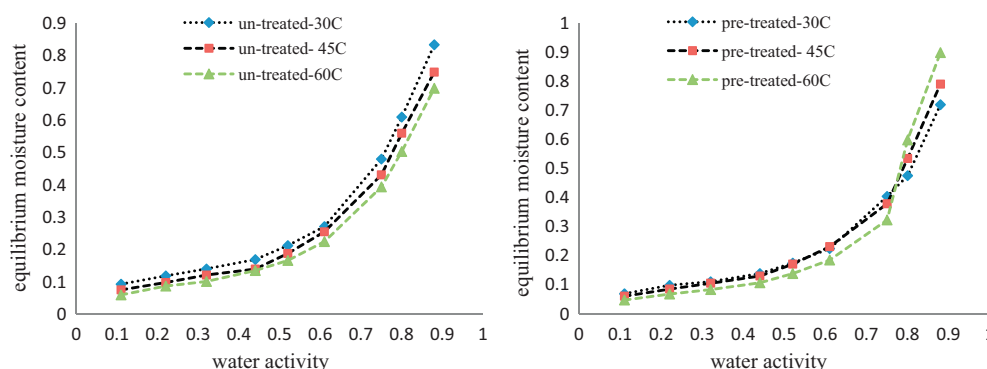


Fig. 3 – Effect of temperature on adsorption isotherm of untreated- and pretreated dried quince slices.

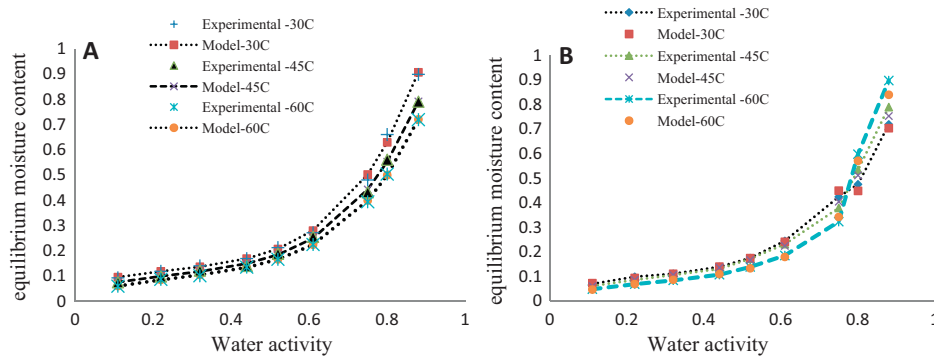


Fig. 4 – Experimental and calculated equilibrium moisture contents by Peleg model of (A) untreated quince and (B) pretreated quince.

Rizvi, 1982). The value for the equilibrium moisture content at a constant water activity is lower when temperature increases. Activation of the water molecules due to the increase in temperature causes them to break away from the water binding sites (McMinn and Magee, 2003), thus a decrease in the degree of water sorption with increasing temperature at a given water activity. This is the reason why the degree of water sorption decreased with the increasing temperature at a given water activity. The decrease in the value for the equilibrium moisture content with the increase of air temperature was also observed for mushroom (Shivhare et al., 2004), apricot, fig and raisin (Tsami et al., 1990), okra (Gus and Maskan, 1999), chillies (Wesley et al., 2000; Hossain and Bala, 2000; Kaleemullah and Kailappan, 2004) and apple (Prothon and Ahmé, 2004). A similar trend was obtained in pretreated dried quince slices until inversion of temperature occurred at $a_w \sim 0.75$. Fig. 3 shows the effect of temperature on adsorption isotherms of pretreated dried quince slices. As shown, crossing of the temperature isotherms occurred at $a_w \sim 0.75$. The ‘unusual’ temperature effect on isotherms above 0.6 (0.75 in this study) was a result of dissolution or increasing solubility of sugars in the high a_w region (Ayranci et al., 1990; Tsami et al., 1990). At water activity values higher than 0.75, there was an inversion in the effect of temperature (i.e., equilibrium moisture content increased with temperature) due to an increase in the solubility of sugars in water. The intersection (or inversion) point depends on the composition of the food and the solubility of sugars (Weisser et al., 1982). For sultana raisin and currant, the inversion point was about 0.55, likewise, 0.65 for fig, 0.70 for prune, 0.75 for apricot (possessing the lowest sugar content

of fruit) (Tsami et al., 1990), and 0.65 for quince jam (tapada nova) (Sa and Sereno, 1993).

3.2. Fitting of sorption models to experimental adsorption data

The values of the parameters for the sorption models of quince are shown in Table 3[b] together with the standard error of estimate (SE), the mean relative percentage deviation modulus (P) and the coefficient of determination (r^2). The goodness of the fit was provided for the higher values of r^2 and the lowest values of SE and P. It can be seen in Table 3 that the Peleg model is the best fit to the experimental data over almost the whole range of water activity and temperature for both fresh- and

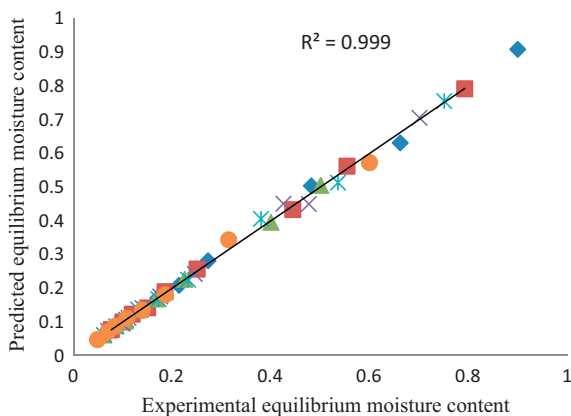


Fig. 5 – Comparison of experimental and calculated equilibrium moisture content values by Peleg model.

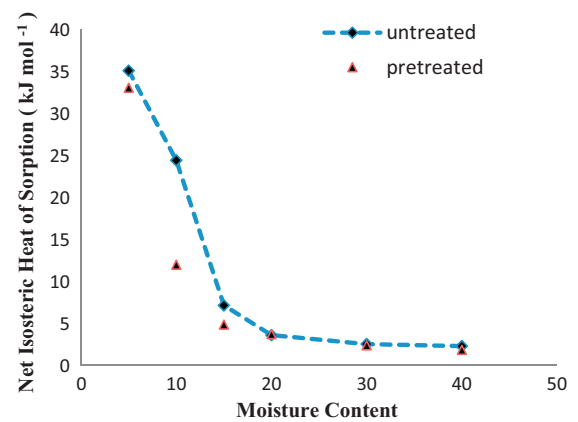


Fig. 6 – Net isosteric heat of adsorption of quince as a function of moisture content.

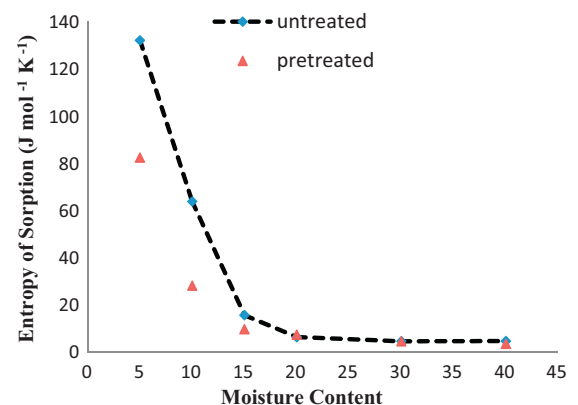
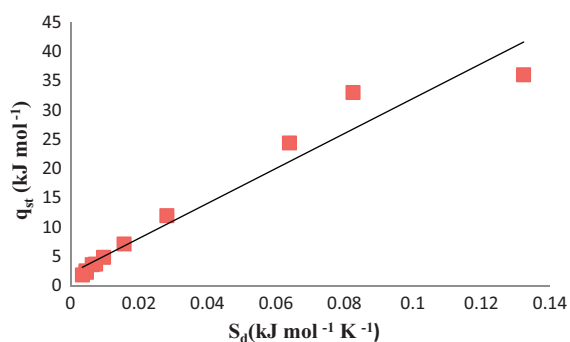


Fig. 7 – Differential entropy of adsorption for quince as a function of moisture content.

Table 3 – Estimated parameters, P (mean relative percentage deviation modules), r^2 (regression coefficient) and SE (standard error of estimate) for several models tested for isotherms of quince at different conditions.

Model	Parameter	Temperature (°C)					
		Untreated			Pretreated		
		30 °C	45 °C	60 °C	30 °C	45 °C	60 °C
GAB	M_0	0.149007	0.13713	0.128028	0.140723	0.127563	0.104572
	C	4.17357	3.417843	2.864514	2.122194	2.794916	2.291893
	K	0.95949	0.952292	0.949384	0.95227	0.957569	0.979394
	P	12.364	11.773	10.761	15.418	11.944	13.693
	r^2	0.986	0.992	0.994	0.988	0.991	0.989
	SE	0.038194	0.0255	0.0201	0.0333	0.0256	0.0259
BET	M_0	0.115432	0.101507	0.0925	0.107199	0.096068	0.089094
	C	16.1325	13.69663	10.69432	7.192299	8.589672	4.017109
	P	7.339416	7.47896	6.2065	9.9962	6.5558	10.189
	r^2	0.979	0.983	0.985	0.982	0.985	0.988
	SE	0.0385	0.0302	0.026	0.0332	0.0272	0.0223
	Chen	K	-0.20373	-0.20107	-0.19781	-0.20616	-0.19492
C		4.69755	3.737229	3.492912	3.827659	3.34584	3.312665
b		10.98341	11.03196	11.84639	11.8689	11.39603	14.07987
P		8.905	10.643	9.284	10.815	9.604	9.185
r^2		0.9786	0.971	0.98	0.973	0.974	0.98
SE		0.0446	0.0513	0.0427	0.0501	0.0445	0.0426
Halsey	a	0.106497	0.10072	0.094834	0.103438	0.097483	0.084704
	r	1.21632	1.148299	1.106163	1.107577	1.094653	1.052979
	P	8.093956	6.9559	4.377	7.7126	4.149	4.369
	r^2	0.989	0.988	0.996	0.988	0.995	0.994
	SE	0.0306	0.0287	0.018	0.0304	0.019	0.0194
	Henderson	A	1.619873	1.71416	1.800668	1.685217	1.771276
B		1.600871	1.725028	1.814247	1.70107	1.79184	1.890552
P		22.41609	20.687	20.305	25.82	21.965	27.47
r^2		0.947	0.956	0.955	0.931	0.942	0.901
SE		0.0656	0.0523	0.0447	0.0685	0.0562	0.0673
Peleg		m_1	0.185474	0.175739	1.063801	0.161894	0.185648
	n_1	0.29851	0.3803	5.089649	0.363075	0.510037	6.236237
	m_2	1.364667	1.164655	0.175704	1.315338	1.156904	0.163107
	n_2	4.912797	4.886916	0.479533	5.095593	5.407081	0.566636
	P	2.422882	2.1154	1.104	2.549	2.6746	3.511
	r^2	0.997	0.999	0.999	0.997	0.997	0.995
	SE	0.018	0.008	0.003	0.017	0.016	0.0182
Caurie	A	-3.50077	-3.61888	-3.77392	-3.86533	-3.85866	-4.42242
	B	3.826462	3.809414	3.879396	4.160437	4.023054	4.581756
	P	17.50686	14.80	14.712	18.078	16.004	22.298
	r^2	0.983	0.988	0.99	0.986	0.986	0.982
	SE	0.0401	0.0287	0.023	0.033	0.0301	0.0331

**Fig. 8 – Relationship between net isosteric heat of sorption and differential entropy of sorption for untreated and pretreated quinces.**

pretreated dried quince slices. According to Peleg (1993), this model fitted as well as or better than the GAB model but its constants had no physical meaning. It is reported that Peleg model gave good fit for isotherms of some foods (Al-Muhtaseb et al., 2004a; Arslan and Togrul, 2005). Figs. 4 and 5 show the experimental and calculated equilibrium moisture contents at different process conditions, that were predicted by the Peleg model. It is apparent from these figures that the predicted data closely band around the straight line, which indicated the sufficiency of the model, proposed in describing the adsorption behaviour of quince.

From Table 3, it is obvious that the monolayer moisture (M_0) content value measure of adsorption possibility for both GAB and BET models decreased with increasing temperature. The temperature dependence of the monolayer value has been linked (Iglesias et al., 1975) to a reduction in sorption active sites as a result of physico-chemical changes induced by tem-

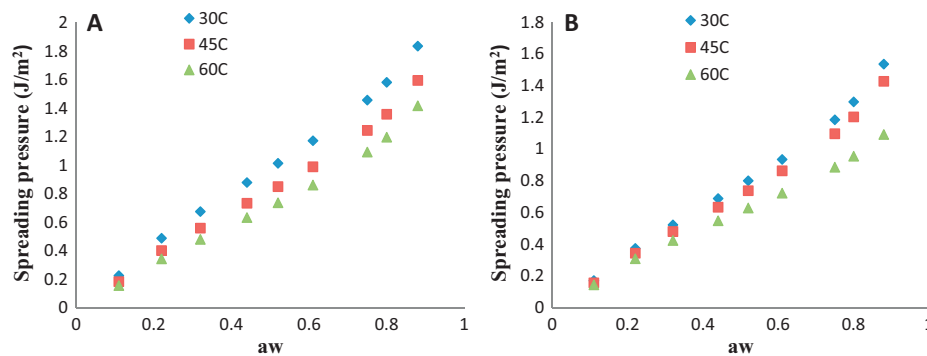


Fig. 9 – Variation of spreading pressure with moisture content and temperature for (A) untreated quince and (B) pretreated quince.

perature (Iglesias and Chirife, 1976; Sopade et al., 1996). M_0 should decrease with increasing temperature as the absorbed molecules gain kinetic energy (Diosady et al., 1996). The samples pretreated have lowered the monolayer moisture (M_0) content as compared to the control sample. A similar result was reported by Mazza (1982) that the addition of sugar lowers the M_0 content of potatoes.

3.3. Isostatic heat of sorption and sorption entropy

The net isosteric heat of adsorption of quince as a function of equilibrium moisture contents is given Fig. 6. As seen from Fig. 6, at low moisture contents, the heat of sorption is higher than at high moisture contents. Tsami et al. (1990) suggested that the rapid increase in the heat of sorption at low moisture content was due to the strongest binding sites on the external surface of the solid. As the moisture contents increase, the number of available binding sites for water adsorption decreases which resulted in lower values of net isosteric heat of adsorption. Untreated samples show the highest heat of sorption at low water content. This means that the energy required for drying quince to a safe water activity will be higher in untreated samples than in pretreated samples.

The differential entropy of adsorption of water, at each moisture content, was determined by applying Eq. (5) to the equilibrium data. Fig. 7 shows the differential entropy for quince as functions of moisture content. The results show the strong dependence of differential entropy on moisture content with an exponential trend similar to that of the net isosteric enthalpy. The differential entropy of the untreated samples exhibits a slightly higher magnitude than that for pretreated samples; however, the difference rapidly decreases to become negligible at high moisture contents. This behaviour indicates that water molecules are more mobile in untreated samples than in pretreated samples.

3.4. Enthalpy–entropy compensation theory

Plotting differential enthalpy versus differential entropy a linear correlation is found (Fig. 8). This means that the theory of compensation could be applied in the range of moisture contents studied. The values for the parameter T_1 (Eq. (6)) calculated from the data by linear regression for adsorption were determined as 364.1 K and 392.6 K for untreated and pretreated samples, respectively. Krug et al. (1976) showed that the compensation theory could be confirmed to apply if the calculated harmonic mean temperature (T_{hm}) was significantly different

from T_1 . The harmonic mean temperature was calculated by Eq. (7) and the obtained results are $T_{hm} = 318$ K for untreated and pretreated samples, as these values are significantly different from the value of T_1 , the suitability of the isokinetic theory is confirmed and, additionally, as in all cases $T_1 > T_{hm}$, the processes can be characterized as enthalpy driven.

3.5. Spreading pressure

The spreading pressures of untreated and pretreated samples at different temperatures were evaluated using Eq. (8). The spreading pressures of quince are plotted in Fig. 9. The results show that the spreading pressure increased with increasing water activity, and decreased with increasing temperature, at a given water activity. Aviara and Ajibola (2002) for melon seed and cassava, Al-Muhtaseb et al. (2004b) for starch powders noted similar changes with respect to temperature and water activity. The value of spreading pressures of untreated samples is higher than that of pretreated quince samples.

4. Conclusions

Adsorption isotherms of untreated and pretreated quince were typical type II sigmoid shape. The equilibrium moisture content decreased with increasing temperature at constant water activity. The osmotic–ultrasonic pretreatment decreased the equilibrium moisture content of the product. The Peleg model described the adsorption data over the range of temperatures and water activities investigated for both fresh- and pretreated dried quince slices. The isosteric heat of sorption was high at low moisture contents decreasing with increasing moisture content; the trend is to reach the latent heat of vaporization of pure water at higher moisture content. The differential entropy has an analogous behaviour to the isosteric heat. The osmotic–ultrasonic pretreatment decreased the value of net isosteric heat, differential entropy. The plot of isosteric heat versus entropy data satisfies the enthalpy–entropy compensation theory.

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