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ORIGINAL PAPER

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Water sorption isotherms of fresh and partially osmotic dehydrated pumpkin parenchyma and seeds at several temperatures

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Abstract Experiments were conducted to determine the equilibrium moisture content of pumpkin (cv *Cucurbita Pepo L.*) at different temperatures (278.1 K, 298.1 K and 318.1 K) and relative humidities (8–91%). Fresh and partially osmotically dehydrated (using sucrose solutions) samples of pumpkin parenchyma were employed. The desorption isotherm of pumpkin seeds at 298.1 K was determined as well and was found to be similar to other sorption isotherms of other seeds with similar fat and protein compositions. No significant dependence of the equilibrium experimental data on the temperature or osmotic pre-treatment was found. Several common mathematical models were used to fit the experimental data. For the parenchyma tissue, statistical analysis proved that those of Halsey, Oswin, Chirife and GAB were the best, while for the seeds, the Henderson, GAB and Peleg models are preferable.

Keywords Water activity · Equilibrium · Sucrose · Modeling

Introduction

Equilibrium sorption data are important for many activities related to food technology, like the prediction of microbiological, enzymatic and chemical activity, selection of packaging materials, design of drying and concentration processes, as well as selection of adequate storage conditions. In all of these cases, the sorption isotherms are required for design purposes.

The shape of a sorption isotherm depends on the structure and composition of the food material, as well as pressure and temperature, and it requires experimental determination, since current prediction methods are not able to simulate systems as complex as food. The sorption isotherms of most foods have a sigmoidal shape, and the isotherm can be divided into three zones as a function of water activity, a_w. At low water activities, physicochemical sorption of moisture is produced, and at higher water activities this is followed by multi-layer adsorption, and finally capillary condensation becomes predominant.

A large number of publications have reported sorption isotherm data for different products, and some important compilations can be found in the literature [1, 2]. Sorption equilibrium data for fresh pumpkin parenchyma tissue (without a clear specification of the variety) is, however, scarce [3], as is data for pumpkin (*Amber* variety) osmotically dehydrated with sucrose solution [4].

Combined methods involving osmotic dehydration and convective air drying or freeze drying are useful for preserving some of the characteristics of fresh food materials (such as colour and texture), and they also have important advantages from an economic point of view. Nevertheless, when osmotic dehydration is employed, while water removal does takes place, the acquisition of osmotic solute occurs in such a way that the composition of the final product is changed and the characteristics of the moisture sorption isotherm may be modified. One of the aims of this work is to determine the effect of sucrose impregnation of pumpkin on its sorption isotherm.

Another objective is to establish the effect of temperature on the desorption isotherm of parenchyma, since this variable is of great importance, taking into account the temperatures used during storage and processing. Temperature affects the mobility of the water molecules and also the corresponding dynamic equilibrium [5].

Pumpkin seeds are a source of oils and other oligocomponents [6]. In this paper, its desorption isotherm at

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Table 1 Sorption models used to fit experimental data

Model	Equation
BET [8]	$X_e = \frac{abaw}{(1-aw)(1+(b-1)aw)}$ (1)
Chirife [9]	$X_e = \frac{1}{a}\left[\ln\left(\frac{b}{RT}\right) - \ln(-\ln(a_w))\right]$ (2)
GAB [10]	$X_e = \frac{abcaw}{(1-caw)[1+(b-1)caw]}$ (3)
Halsey [11]	$X_e = \left[\frac{-a}{\ln(aw)}\right]^{(1/b)}$ (4)
Harkins [12]	$X_e = \frac{1}{\sqrt{a+b\ln(aw)}}$ (5)
Henderson [13]	$X_e = \left[\frac{\ln(1-aw)}{a}\right]^{(1/b)}$ (6)
Kühn [12]	$X_e = a + \frac{b}{\ln(aw)}$ (7)
Mizrahi [12]	$X_e = a\left[\frac{aw}{(1-aw)} + \frac{b}{(1-aw)}\right]$ (8)
Oswin [14]	$X_e = a\left[\frac{aw}{1-aw}\right]^b$ (9)
Peleg [15]	$X_e = a(a_w)^b + c(a_w)^d$ (10)
Smith [16]	$X_e = a - b\ln[1 - a_w]$ (11)

298.1 K was experimentally determined and compared with bibliographic data for other seed products.

An important number of mathematical models have been proposed to describe sorption isotherms, and they can be found in the literature. In this work, a selection of the most common models with two (BET, Halsey, Harkins, Henderson, Kühn, Mizrahi, Oswin and Smith), three (Chirife and GAB) and four (Peleg) parameters were considered. The mathematical expressions of each model are collected in Table 1. In general, most of them are empirical or based on semitheoretical assumptions.

Materials and methods

Sample preparation

Pumpkins (*Cucurbita pepo L.*), stored at 278 K and at similar stages of ripeness, were selected for the equilibrium experiments. Cylinders with fixed dimensions (length: 25 mm; diameter: 15 mm) were obtained from parenchyma tissue using a cork borer. The initial moisture content, X_0 (from 95% to 97%, wet basis), and Brix (from 3° to 4° Brix) of the samples were used as control values for the fresh pumpkin. Pumpkin seeds were carefully separated from the fruit and stored. The seeds were cut into slices before the equilibrium experiment. In both cases, the moisture content was determined in a vacuum oven at 343 K and 10^4 Pa [7] until a constant weight was achieved.

Osmotic dehydration

Some of the cylinders of pumpkin parenchyma were immersed into a sucrose solution (60% w/w) with agitation (250 rpm) at 298.1 K for 3 h and with a large ratio of solution/samples (w/w) in order to avoid dilution effects. After this contact with the solution, the tissue was partially dehydrated and acquired different contents of osmotic solute.

Equilibrium experiments

Experiments with fresh and osmotic dehydrated parenchyma and raw seeds were carried out in the same way. Each experimental equilibrium moisture content, X_e (d.b.), was determined using a gravimetric technique: the static equilibrium method [17]. All measurements were done in triplicate using a 2 g of each sample. Various water activities, a_w, were selected (from 0.08 to 0.91) using several saturated salt solutions at several temperatures (278.1 K, 298.1 K and 318.1 K) following the recommendations proposed in [17]. The salts selected to obtain a wide and well-covered range were KOH, LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaBr, $SrCl_2$, NaCl, $(NH_4)_2SO_4$, KCl, $BaCl_2$ and KNO_3. Values for the water activity of the salt solutions at each temperature were obtained from the literature [18, 19], and where no data were found, they were experimentally measured with a Novasina Thermoconstanter apparatus. For water activities above 0.65, some thymol crystals were put in the sorption container to avoid microbial growth. When equilibrium was reached (after eight weeks, approximately), the equilibrium moisture content of the samples was determined as described before.

Data analysis

Non-linear least square regression analysis was used to evaluate the parameters of the selected model with the software package Tablecurve (AISN Software). The goodness of fit was determined using the correlation coefficient, the average residual (A), the percent average relative deviation (P), and the standard deviation (S). Each parameter is given by Eqs. (12)–(14), respectively, as:

$$A = \sum_{i=1}^{n}\left[\frac{X_i^{cal} - X_i^{exp}}{n}\right] \quad (12)$$

$$P(\%) = \frac{100}{n}\sum_{i=1}^{n}\left[\frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}}\right] \quad (13)$$

$$S = \sqrt{\sum_{i=1}^{n}\left[\frac{((X_i^{cal} - X_i^{exp}) - A)^2}{n-p-1}\right]} \quad (14)$$

where X_i^{cal} and X_i^{exp} are the calculated and experimental equilibrium moisture content values, n is the number of experimental data points, and p is the number of parameters of the model.

Results and discussion

Equilibrium data

Experimental equilibrium data for pumpkin parenchyma at 278.1 K, 298.1 K and 318.1 K are shown in Fig. 1. The equilibrium moisture content at each water activity is the mean value of three replications. All isotherms show an increase in equilibrium moisture content with increasing water activity, at each temperature. The shape of each isotherm is a very light sigmoidal curve of somewhere between type II and type III following Brunauer's classification [20]. Taking into account the composition of pumpkin parenchyma tissue (82.7% carbohydrate and 9.6% protein, both values measured on a dry basis) [21], the sorption isotherm is very similar to the corresponding average sorption isotherms of glucose and fructose (the main sugars present in the pumpkin with similar composition values), and the end is also similar to the sucrose

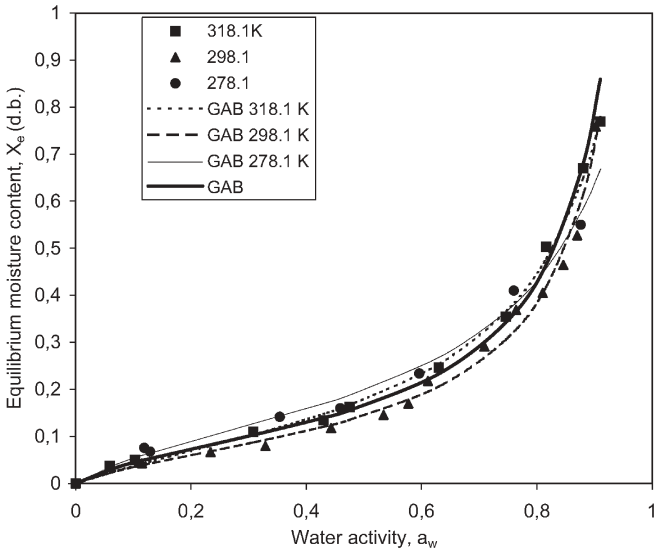

Fig. 1 Experimental equilibrium data at different temperatures and GAB sorption isotherms (Eq. 3) for fresh pumpkin parenchyma

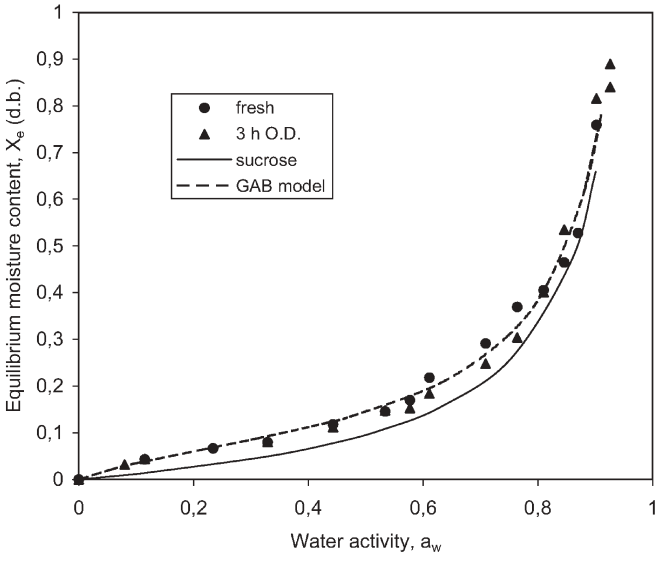

Fig. 2 Experimental equilibrium data for fresh and osmotically-treated pumpkin parenchyma tissue with sucrose solution, with the GAB model (Eq. 3) and the sucrose isotherm [22] also plotted at 298.1 K

isotherm (included in Fig. 2) [22]. Moisture content increases considerably at high water activity values. This fact is related to the the crystalline sugars' transition to the amorphous state [23].

Practically no effect of temperature on the sorption isotherm is observed. The dependence with temperature is clearer at higher temperatures and when a wide range of temperatures are studied. These results indicate that, over the range of temperatures studied, the pumpkin tissue exhibits similar hygroscopicities. When low temperatures are employed, no physical or chemical changes are produced, and the energy levels reached are insufficient to allow great water mobility. This behaviour is also shown

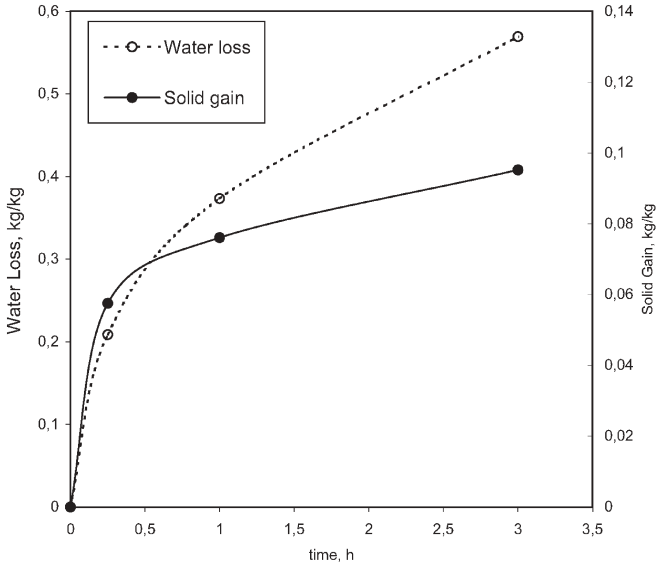

Fig. 3 Water loss and solid gain kinetics for the simultaneous dehydration/sucrose impregnation of pumpkin parenchyma with 60º Brix sucrose solution at 298.1 K

for other products [24]. As sorption characteristics have practically no dependence on temperature, this fact indicates that pumpkin can be stored in the same atmosphere at any temperature within the studied range (these are common conditions for storing).

Figure 2 shows the equilibrium desorption data for fresh pumpkin parenchyma and that partially dehydrated by osmotic dehydration using a sucrose solution. During soaking, the composition of the pumpkin is changed, not only through water loss, but also by acquisition of solutes from the osmotic solution. The osmotic agent acquisition and water removal kinetics of pumpkin with 60° Brix sucrose solution at 298.1 K are shown in the Fig. 3. Both processes are fast and 0.095 kg sucrose/kg initial wet mass was gained by the pumpkin after 3 h. The uptake of solids is most rapid over the first hour, after which it slows down because a pseudo-equilibrium is achieved, but the water loss continues to be fairly rapid (reaching 0.58 kg water/kg initial wet basis) after 3 h. The sorption isotherms of these pre-osmotic products are very similar. In Fig. 2, the sorption isotherm of pure sucrose is shown for comparison [22], and the equilibrium data for the pumpkin impregnated with sucrose over 3 h correlates closely to the sucrose sorption isotherm, although the values of equilibrium moisture content are slightly higher, probably due to the presence of proteins and other more hygroscopic compounds in the pumpkin [25]. Taking into account the previous considerations, it is reasonable to assume that the sorption isotherms are very similar, and from a practical point of view this means that all pumpkins can be dried, stored and preserved in the same way.

Figure 4 shows equilibrium experimental data for the sorption isotherm of pumpkin seeds. The shape classification of the isotherm is type II. The high oil concentration in the seeds facilitates a lower equilibrium moisture

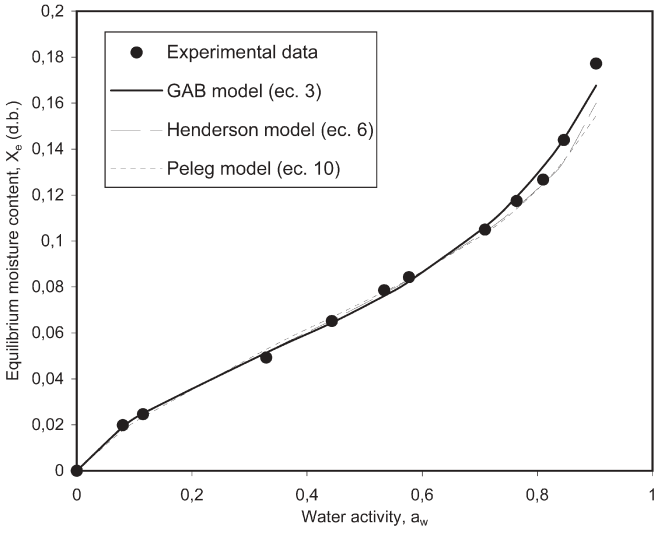

Fig. 4 Experimental equilibrium data and several models for the sorption isotherm of pumpkin seed at 298.1 K

content compared to parenchyma tissue at the same water activity. The results obtained are similar to those found for seeds of other food materials reported by other authors [26].

Modeling of sorption isotherms

The experimental data were modeled using several models found in the literature. Taking into account that equilibrium moisture content did not depend on the temperature for the pumpkin parenchyma in the studied range for the osmotic pretreatment, the modeling incorporated all of the experimental data in order to obtain a single equation valid over the interval of interest. This equation is very useful from a practical point of view. The values of the fit parameters for each model and their associated statistics are collected in Table 2a. Several models gave the same results when fitting the experimental data; from this point of view, the Halsey and Oswin models with two parameters (simpler models) and the Chirife and GAB models with three parameters may be recommended. The values of the fit statistics for each model are satisfactory, taking into account the wide range of application of these equations. Specifically, the GAB model (also known as the kinetic model based on a multilayer and condensed film) is considered to be the most versatile, and it has been adopted by many researchers to model sorption isotherms of many food materials, due to the physical meaning often attached to its parameters.

Table 2b shows the fit parameters and associated statistics for the GAB model at each temperature considered. The results are in the typical range for this type of product [1, 27] and the quality of the fits are good (but useful only for each temperature). Figure 1 shows the GAB model fits at each temperature (values of the parameters are shown in Table 2b), as well as the GAB model for all experimental data (values of the parameters are shown in Table 2a). Also, for comparison, the average GAB model is plotted in Fig. 2.

The results from modeling the sorption isotherm for pumpkin seeds are collected in Table 3. Analyzing the results, the Henderson, GAB and Peleg models are the best. Figure 4 shows the sorption isotherms obtained with these models.

Conclusions

The shape of the desorption isotherm of fresh pumpkin parenchyma tissue is intermediate between types II and III (slight sigmoidal shape); for seeds it is clearly type II. Over the range of the low temperatures studied, the isotherms for parenchyma tissue show no clear dependence on the temperature. The equilibrium data are satisfactorily fitted by several models. Specifically, the parameter *a*

Table 2a Estimated values for the fit parameters (and associated statistics) for sorption models applied to sorption data for pumpkin parenchyma in the range 278.1–318.1 K

Model	*a*	*b*	*c*	*d*	R^2	*P* (%)	*A*	*S*
BET (a_w<0.4)	0.0779	31.864			0.966	17.28	0.0334	0.02012
Chirife	2.0799	–0.8025	–0.0015		0.975	15.47	0.0289	0.01745
GAB	0.0961	0.9756	8.0626		0.974	12.95	0.0287	0.01761
Halsey	0.0762	1.2361			0.975	15.29	0.0288	0.01744
Harkins	2.0881	–38.702			0.959	31.90	0.0374	0.02509
Henderson	–2.759	0.7046			0.972	20.69	0.0304	0.01760
Kühn	0.0453	–0.0766			0.965	19.43	0.0342	0.01995
Mizrahi	0.0737	0.1710			0.957	32.91	0.0582	0.02900
Oswin	0.1636	0.7051			0.974	14.70	0.0292	0.01754
Peleg	0.3663	1.0000	1.617	12.047	0.982	16.17	0.0323	0.01941
Smith	–0.0044	0.3106			0.958	26.48	0.0506	0.02687

Table 2b Estimated values for the fit parameters (and associated statistics) for the GAB model applied to sorption data for pumpkin parenchyma tissue at several temperatures

Temperature (K)	*a*	*b*	*c*	R^2	*P* (%)	*A*	*S*
278.1	0.1343	0.887	5.831	0.993	4.23	0.00897	0.00231
298.1	0.0894	0.976	4.990	0.990	5.02	0.01050	0.00264
318.1	0.1165	0.928	3.553	0.997	3.53	0.00781	0.00147

Table 3 Estimated values for the fit parameters and associated statistics for various sorption models fitted to sorption data for pumpkin seeds at 298.1 K

Model	*a*	*b*	*c*	*d*	R^2	*P* (%)	*A*	*S*
Chirife	−2.3076	−1.2960	0.6125		0.993	4.07	0.00273	0.00369
GAB	0.0565	7.4430	0.7287		0.995	2.90	0.00231	0.00353
Halsey	0.00148	2.2989			0.951	14.69	0.00826	0.00712
Harkins	14.219	−263.37			0.968	13.07	0.00715	0.00602
Henderson	−47.548	1.6136			0.996	2.30	0.00213	0.00298
Oswin	0.0715	0.3532			0.981	10.37	0.00559	0.00378
Peleg	0.1251	0.7758	0.0791	6.8428	0.995	4.14	0.00263	0.00324
Smith	0.0218	0.0599			0.960	11.31	0.00839	0.00569

(corresponding to the monolayer moisture content, an important value for correct preservation) of the GAB model, resulted in values of 0.096 and 0.057 (kg water)/(kg dry solid) for parenchyma and seed, respectively. The equilibrium values for the moisture content of both parenchyma and seed have water activity values that are very similar (0.30–0.35), indicating that both products can be stored in the same atmosphere. When pumpkin parenchyma is osmotically treated, the sorption isotherm is not significantly changed because the self-dried composition of pumpkin is practically a mixture of sugars (glucose and fructose, monosaccharides of sucrose). With more sucrose content, the pumpkin has a sorption isotherm similar to the sucrose sorption isotherm, but with a higher equilibrium moisture content, probably due to the presence of proteins in the pumpkin. The results indicate that both products, fresh or osmotically-treated, can be stored in the same way.

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