PAPER

FREEZE DRYING AND MOISTURE ADSORPTION KINETICS OF KEFIR POWDER

H. ISLEROGLU
Tokat Gaziosmanpasa University, Faculty of Natural Sciences and Engineering, Food Engineering Dept., 60150, Tokat, Turkey
E-mail address: hilal.isleroglu@gop.edu.tr

ABSTRACT

Freeze drying and moisture adsorption behaviour of kefir powder were investigated by fitting the experimental drying data to ten thin layer drying and sorption isotherm models. Moisture adsorption isotherms of kefir powder were determined at 5-35°C and within the range of 0.11–0.88 water activity. By statistical comparison of the values, Midilli et al. was found to be the best model describing the freeze drying behaviour. The GAB and Oswin equations gave the closest fit to the adsorption data over the tested range of temperatures and water activities. Additionally, adsorption isotherms data were used to determine the thermodynamic properties such as isosteric heat, sorption entropy and Gibbs free energy. The enthalpy-entropy compensation was valid for the adsorption process and showed that the process was controlled by the enthalpy. Gibbs free energy was negative at all of the tested temperatures, which indicates that moisture adsorption of kefir powder was a spontaneous process.

Keywords: adsorption isotherm, compensation theory, freeze drying, Gibbs free energy, kefir powder

1. INTRODUCTION

Kefir is a fermented milk drink with a unique acidic aromatic taste and it is a complex probiotic containing numerous bacterial species such as acetic acid bacteria, *Leuconstoc, Lactobacillus*, *Lactococcus*, and also yeasts (CHIFIRIUC *et al.*, 2011). Kefir also contains small amounts of acetic acid, ethanol, acetaldehyde, lactic acid, diacetyl, carbon dioxide, and acetoin that characterized its specific flavour (GRONNEVIK *et al.*, 2011; ARSLAN, 2014). Kefir grains or commercially available dairy cultures were used to inoculate milk for producing kefir (TAMIME *et al.*, 2011). Since kefir has several health promoting and therapeutic effects, consumer's interests are increasing about consuming it.

The health beneficial effects are identified with bioactive compounds such as exopolysaccharides and bioactive peptides produced during fermentation process (FARNWORTH, 2005). However, kefir has a short shelf-life even in refrigerator conditions due to its biologically active components. Therefore, improvements in the shelf-life of kefir can be achieved by changing it into a shelf-stable powder. Also, kefir powder enables easier transportation and storage, and it can be used as an ingredient in various formulations. ATALAR and DERVISOGLU (2015) produced kefir powder by spray drying and determined the optimum drying conditions. However, there are no reports related freeze drying characteristics and sorption properties of kefir in the literature.

Compared to spray drying process, freeze drying generally results in better survival of starter culture and improved reconstitution properties (KUMAR and MISHRA, 2004). In freeze drying process, moisture is removed at low temperature which prevents thermal inactivation and material structure is maintained i.e. particles and cells are not damaged (ADAMIEC *et al.,* 2015).

Moisture sorption isotherm (MSI) measured experimentally under isothermal conditions characterizes the relationship between the equilibrium moisture content (EMC) and water activity (a_w) of foods at constant temperature and pressure (KAYMAK-ERTEKIN and GEDIK, 2004). MSI provides information about hygroscopic properties of a product and it can be used in modelling drying process, calculating changes in moisture content during storage and estimating shelf-life by theoretical calculation (RIZVI, 1995). EMC depends on many factors such as physical structure and chemical composition of the product, and the environmental air conditions. Wide range of equations (theoretical, semi-empirical, empirical) have been suggested; however, no one equation provides precise results over the entire range of water activity (WANG *et al.,* 2013). Some of the best known equations are Brunauer-Emmet-Tetter (BET) equation which has been successfully applied to almost all kinds of materials, but especially to hydrophilic polymers for $a_w< 0.5$ and Guggenheim-Anderson-Boer (GAB) equation which is evaluated as the most useful sorption model present in the literature, capable of application to circumstances over a wide range of water activities ($0.1< a_w< 0.9$) (KOÇ et al., 2010).

Temperature dependence of MSI is very important because the foods are subjected to different temperatures during storage and also processing (KAYMAK-ERTEKIN and SULTANOGLU, 2001). Thermodynamic properties such as the isosteric heat of sorption, differential entropy and Gibbs free energy are important parameters for processing and storage, and they provide a conception about water properties and energy requirements related to sorption behaviour and these properties can be calculated from sorption isotherms (RIZVI, 1995; TOLABA *et al.,* 2004).

The aims of the current study were to examine a proper thin-layer drying model for describing the freeze drying of kefir, to achieve the adsorption isotherms of kefir powder at different temperatures, to determine the best model describing adsorption behaviour and to estimate thermodynamic properties such as net isosteric heat (q_{st}), differential entropy (ΔS) and Gibbs free energy (ΔG) for kefir powder.

2. MATERIAL AND METHODS

2.1. Materials

Ultra-high temperature (UHT) sterilized milk with 3.0 % milkfat was used for kefir production. Milk (3 liters) was fermented with a commercial kefir starter (~1 g of powder) (Maysa A.S., Turkey) and fermentation was performed at 30°C for 20 hours, which were the declared optimal conditions according to producers' information. Final pH value of kefir was 4.55 and it was refrigerated until drying.

2.2. Freeze drying characteristics

Drying experiments were carried out in a laboratory scale freeze dryer (CHRIST, Alpha 1-4 LSC, Germany). Kefir was poured in to drying pans as 3 mm thickness and then frozen at -20°C for a night. Freeze drying processes were performed at 1 mbar absolute pressure and -55°C condenser temperature. Each experiment for incrementing time periods was conducted with incipient samples of equal mass (~30 g of frozen sample), and the moisture loss was established by weighing drying pans using a digital balance. Weight of sample was saved at 2 hours intervals until constant weight was achieved. All drying experiments were duplicated.
The dimensionless moisture ratio (MR) of the samples was determined using Eq. (1).

$$\mathrm{MR} = \frac{M-M_e}{M_0-M_e} \qquad (1)$$

where, M_0 is the initial moisture content, M_e is the equilibrium moisture content and M is the moisture content at time t. The moisture content of the samples were determined using an infrared moisture analyser (Shimadzu, MOC 63u, Japan) at 90°C as two parallels and the results were confirmed by the standard oven method. To determine drying characteristics the experimental data was fitted to ten different thin layer drying models given in Table 1.
Fick's second law of diffusion for an infinite slab was used to describe moisture diffusion (Eq. 2) and it was assumed that the moisture was migrating only by diffusion; shrinkage and external mass transfer resistance were negligible.

$$\mathrm{MR} = \frac{M-M_e}{M_0-M_e} = \frac{8}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left[-(2n+1)^2\frac{\pi^2}{4}\frac{D_{eff}t}{L^2}\right] \qquad (2)$$

where, D_{eff} is the effective diffusion coefficient and L is the thickness of the slab. At sufficiently large drying times, only the first term of the Eq. (2) is taken into consideration to calculate the effective diffusion coefficient (Eq. 3).

$$\mathrm{In\ MR} = In\ \frac{8}{\pi^2} - \frac{\pi^2 D_{eff}t}{4L^2} \qquad (3)$$

2.3. Adsorption characteristics of kefir powder

Moisture adsorption isotherms of kefir powder were established by a gravimetric method at ten relative humidities between the range of 0.11 and 0.88. To obtain desired relative humidity, hermetic jars containing saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, NaBr, $SrCl_2$, NaCl, KCl and $BaCl_2$ were prepared (GREENSPAN, 1977; SPIESS and WOLF, 1983). A test tube consisting of 5 ml toluene was put into every jar which had relative humidity higher than 50 % to avoid microbial growth (LABUZA, 1984). Triplicate samples of ~0.3 g of kefir powder were put into measuring bottles and afterward into glass jars containing the saturated salt solutions. The glass jars were placed in controlled temperature cabinets at selected temperatures of 5, 25 and 35°C. The samples were weighed at certain intervals until a change of less than 0.001 g was observed. The equilibrium moisture content (EMC) of samples was obtained by drying in an oven at 102°C for 2 hours (AOAC, 1990). The experimental sorption data at three temperatures was fitted to the most widely used sorption models given in Table 2.

Table 1. Equations for different thin layer drying models.

Model name	Model equation	Reference
Midilli *et al.*	$\mathrm{MR} = a\,exp(-kt^n) + bt$	MIDILLI *et al.* (2002)
Parabolic	$\mathrm{MR} = a + bt + ct^2$	SHARMA and PRASAD (2004)
Wang and Singh	$\mathrm{MR} = 1 + at + bt^2$	WANG and SINGH (1978)
Logarithmic	$\mathrm{MR} = a\,exp(-kt) + c$	GOYAL *et al.* (2007)
Verma	$\mathrm{MR} = a\,exp(-kt) + (1-a)\exp(-bt)$	VERMA *et al.* (1985)
Page	$\mathrm{MR} = exp(-kt^n)$	ZHU and XINQI (2014)
Two term exponential	$\mathrm{MR} = a\,exp(-kt) + (1-a)\exp(-kat)$	SHARAF-ELDEEN *et al.* (1980)
Henderson and Pabis	$\mathrm{MR} = a\,exp(-kt)$	WANG *et al.* (2007)
Two term	$\mathrm{MR} = a\,exp(-k_0 t) + b\,exp(-k_1 t)$	MADAMBA and DRISCOLL (1996)
Lewis	$\mathrm{MR} = exp(-kt)$	AVHAD and MARCHETTI (2016)

Table 2. Adsorption models for kefir powder.

Model name	Model equation	References
GAB	$\mathrm{M} = \frac{M_0 CKa_w}{[(1-Ka_w)(1-Ka_w+CKa_w)]}$	VAN DEN BERG (1985)
BET	$\mathrm{M} = \frac{M_0 ca_w}{[(1-a_w)+(c-1)(1-a_w)a_w]}$	BRUNAUER *et al.* (1938)
Oswin	$\mathrm{M} = k(a_w/1-a_w)^n$	OSWIN (1946)
Halsey	$a_w = exp(-k/M^n)$	HALSEY (1948)
Modified Halsey	$a_w = exp(-\exp(kT+c)M^{-n})$	IGLESIAS and CHIRIFE (1976c)
Henderson	$1 - a_w = exp(-kTM^n)$	HENDERSON (1952)
Modified Henderson	$\mathrm{M} = \{ln(1-a_w)\,/\,[-k(T+c)]\}^{(1/n)}$	HENDERSON (1952)
Chen	$a_w = exp[k - c\,exp(-bM)]$	CHEN (1971)
Peleg	$\mathrm{M} = (k\,a_w{}^n) + (c\,a_w{}^b)$	PELEG (1993)
Iglesias–Chirife	$ln[M + (M^2 + M_{0.5})^{1/2}] = k\,a_w + c$	IGLESIAS and CHIRIFE (1978)

2.4. Thermodynamic properties of adsorption

The net isosteric heat (differential enthalpy, q_{st}) and differential entropy (ΔS) of sorption can be determined from Clausius-Clapeyron equation (Eq. 4) for constant EMC and with the assumption of heat of vaporization and heat of sorption don't change with temperature (AL-MUHTASEB *et al.*, 2004).

$$\left(\frac{\partial(\ln a_w)}{\partial(1/T)}\right)_{X_e} = -\frac{q_{st}}{R} \quad (4)$$

where, q_{st} is the net isosteric heat of sorption (kJ/mol), T is the absolute temperature (K), and R is the universal gas constant (8.314×10^{-3} kJ/mol K). The Eq. (5) was obtained by integration of the Clausius-Clapeyron equation. Net isosteric heat (q_{st}) and differential entropy (ΔS) were determined by generating ln (a_w) versus $1/T$ graph for a selected EMC (X_e) of material and then q_{st} was calculated from the slope and ΔS was determined from the intercept.

$$\ln a_w = -\left(\frac{q_{st}}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \quad (5)$$

The enthalpy-entropy compensation theory suggests a linear relationship between the differential entropy (ΔS) and enthalpy (q_{st}) (Eq. 6) for a specific reaction.

$$q_{st} = T_\beta \Delta S + \Delta G_\beta \quad (6)$$

where T_β s the isokinetic temperature and ΔG_β is the Gibbs free energy at the specific temperature of T_β. The isokinetic temperature was compared with the harmonic mean temperature (T_{hm}) in order to validate the enthalpy-entropy compensation theory.

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

where, n is the number of isotherms. The compensation theory only applies if $T_\beta \neq T_{hm}$. If $T_\beta > T_{hm}$ the process is controlled by enthalpy, while if $T_\beta < T_{hm}$ the process is entropy driven (NOSHAD *et al.*, 2012).
Gibbs free energy (ΔG, kJ/mol) was determined using the change in a_w data estimated by the GAB model and was calculated according to Eq. (8) (YAZDANI *et al.*, 2006).

$$\Delta G = R \cdot T \cdot \ln(a_w) \quad (8)$$

2.5. Data analysis

Nonlinear regression analysis was used to evaluate the drying and adsorption model parameters using MATLAB software version 9.1.0 (MathWorks Inc., USA). To evaluate the quality of fit, regression coefficient (R^2), root mean square error (RMSE), chi-square (χ^2) and the mean relative percentage deviation (P %) between predicted and experimental values were calculated using Eq.s (9), (10), (11) and (12), respectively.

$$R^2 = \frac{\sum_{i=1}^{N}(M_i - M_{pre,i}).(M_i - M_{exp,i})}{\sqrt{\left[\sum_{i=1}^{N}(M_i - M_{pre,i})^2\right].\left[\sum_{i=1}^{N}(M_i - M_{exp,i})^2\right]}} \quad (9)$$

$$\mathrm{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(M_{exp,i} - M_{pre,i})^2\right]^{1/2} \quad (10)$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(M_{exp,i} - M_{pre,i})^2}{N-n} \quad (11)$$

$$P\ (\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|M_{exp,i}-M_{pre,i}|}{M_{exp,i}} \quad (12)$$

where, M_{exp} and M_{pre} express the experimental and predicted moisture ratio for drying and moisture content for adsorption process, respectively. N is the number of observations and n is the number of constants of the model. The best models defining the thin-layer drying and adsorption behaviour were chosen as the one with the highest R^2, and the lowest RMSE and χ^2 value. A model was accepted to be valid if the P value was lower than 10 % for the adsorption process (KAYMAK-ERTEKIN and GEDIK, 2004).

3. RESULTS AND DISCUSSION

3.1. Drying characteristics

The drying characteristic of kefir during freeze drying was evaluated using the moisture ratio data and the change in the moisture ratio of samples versus time was illustrated in Fig. 1. Obviously, the higher level of weight reduction happens in the beginning periods of the drying and the moisture content decreased extensively with increasing drying time. Total drying time was achieved to be as 10 hours by monitoring the changes in the weight of the samples. The equilibrium moisture content was found to be 4.58 (±0.20) %. It was observed that the constant rate period was absent and the complete drying process of kefir took place during the falling rate period (Fig 1).

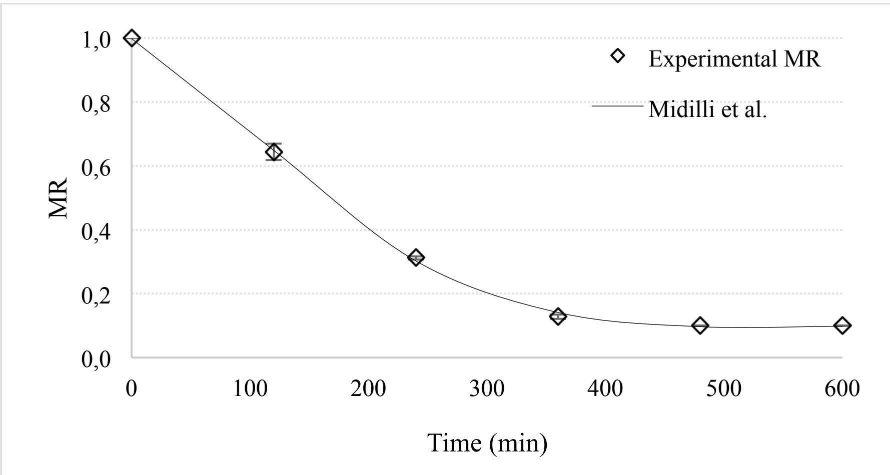


Figure 1. Experimental and predicted moisture ratios for freeze dried kefir.

The curve fitting processes were performed with ten well-known thin layer drying models. Estimated model constants and curve fitting data including regression coefficient (R^2), root mean square error (RMSE) and chi-square (χ^2) values are given in Table 3. The model giving the highest R^2, and the lowest RMSE and χ^2 values was considered as the best model defining the drying characteristic of kefir as in different studies (ERGÜN *et al.*, 2016; İZLI, 2017; ANTAL and KEREKES, 2016). According to the selection criteria, MIDILLI *et al*. model was found to be the best model representing the drying characteristics of kefir with its highest R^2 (0.999), and the lowest RMSE (0.012) and χ^2 ($1.51*10^{-4}$) values. Likewise, MIDILLI *et al*. model was selected as the best model for defining the freeze drying

behaviour of soluble coffee (GHIRISAN *et al.,* 2017) and kiwi (İZLI *et al.,* 2017). Furthermore, Parabolic and Wang and Singh models were also satisfactory for describing the freeze drying characteristics of the kefir owing to high R^2, and low RMSE and χ^2 values (Table 3). Page and Two-term exp. models which gave fairly well statistical results were also reported by some researchers as the most appropriate model for freeze drying processes (İZLI, 2017; MARQUES and FREIRE, 2005; ACAR *et al.,* 2015; İZLI *et al.,* 2018), but they did not exactly match the experimental data in the current study.
The effective moisture diffusivity (D_{eff}) of the kefir was achieved from Fick's Law of Diffusion model and calculated from the slope of the natural logarithm of MR (ln MR) against drying time (s) plot, and found to be as $2.61x10^{-10}$ m^2/s.

Table 3. Estimated parameters and statistical analysis of drying models.

Model	Parameters	R^2	RMSE	$\chi^2 *10^4$
Midilli *et al.*	a= 0.999 b= 0.0001558 k= 0.0003095 n= 1.526	0.999	0.012	1.51
Parabolic	a= 1.01 b= -0.003731 c= 3.711*10-6	0.997	0.028	7.69
Wang and Singh	a= -0.00367 b= 3.634*10-6	0.996	0.025	6.08
Two term	a= 0.9523 b= 0.06838 k0= 0.004697 k1= 0.004699	0.985	0.071	49.81
Page	k= 0.001535 n= 1.2	0.990	0.042	17.35
Logarithmic	a= 1.026 c= -0.005806 k= 0.004633	0.985	0.058	33.14
Henderson	a= 1.021 k= 0.004699	0.985	0.050	24.91
Two term exp.	a= 1.819 k= 0.006567	0.991	0.040	15.80
Lewis	k= 0.004611	0.985	0.046	20.90
Verma	a= 1.008 b= 0.004233 k= 0.004608	0.985	0.059	34.83

3.2. Adsorption characteristics

Adsorption isotherms were constructed in which the moisture bound by adsorption per unit weight was plotted against water activity (Fig 2). As seen in Fig. 2, the moisture adsorption isotherms of kefir powder are temperature-dependent and the sorption ability of the samples was lower at higher temperatures. At increasing temperatures, the binding forces decrease; hence less moisture is absorbed at the same water activity at higher temperatures (MULET *et al.,* 2002). The decreasing sorptivity of kefir powder with increasing temperature can be also explained by its rich composition in terms of proteins and polysaccharides which have higher water-binding capacity at low temperatures in comparison with high temperatures (KAYMAK-ERTEKIN and GEDIK, 2004). This demonstrates the kefir powder turned out to be less hygroscopic at high temperatures. These results are similar to those of other studies about the obtaining of sorption isotherms of yoghurt powder (KOÇ *et al.,* 2010; STENCL, 2004; KUMAR and MISHRA, 2006). The type III isotherm was observed for kefir powder, which indicated that binding energy was so high that water activity was suppressed while water was absorbed. This phenomenon is characteristic for these types of materials and when all the binding sites are filled, the increase in moisture content causes a significant increase in water activity (RAHMAN, 1995). Bioactive peptides and exopolysaccharides are the main components of kefir and their concentration depends on milk and the applied culture type (BARUKČIĆ *et al.*, 2017). Foods rich in soluble components such as kefir were found to exhibit type III behaviour (RAO and RIZVI, 1995).

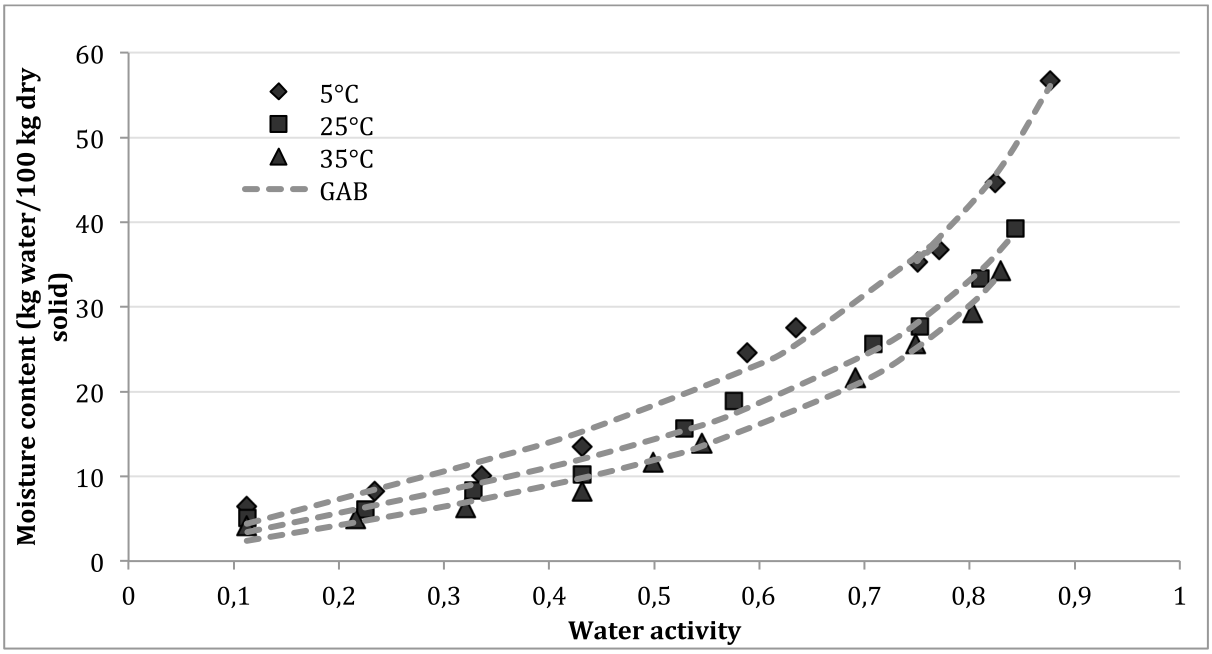


Figure 2. Moisture adsorption isotherms of kefir powder at different temperatures.

To represent water adsorption characteristics of kefir powder, the sorption data were fitted to ten sorption isotherm equations. Non-linear regression analysis was used to determine the best-fitted values of model constants and they are given in Table 4 and Table 5 for the model that account for temperature effect or not. The regression coefficient (R^2), root mean square error (RMSE) and the mean relative percentage deviation (*P %*) are also represented in Table 4 and Table 5 as the fitting criteria. The selection criteria of the most appropriate adsorption model were the simplicity of the model and the degree of fit to the experimental data. It can be seen that GAB, Oswin and Peleg equations gave the best fit to the experimental data of kefir powder (Table 4).

Peleg equation is a four-parameter, easy-to-solve semi-empirical model, and is based on the explicit denial of water monolayer presence (PELEG, 1993). Although this equation has been successfully applied at all temperatures in a wide range of water activity at all types of isotherms (MOREIRA *et al.*, 2005), it gave higher *P* (%) value (> 10%) at 5°C (Table 4).

Oswin equation is an empirical model and considered as the best model for defining the isotherms of starchy foods (OSWIN, 1946). Both Oswin and GAB equations showed a high goodness of fit with $R^2 > 0.99$ and low *P* (< 10%) values for all temperatures (Table 4).

Table 4. Estimated parameters and statistical analysis of the sorption models which are invariant with temperature.

Model	Parameters	5°C	25°C	35°C
GAB	M_0	13.530	10.94	9.776
	C	3.742	3.509	2.510
	K	0.885	0.881	0.899
	R^2	0.992	0.991	0.992
	P (%)	8.635	8.438	9.591
	RMSE	1.714	1.283	1.124
*BET	M_0	7.884	6.146	5.963
	C	17.220	18.000	8.373
	R^2	0.964	0.968	0.921
	P (%)	5.122	4.812	10.439
	RMSE	0.698	0.508	0.971
Oswin	k	18.320	14.290	11.890
	n	0.581	0.601	0.670
	R^2	0.992	0.991	0.992
	P (%)	8.500	8.145	8.116
	RMSE	1.640	1.199	1.050
Halsey	k	15.910	11.86	8.450
	n	1.120	0.601	0.670
	R^2	0.985	0.984	0.988
	P (%)	10.257	9.767	8.330
	RMSE	0.034	0.034	0.030
Chen	k	-0.119	-0.155	-0.206
	c	2.492	2.637	2.718
	b	0.078	0.110	0.148
	R^2	0.976	0.976	0.972
	P (%)	13.894	12.879	15.049
	RMSE	0.046	0.045	0.047
Peleg	k	75.470	8.715	48.110
	n	10.800	0.278	2.859
	c	45.140	47.850	5.040
	b	1.238	2.863	0.097
	R^2	0.991	0.992	0.995
	P (%)	10.832	4.756	2.866
	RMSE	1.996	1.306	0.813
Iglesias–Chirife	$M_{0.5}$	19.113	13.679	11.725
	k	2.785	2.746	2.901
	c	2.211	1.995	1.758
	R^2	0.989	0.989	0.985
	P (%)	7.415	7.450	8.684
	RMSE	0.029	0.508	0.033

*a_w range for BET equation was 0.11-0.50. The first four data points were used.

GAB equation is a semi-theoretical and multi-molecular and homogeneous adsorption model and capable of application to situations over a wide variety of conditions. Therefore, it is the most suitable equation for the design of drying process because of its reliability, simple mathematical form, and the possibility of being used in a wide range (AL-MUHTASEB *et al.*, 2002). GAB equation includes the monolayer moisture content (M_0) as well as the C and K constants associated with the energies of interaction between first and further molecules at the particular sorption sites (BASTIOĞLU *et al.*, 2017); hence the predicted EMC values using GAB model was selected and shown in Fig. 2 because of the physical meaning of the coefficients in the GAB model. The monolayer moisture contents of kefir powder were determined in the range of ~9.8-13.5 kg water/100 kg dry solid and decreased as temperature increased from 5 to 35°C. These M_0 values indicate the theoretical moisture at which kefir powder could present maximum stability during storage. It was observed that the C parameter decreased with increasing temperature (Table 4) and it could be explained by the strong adsorbent-adsorbate interaction at lower temperature. The K parameter assumes that multilayer molecules have interactions with the sorbent and it is in tendency to decrease between energy values of the molecules in the monolayer and liquid water (AL-MUHTASEB *et al.*, 2002). All K values of kefir powder were found to be higher than 0.88, and these high values of K show that the monolayer and multilayer molecules were not very different and that the multilayer molecules act like liquid water. The multilayers have the same properties of liquid water when the K value is equal to 1, hence the sorption behaviour can be modelled by BET equation (GABAS *et al.*, 2007). BET equation also provides an estimation of the monolayer moisture adsorbed on the surface and according to BET equation M_0 values were in the range of ~6.0-7.9 kg water/100 kg dry solid. It was observed that the M_0 values achieved by the GAB model were higher than that achieved by the BET equation (Table 4). BASU *et al.* (2006) stated that the M_0 value estimated by the BET model is always lower than the monolayer value given by GAB and similar results were achieved by KOÇ *et al.* (2010) for yoghurt powder produced using spray drying process. Although BET equation is one of the most effective methods for evaluating the measure of bound water to particular polar sites in dry foods, it gave the lowest R^2 values among the tested models (Table 4).
The Halsey model is favourable for the materials of types I, II, and III and Iglesias-Chirife has been effectively used for type III isotherms (i.e. foods rich in soluble components) (AL-MUHTASEB *et al.*, 2004). Halsey and Iglesias-Chirife equations gave a satisfying estimation of the adsorption for a wide range of water activity (0.11-0.88) (Table 4). Modified Halsey, Henderson and Modified Henderson, which account for temperature effect failed to describe the sorption behaviour at high temperature (Table 5). Furthermore, Chen equation failed to predict the sorption characteristic at all temperatures due to high mean relative percentage deviation values (>10%).

3.3. Thermodynamic properties

Thermodynamic properties of foods give a comprehension of hygroscopic properties and energy requirements related with the sorption behaviour; hence they are important parameters for both processing and storage. Isosteric heat of sorption ensures an indication of the state of the sorbed water and gives information about the stability of the food during handling, storage and processing. Also, the change in heat of sorption with moisture content enables important data for energy consumption calculations and following drying equipment designs (TOLABA *et al.*, 2004). The net isosteric heat of sorption (q_{st}, kJ/mol) values were estimated using Clausius-Clapeyron equation with the equilibrium data at different temperatures and calculated at different equilibrium moisture contents. The variation of the isosteric heat of sorption of the kefir powder with

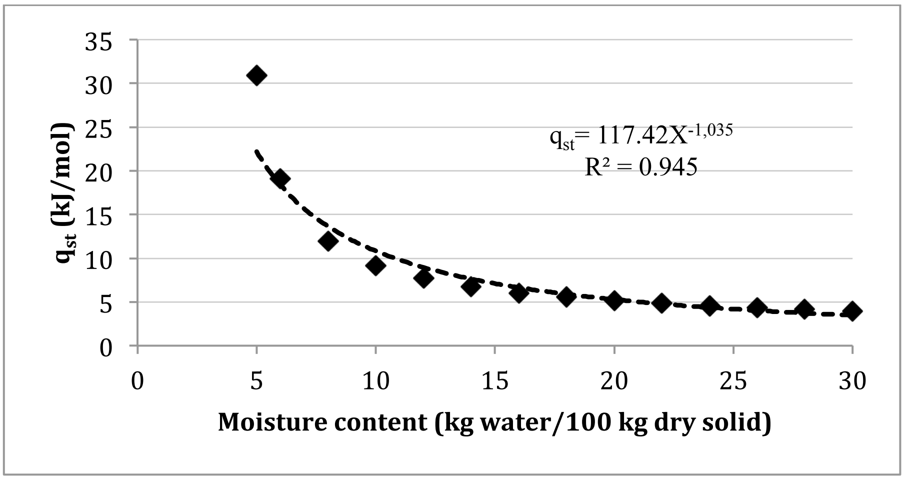
EMC is illustrated in Fig. 3a. The heat of sorption decreased with increasing moisture content. It was observed that the isosteric heat has a strong relationship with moisture content and decreased with a steep slope at lower moisture contents (5-10 kg water/100 dry solid). Sorption initially occurs in highly active polar sites on the surface with the highest interaction energy and pursue by the progressive filling of the less favourable sites with lower binding activation energies (SINIJA and MISHRA, 2008). As the moisture content increases, the net heat of adsorption approaches to zero, hence the heat of adsorption tends to that of pure water (MOREIRA *et al.*, 2008). Similar patterns have been accounted for the net isosteric heats of other milk-based materials (RÜCKOLD *et al.*, 2000; YU and LI, 2012; SAWHNEY *et al.*, 2014; TADAPANENIA *et al.*, 2017).

Table 5. Estimated parameters and statistical analysis of the sorption models that account for temperature effect.

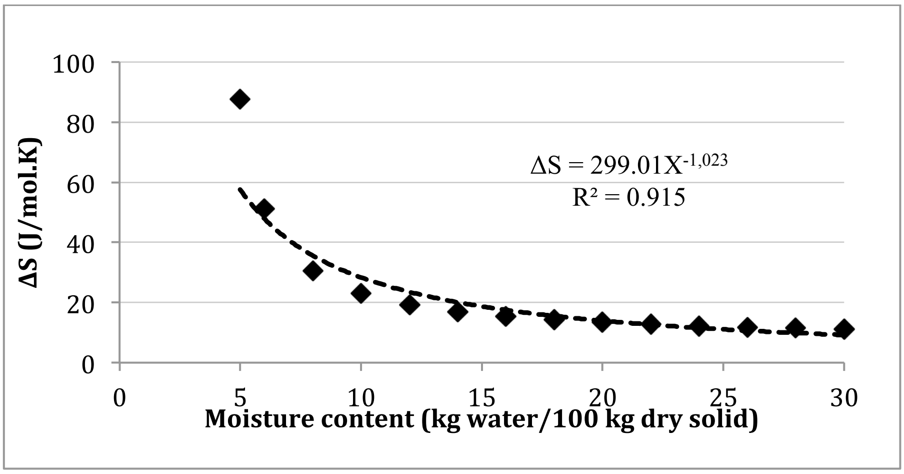
Model	Parameters	5°C	25°C	35°C
Modified Halsey	k	0.130	0.107	-0.092
	c	-33.410	-29.500	30.000
	n	1.150	1.095	0.905
	R^2	0.985	0.984	0.975
	P (%)	8.984	9.749	14.767
	RMSE	0.037	0.036	0.045
Henderson	k	0.0001020	0.0001230	0.0001773
	n	1.087	1.089	1.005
	R^2	0.981	0.979	0.972
	P (%)	9.847	9.218	11.837
	RMSE	0.039	0.039	0.044
Modified Henderson	k	0.0001426	0.0001340	0.0002119
	c	-87.500	-32.590	-46.640
	n	1.100	1.100	1.000
	R^2	0.981	0.979	0.972
	P (%)	9.797	9.451	11.687
	RMSE	0.041	0.041	0.047

The estimated differential entropy values showed a tendency to stabilize at high moisture contents as similar to the isosteric heat of sorption pattern (Fig. 3b).
The entropy of a material is proportional to the quantity of sorption sites present at a given energy level, which gives an indication of the mobility state of water molecules (TELIS *et al.*, 2000). At higher EMC values of kefir powder, the active sites on the surface were occupied by the water molecules, so they had less capacity for sorption and therefore entropy was reduced.
Enthalpy-entropy compensation theory is used to investigate physical and chemical phenomena such as sorption reactions. According to this theory, the relationship between the enthalpy and entropy for a given reaction is linear as a result of the nature of the solute and solvent interaction, which causes the reaction (FASINA, 2006).

a



b



c

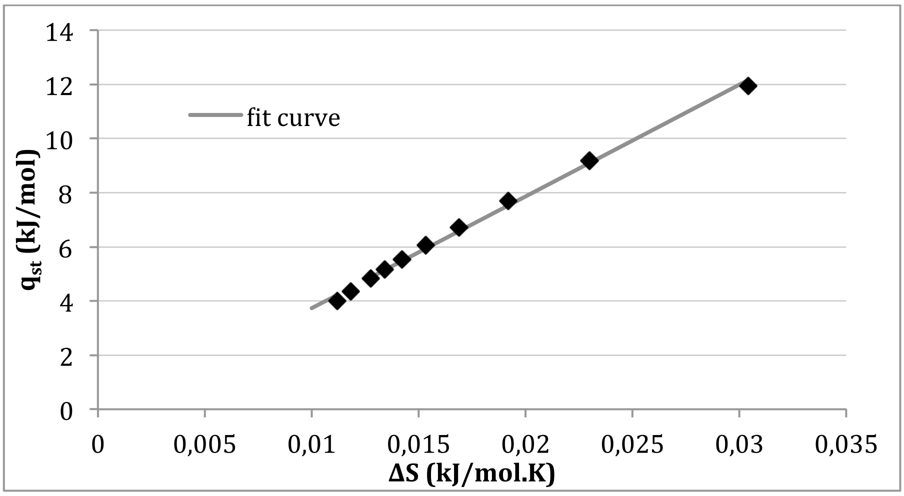


Figure 3. Enthalpy-entropy compensation a) isosteric heat of adsorption, b) differential entropy versus moisture content, c) relationship between enthalpy and entropy. Dashed lines represent the estimated values obtained by a power law relation.

Fig. 3c shows a strong correlation between isosteric heat and differential entropy for the adsorption, which indicates that compensation exists and confirms the enthalpy-entropy compensation theory. The isokinetic temperature (T_{β}) indicates the temperature at which all reactions in the series continue at the same rate. The isokinetic temperature determined from the data by linear regression for adsorption was calculated as 412.7 K and the harmonic mean temperature (T_{hm}) was calculated as 294.1 K, hence a significant difference was observed, the suitability of the compensation theory was reconfirmed. Furthermore, as the T_{β} value was higher than T_{hm} the adsorption process of kefir powder was driven by enthalpy, hence the process was controlled by energy interactions in conjunction with chemical composition of the product (AZURA-NIETO and BERISTAIN-GUEVARA, 2007; CORRÊA *et al.*, 2012). The ΔG_{β} represents the Gibbs free energy at the isokinetic temperature and the negative sign of ΔG_{β} indicates that the water adsorption reaction is spontaneous, and the positive sign represents that it is a non-spontaneous process. The sign of ΔG_{β} was determined as negative (-393.3 J/mol) for kefir powder showing a spontaneous adsorption process.

Gibbs free energy is a thermodynamic parameter related to the amount of process free energy at constant temperature and pressure which is an indication of whether the water sorption is a spontaneous process and indicates the affinity of the sorbents to the water (TELIS *et al.*, 2000). Fig. 4 shows the estimated Gibbs free energy values as a function of the moisture content at each temperature during the adsorption process of kefir powder. Gibbs free energy decreased with increasing temperatures and EMC (Fig. 4). Additionally, Gibbs free energy was noticeably negative at all temperatures, thus showing that water adsorption is a spontaneous process. These results corroborate the findings of SOUZA *et al.* (2015), SILVA *et al.* (2014) and MUNIO *et al.* (2015) in their studies of mango skin, rosemary essential oil micro-particles and spray-dried cherimoya puree, respectively.

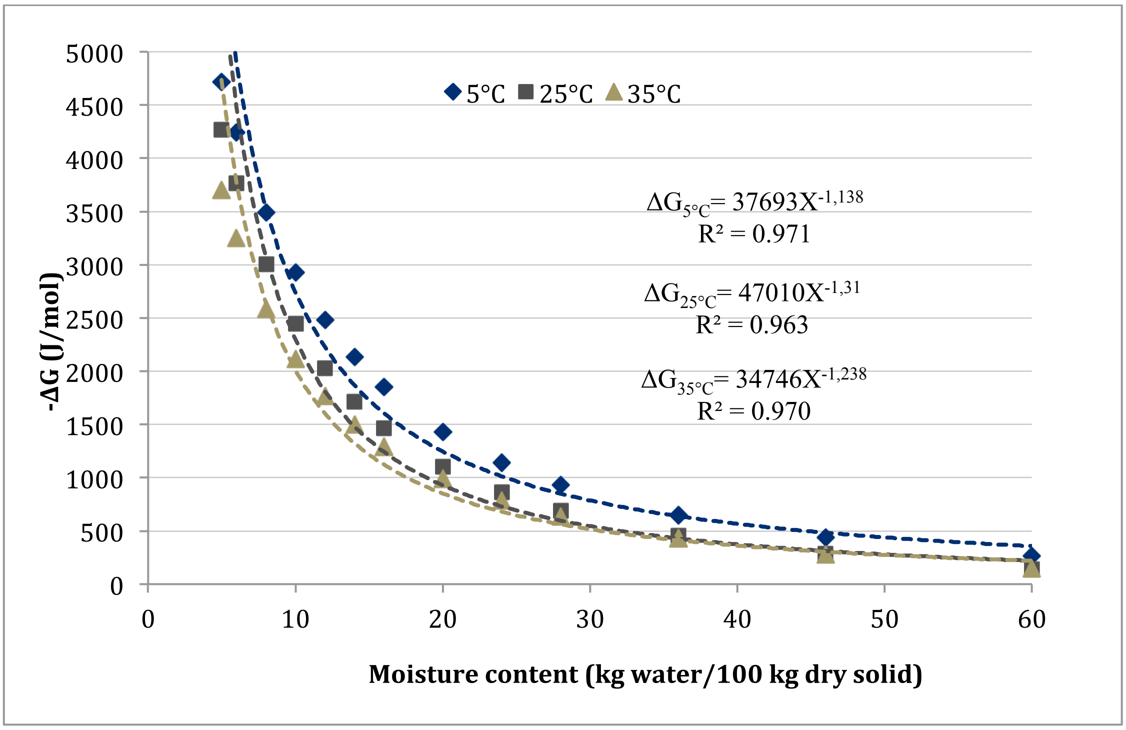


Figure 4. Gibbs free energy of kefir powder at different temperatures. Respective dashed lines indicate the estimated values obtained by a power law relation.

4. CONCLUSIONS

In this study, instant kefir powder was obtained by freeze drying process and drying kinetics of kefir were investigated. Midilli et al. model was chosen to describe the drying behaviour of kefir with great accuracy. To provide information about hygroscopic properties of kefir powder, moisture adsorption isotherms were achieved at different temperatures. The equilibrium moisture content increased with decreasing temperature at constant water activity. Among the sorption models, GAB and Oswin models described well the adsorption behaviour of kefir powder for all experimental conditions. Net isosteric heat and differential entropy estimated using the Clausius-Clapeyron equation increased with decreasing moisture content. Furthermore, compensation enthalpy-entropy theory was confirmed and it can be concluded that the adsorption mechanism for the kefir powder is controlled by enthalpy.

The Gibbs free energy decreased with increasing equilibrium moisture contents and temperatures, and showed that the moisture adsorption of kefir powder is a spontaneous process. It is thought that the data obtained in this study can be used to establish drying and storage conditions of instant kefir powder, which may be a new and alternative product.

REFERENCES

Acar B., Sadikoglu H. and Doymaz I. 2015. Freeze-Drying Kinetics and Diffusion Modeling Of Saffron (*Crocus Sativus* L.). J. Food Proces. Pres. 39:142.

Adamiec J., Kaminski W., Markowski A.S. and Strumillo C. 2015. Drying of Biotechnological Products in Handbook of Industrial Drying, 4th edn. (CRC Press, Taylor&Francis Group)

Al-Muhtaseb A.H., McMinn W.A.M. and Magee T.R.A. 2002. Moisture sorption isotherm characteristics of food products:A review. Food Bioproducts Proces. 80:118.

Al-Muhtaseb A.H., McMinn W.A.M. and Magee T.R.A. 2004. Water sorption isotherms of starch powders. Part 1:Mathematical description of experimental data. J. Food Eng. 61, 297.

Al-Muhtaseb A.H., McMinn W.A.M. and Magee T.R.A. 2004. Water sorption isotherms of starch powders: Part 2: Thermodynamic characteristics. J. Food Eng. 62 (2):135.

Anonymous. 1990. Official Methods for Analysis, Vol. 2, 15th ed.; AOAC. Arlington, VA.

Antal T. and Kerekes B. 2016. Investigation of Hot Air- And Infrared-Assisted freeze-Drying Of Apple. J. Food Process Pres. 40:257.

Arslan S. 2014. A review: chemical, microbiological and nutritional characteristics of kefir. CyTA- J. Food. 13:1.

Atalar I. and Dervisoglu M. 2015. Optimization of spray drying process parameters for kefir powder using response surface methodology. LWT - Food Sci. Technol. 60:751.

Avhad M.R. and Marchetti J.M. 2016. Mathematical modelling of the drying kinetics of Hass avocado seeds. Ind. Crops Prod. 91:76.

Azura-Nieto E. and Beristain-Guevara C.I. 2007. Thermodynamic and kinetic study of water adsorption on whey protein. Rev. Mex. Ing. Quím. 6:359.

Barukčić I., Gracin L., Jambrak A.R. and Božanić R. 2017. Comparison of chemical, rheological and sensory properties of kefir produced by kefir grains and commercial kefir starter. Mljekarstvo. 67 (3):169.

Bastıoğlu A.Z., Koç M. and Kaymak-Ertekin F. 2017. Moisture sorption isotherm of microencapsulated extra virgin olive oil by spray drying. Food Measure. 11:1295.

Basu S., Shivhare U.S. and Mujumdar A.S. 2006. Models for sorption isotherms for foods:A review. Dry. Technol. 24:917.

Brunauer S., Emmett P.H. and Teller E. 1938. Adsorption of gases in multimolecular layer. J. Am. Chem. Soc. 60:309.
Chen, C.S. 1971. Equilibrium moisture curves for biological materials. Transaction of the ASEA. 14:924.

Chifiriuc M.C., Cioaca A.B. and Lazar V. 2011. In vitro assay of the antimicrobial activity of kefir against bacterial and fungal strains. Anaerobe. 17:433.

Corrêa P.C., Oliveira G.H.H. and Santos E.S. 2012. Thermodynamic properties of agricultural products processes. In Physical properties of foods: Novel measurement techniques and applications, ed. by I. Arana, (CRC Press, Boca Raton), p.131-141

Ergün K., Çalıskan G., and Dirim S.N. 2016. Determination of the drying and rehydration kinetics of freeze dried kiwi (*Actinidia deliciosa*) slices. Heat Mass Transf. 52:2697.

Farnworth E.R. 2005. Kefir a complex probiotic. Food Sci. Technol. 2:1.

Fasina O.O. 2006. Thermodynamic properties of sweetpotato. J. Food Eng. 75:149.

Gabas A.L., Telis V.R.N., Sobral P.J.A. and Telis-Romero J. 2007. Effect of maltodextrin and arabic gum in water vapor sorption thermodynamic properties of vacuum dried pineapple pulp powder. J. Food Eng. 82:246.

Ghirisan A., Drăgan S. and Miclăuş V. 2017. Freeze-Drying Kinetics Approach Of Soluble Coffee: Mass Transfer Parameters Estimation. Studia Ubb Chemia. 1:7.

Goyal R.K., Kingsly A.R.P., Manikantan M.R. and Ilyas S.M. 2007. Mathematical modelling of thin layer drying kinetics of plum in a tunnel dryer, J. Food Eng. 79 (1):176.

Greenspan L. 1977. Humidity fixed points of binary saturated aqueous solutions. J. Res. Natl. Bur. Stand. 81:89-112.

Gronnevik H., Falstad M. and Narvhus J.A. 2011. Microbiological and chemical properties of Norwegian kefir during storage. Int. Dairy J. 21:601.

Halsey G. 1948. Physical adsorption on non-uniform surfaces. J. Chem. Phys. 16:931.

Henderson S.M. 1952. A basic concept of equilibrium moisture. Agric. Eng. 33:29.

Iglesias H.A and Chirife J. 1976c. Prediction of the effect of temperature on water sorption isotherms of food material. J. Food Technol. 11:109.

Iglesias H.A. and Chirife J. 1978. An empirical equation for fitting water sorption isotherms of fruits and related products. Can. Inst. Food Sci. Technol. J. 11:12.

İzli G. 2017. Total phenolics, antioxidant capacity, colour and drying characteristics of date fruit dried with different methods. Food Sci. Technol. 37(1):139.

Izli N., Izli G. and Taskin O. 2017. Drying kinetics, colour, total phenolic content and antioxidant capacity properties of kiwi dried by different methods. Food Measure. 11:64.

Izli N., Izli G. and Taskin O. 2018. Impact of different drying methods on the drying kinetics, color, total phenolic content and antioxidant capacity of pineapple. CYTA- J. Food. 16 (1):213.

Kaymak-Ertekin F. and Gedik A. 2004. Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes. LWT - Food Sci. Technol. 37(4):429.

Kaymak-Ertekin F. and Sultanoglu M. 2001. Moisture sorption isotherm characteristics of peppers. J. Food Eng. 47:225.

Koç B., Sakin-Yilmazer M., Balkır P. and Kaymak-Ertekin F. 2010. Spray drying of yoghurt: optimization of process conditions for improving viability and other quality attributes. Dry. Technol. 28:495.

Kumar P. and Mishra H.N. 2004. Yogurt powder. A review of process technology, storage and utilization. Food Bioprod. Process. 82 (2):133.

Kumar P. and Mishra H.N. 2006. Moisture sorption characteristics of mango–soy-fortified yogurt powder. Int. J. Dairy Technol. 59:22.

Labuza T.P. 1984. Moisture Sorption: Practical Aspects of Isotherm Measurement and Use, AACC. St. Paul.

Madamba P.S., Driscoll R.H. and Buckle K.A. 1996. The thin-layer drying characteristics of garlic slices. J. Food Eng. 29 (1):75.

Marques L.G. and Freire J.T. 2005. Analysis of Freeze-Drying of Tropical Fruits. Dry. Technol. 23:2169.

Midilli A., Kucuk H. and Yapar Z. 2002. A new model for single-layer drying. Dry. Technol. 20 (7):1503.

Moreira R., Chenlo F., Torres M.D. and Vallejo N. 2008.Thermodynamic analysis of experimental sorption isotherms of loquat and quince fruits. J. Food Eng. 88:514.

Moreira R., Chenlo F., Vázquez M.J. and Cameán P. 2005. Sorption isotherms of turnip top leaves and stems in the temperature range from 298 to 328 K. J. Food Eng. 71:193.

Mulet A., Garcia-Pascual P., Sanjuán N. and Garcia-Reverter J. 2002. Equilibrium isotherms and isosteric heats of morel (*Morchella esculenta*). J. Food Eng. 53 (1):75.

Munio M.M., Guadix E.M. and Guadix A. 2015. Modeling of Water Sorption Isotherms Characteristics of Spray-Dried Cherimoya (*Annona cherimola*) Puree. Particl. Sci. Technol. 33:264.

Noshad M., Mohebbi M., Shahidi F. and Mortazavi S.A. 2012. Effect of osmosis and ultrasound pretreatment on the moisture adsorption isotherms of quince. Food Bioprod. Process. 90:266.

Oswin C.R. 1946. The kinetics of packing life. III. The isotherm. J. Chem. Ind. 65:419.

Peleg M. 1993. Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. J. Food Process. Eng. 16:21.

Rahman S. 1995. Water activity and sorption properties of foods, in Food Properties Handbook ed. By S. Rahman, (CRC Press, Boca Raton, FL), pp. 1–86

Rao M.A. and Rizvi S.S.H. 1995. Engineering Properties of Foods (Marcel Dekker Inc, New York, USA).

Rizvi S.S.H. 1995. Thermodynamic properties of foods in dehydration. In Engineering Properties of Foods; ed. by M. Dekker (New York) pp. 223-309.

Rückold S., Grobecker K.H. and Isengard H.D. 2000. Determination of the contents of water and moisture in milk powder. Fresenius J. Anal. Chem. 368:522.

Sawhney I.K., Sarkar B.C., Patil G.R. and Sharma H.K. 2014. Moisture sorptıon isotherms and thermodynamic properties of whey proteın concentrate powder from buffalo skim milk. J. Food Proces. Pres. 38:1787.

Sharaf-Eldeen Y.I., Blaisdell J.L. and Hamdy M.Y. 1980. A model for ear corn drying, Transactions of the ASAE. 23 (5):1261.

Sharma G.P. and Prasad S. 2004. Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying. J. Food Eng. 65 (4):609.

Silva E.K., Fernandes R.V.B., Borges S.V., Botrel D.A. and Queiroz F. 2014. Water adsorption in rosemary essential oil microparticles: Kinetics, thermodynamics and storage conditions. J. Food Eng. 140:39.

Sinija V.R. and Mishra H.N. 2008. Moisture sorption isotherms and heat of sorption of instant (soluble) green tea powder and green tea granules. J. Food Eng. 86:494.

Souza S.J.F., Alves A.I., Vieira E.N.R. Vieira J.A.G., Ramos A.M. and Telis-Romero J. 2015. Study of thermodynamic water properties and moisture sorption hysteresis of mango skin. Food Sci. Technol. 35 (1):157.

Spiess W.E.L. and Wolf W. 1983. The results of the COST 90 project on water activity, in Physical properties of foods ed. By R. Jowitt, F. Escher, B. Hallström, H. Mefert, W. Spiess, G. Vos (Elsevier Applied Science, London), pp. 65–91

Stencl J. 2004. Modelling the water sorption isotherms of yoghurt powder spray. Math. Comput. Simul. 65:157.

Tadapanenia R.K., Yanga R., Carterb B. and Tanga J. 2017. A new method to determine the water activity and the net isosteric heats of sorption for low moisture foods at elevated temperatures. Food Res. Int. 102:203.

Tamime A.Y., Wszolek M., Božanić R. and Özer B. 2011. Popular ovine and caprine fermented milks. Small Ruminant Res. 101:2.

Telis V.R.N., Gabas A.L., Menegalli F.C. and Telis-Romero J. 2000. Water sorption thermodynamic properties applied to persimmon skin and pulp. Thermochimica Acta. 343:49.

Tolaba M.P., Peltzer M., Enriquez N. and Pollio M.L. 2004. Grain sorption equilibria of quinoa grains. J. Food Eng. 61:365.

Van den Berg C. 1985. Development of B.E.T. like models for sorption of water of foods; theory and relevance, in Properties of water in foods, ed. by D. Simatos, J.L. Multon (Martinus Nijhoft Publishers, Dordrecht), pp. 119–135.

Verma L.R., Bucklin R.A., Endan J.B. and Wratten F.T. 1985. Effects of drying air parameters on rice drying models, Transactions of the ASAE. 28 (1):296.

Wang C.Y. and Singh R.P. 1978. A single layer drying equation for rough rice, ASAE. 78:3001.

Wang X., Shi Q., Zhao Y., Wang X. and Zheng Y. 2013. Moisture Adsorption Isotherms And Heat Of Sorption Of Agaricus Bisporus. J. Food Process. Preserv. 37:299.

Wang Z., Sun J., Liao X., Chen F., Zhao G., Wu J. and Hu X. 2007. Mathematical modeling on hot air drying of thin layer apple pomace. Food Res. Int. 40 (1):39.

Yazdani M., Sazandehchi P., Azizi M. and Ghobadi P. 2006. Moisture sorption isotherms and isosteric heat for pistachio. Eur. Food Res. Technol. 223:577.

Yu H. and Li Y. 2012. Sorption isotherms and thermodynamic properties of freeze-dried colostral whey powders with different additives. Int. J. Food Sci. Technol. 47:613.

Zhu A. and Xinqi S. 2014. The model and mass transfer characteristics of convection drying of peach slices. Int. J. Heat Mass Transfer. 72:345.

Paper Received September 19, 2018 Accepted January 8, 2019