Moisture sorption characteristics of full fat and defatted pistachio kernel flour

Ling Bo[1], Li Rui[1], Gao Haiyan[2,3], Shaojin Wang[1,4*]

(1. *College of Mechanical and Electronic Engineering, Northwest A&F University, Yangling 712100, China*;
2. *Institute of Food Science, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, China*;
3. *Key Laboratory of Fruits and Vegetables Postharvest and Processing Technology Research of Zhejiang Province, Hangzhou 310021, China*; 4. *Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164-6120, USA*)

Abstract: The sorption isotherms of full-fat (FPKF), partially defatted (PDPKF), and totally defatted (TDPKF) pistachio kernel flour were performed in the range of water activity (a_w) from 0.113 to 0.859 at 15°C, 25°C and 35°C, and the applicability of six mathematical models (Smith, Oswin, Henderson, GAB, Halsey and BET) in data prediction was evaluated. Sorption isotherms were type Ⅱ, according to Brunauer's classification. Equilibrium moisture content (EMC) increased with an increase in a_w at constant temperatures. The sorption isotherms of all three flour samples exhibited hysteresis. Significant differences were found among equilibrium data of FPKF, PDPKF and TDPKF samples. TDPKF showed higher hygroscopic characteristics than PDPKF, and PDPKF showed higher hygroscopic characteristics than FPKF at any temperature and a_w studied. It was found that the Smith model was the most satisfactory one for representation of the sorption data of full fat sample, but for defatted samples, Halsey was the best model. The average monolayer moisture content (MMC) calculated by GAB model were 2.443-3.781 g/100 g (d.b.), 3.585-4.886 g/100 g (d.b.) and 5.093-6.918 g/100 g (d.b.) for FPKF, PDPKF and TDPKF, respectively. The isosteric sorption heat (Q_{st}) calculated by means of Clausius-Clapeyron equation decreased with increasing moisture content. The Q_{st} values were 44.76-74.67 kJ/mol, 44.75-99.44 kJ/mol and 44.80-133.28 kJ/mol for FPKF, PDPKF and TDPKF, respectively, in the range of moisture content of 2% to 41% (d.b.) at 25°C.

Keywords: pistachio kernel flour, equilibrium moisture content, sorption isotherm, isosteric sorption heat, monolayer moisture content

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1 Introduction

Pistachio kernel oil (PKO) is one of the most valued edible oil owing to its price and beneficial effects on human health. Traditionally, PKO are prepared from raw or roasted kernels using cold pressing or pre-press-solvent extraction because nut seeds are high oil-bearing materials[1]. After extracting oil from nut kernels, the residuals are known as partially (cold pressing) or totally (pre-press-solvent extraction) defatted pistachio kernel flour (PKF), which is commonly wasted. Although PKF creates a disposal problem for the industry, they probably retain nutrients and bioactive compounds present in original kernels, which may provide some potential products of various functional ingredients[2,3]. However, the moisture content (MC) of the PKF as a hygroscopic material exerts a strong influence on its nutritional quality and functional properties. Therefore,

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Biographies: Ling Bo, PhD, Lecturer, research interests: processing and storage of agricultural products, Email: 6lb6lb@163.com; **Li Rui**, Research Assistant, research interests: processing and storage of agricultural products, Email: ruili1216@nwsuaf.edu.cn; **Gao Haiyan**, PhD, Researcher, research interests: processing and storage of agricultural products, Email: ruili1216@nwsuaf.edu.cn.

***Corresponding author: Shaojin Wang**, PhD, Professor, research interests: processing and storage of agricultural products, disinfestation and pasteurization of postharvest products using radio frequency heating. College of Mechanical and Electronic Engineering, Northwest A&F University, Yangling 712100, China. Tel: +86-29-87092319, Email: shaojinwang@nwsuaf.edu.cn.

this product needs to be dried to extend the storage stability and preserve its market values.

Knowledge of the sorption properties (equilibrium moisture content, monolayer moisture, and heat of sorption) of foodstuffs are essential for the design and optimization of many processes, such as drying, packaging and storage, especially with regard to quantitative approaches for predicting the shelf life of dried foods. PKF can be used as a functional ingredient in foods to improve desirable properties[4]. In fact, the majority of the sensorial properties of foods in which MC has been reduced depending on the amount of water absorbed by the product. Since these powdered materials are characterized by their naturally high hygroscopicity and the storage environment could strongly influence its quality and technological properties, moisture sorption is of great importance in maintaining powdered product stability[2,5].

The relationship between the equilibrium moisture content and water activity (a_w) of food at constant temperature and pressure is known as the moisture sorption isotherm (MSI)[6]. These isotherms are an extremely important tool in the microbiological stability and acceptability of food products, drying process modeling and equipment design, calculation of moisture changes that may occur during storage, and for the selection of packaging materials[7].

Several researchers have conducted equilibrium isotherm studies on pistachio products, such as whole nuts, kernels, and paste[8-10]. However, no data related to the sorption process have been reported for PKF. As PKF is a dried flour product derived from pistachio kernels, with different morphological and functional properties in comparison to the other pistachio products, more sorption information is needed on these products.

The objectives of the present study were to: (1) obtain experimental equilibrium data of full-fat (FPKF), partially defatted (PDPKF), and totally defatted (TDPKF) PKF at three different temperatures, (2) find out the suitable model describing the isotherms, (3) calculate the monolayer moisture content (MMC), and (4) determine the sorption isosteric heat of the PKF.

2 Materials and methods

2.1 Materials

Raw and dried pistachio nuts (4.0 kg) of the *Kerman* variety were obtained from Paramount Farm Company (Lost Hills, CA, USA). After removing shells, about 2.0 kg kernels (MC: 3.35±0.12 g/100g in wet basis, w.b.) were sorted to remove any damaged samples and then sealed into polyethylene bags at 4°C until use. All chemicals used in this study were reagent grade purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Preparation of PKF

To produce full-fat flours, each batch of 100 g kernels were milled in a stainless steel grinder (FLB-100, Shanghai Feilibo Food Machinery Co., Ltd, Shanghai, China) for 30 s and sifted through a 50 mesh sieve to obtain full fat flour (FPKF, Figure 1a). To produce partially defatted flours, oil was separated from the FPKF using a hydraulic press (Lefen T-50, Daohang Food Machinery Company, Dezhou, China) at 60 kg/cm^2 for 15 min without additional heat treatment, which could obtain a residual fat content of ~22% (dry basis, d.b.). The resulting press-cake was ground to be sifted through 50 mesh sieve as partially defatted flour (PDPKF, Figure 1b). For totally defatted flours, the resulting PDPKF was defatted for 24 h in a Soxhlet apparatus using petroleum (boiling point range of 38.2°C-54.3°C) to obtain less than 1% (d.b.) of residual fat. Then resulting flours were air-dried at ambient temperature in a fume hood, powered again to be sifted through 50 mesh sieve as totally defatted flour (TDPKF, Figure 1c). All flours were placed in airtight containers and stored in a refrigerator at 4°C until use.


a. FPKF b. PDPKF c. TDPKF

Figure 1 Photographs of the full-fat and defatted pistachio kernel flour

2.3 Composition analysis

The proximate compositions of flour samples were analyzed for determining their MC (at 105°C under pressure≤100 mm Hg, 13.3 kPa), ash (Muffle furnace, 550°C), fat (Soxhlet, petroleum ether, 16 h), and protein (N×5.30) contents according to the AOAC Official Method[11]. Total carbohydrate content was estimated by the difference from the total contents.

2.4 Determination of moisture sorption isotherm

The equilibrium moisture content (EMC) of PKF was determined using the static gravimetric method standardized by "The European Cooperative Project COST 90"[12], which was based on the use of saturated salt solutions so as to obtain constant a_w. The detailed information about the a_w and temperatures to obtain sorption isotherms is listed in Table 1. For the adsorption process, flour samples (with its original MC) were first dehydrated in a desiccator with P_2O_5 at 40°C until the weight loss was negligible, which resulted in flour samples with a_w<0.07 (35°C) determined using a hygrometer (Aqualab 3TE, Decagon Devices, Inc., Pullman, WA, USA). For the desorption process, flour samples (with its original MC) were first hydrated in a desiccator over distilled water at 25°C until no significant weight gain was noticed, which resulted in flour samples with a_w>0.87 (15°C). Triplicate samples of above dehydration or rehydration flour (about 3.0 g) were introduced in weighting bottles (Ø 40 mm × H 25 mm) and placed in eight desiccators (Ø 210 mm × H 120 mm) (Figure 2a), each one containing the oversaturated salt solutions of known a_w at the studied temperature as described in Table 1. At a_w greater than 0.6, crystalline thymol was placed inside desiccators to inhibit fungal growth. All desiccators were placed in a temperature-controlled incubator (SH-045B, Shanghai Laboratory Instrument Works Co., Ltd. Shanghai, China) (Figure 2b) at 15°C, 25°C and 35°C. These temperatures were selected because they are often used in the storage and drying processes of nut products. Samples were weighed every three days until they reached a constant weight (±0.001 g) using an electronic balance (PTX-FA210, Huazhi Scientific Instrument, Co., Ltd. Fuzhou, China) with a sensitivity of 0.1 mg. The EMC of each sample was determined by the AOAC Official Method 925.40 mentioned above.

Table 1 Water activities of selected saturated salt solutions at 15°C, 25°C and 35°C[13]

Salt	a_w at 15°C	a_w at 25°C	a_w at 35°C
LiCl	0.113	0.113	0.113
CH_3COOK	0.234	0.225	0.230
$MgCl_2$	0.333	0.328	0.321
K_2CO_3	0.432	0.432	0.410
$Mg(NO_3)_2$	0.559	0.529	0.499
$CuCl_2$	0.680	0.670	0.670
NaCl	0.756	0.753	0.749
KCl	0.859	0.843	0.830

a b

Figure 2 Sealed desiccators (a) and temperature controlled incubator (b) used in the experiments

2.5 Data analysis

2.5.1 Modeling of sorption isotherms

Six mathematical models including five two-parameter and one three-parameter models were used for describing desorption and adsorption isotherms of PKF in the range of temperature varying from 15°C to 35°C as shown in Table 2. The curve fitting and regression analysis were performed using SPSS 17.0 statistical package software (SPSS Inc., Chicago, IL, USA). To evaluate the ability of each model to fit the experimental data, the coefficient of the determination (R^2), standard error of estimate (SEE) and mean relative deviation (MRD) were determined as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(m_{ep} - m_{pre})^2}{\sum_{i=1}^{N}(m_{ep} - \overline{m_{ep}})^2} \tag{1}$$

$$SEE = \sqrt{\frac{1}{N - n_\mathrm{c}}\sum_{i=1}^{N}(m_{ep} - m_{pre})^2} \tag{2}$$

$$MRD = \frac{1}{N}\sum_{i=1}^{N}\frac{|\, m_{ep} - m_{pre}\,|}{m_{ep}} \tag{3}$$

where, N is the number of experimental observations and n_c is the number of constants in each model; m_{ep} represents experimental moisture content values; m_{pre}

denotes predicted moisture value from the model. These parameters helped the calculation of EMC within the temperature and a_w ranges used in this study. Lomauro et al.[14] pointed out that when *MRD* values below 10% indicate an adequate fit for practical purposes. It is well-known that the fit becomes better as the R^2 approaches to 1. Finally, the smaller the *SEE* of models the better is the fit.

Table 2 Mathematical models used to fit the sorption isotherms of PKF

Name of the model§	Model equation
Smith[15]	$\mathrm{EMC} = A - B\ln(1-a_w)$
Oswin[16]	$\mathrm{EMC} = A\left(\frac{a_w}{1-a_w}\right)^B$
Henderson[17]	$\mathrm{EMC} = \left[\frac{-\ln(1-a_w)}{A}\right]^{1/B}$
GAB*[18]	$\mathrm{EMC} = \frac{ABCa_w}{(1-Ca_w)(1-Ca_w+BCa_w)}$
Halsey[19]	$\mathrm{EMC} = \left(\frac{-A}{\ln a_w}\right)^{1/B}$
BET*[20]	$\mathrm{EMC} = \frac{ABa_w}{(1-a_w)[1+(B-1)a_w]}$

Note: § All the models were applied to the sorption data of full range of a_w (0.113-0.859) except for BET model fitted for $a_w \leq 0.5$ as it is reported to be successful only in this a_w range[5].

* The parameter A represents monolayer moisture content (MMC) in BET and GAB models, respectively.

2.5.2 Determination of the isosteric heat of sorption

Isosteric heat of sorption is the amount of energy required to change unit mass of a product from liquid to vapor at a particular temperature and a_w. The net isosteric heat is the amount of energy by which the heat of moisture vaporization in a product exceeds the latent heat of pure water. Water sorption data from the best-fitting equation at three temperatures could be used to calculate the net isosteric heat of sorption (q_{st}, kJ/mol) by using the following equation, which is derived from Clausius-Clapeyron Equation[21]:

$$\ln\left(\frac{a_{w2}}{a_{w1}}\right) = \frac{1000q_{st}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (4)$$

where, a_{w1} and a_{w2} are the water activities at temperatures T_1 and T_2 (K), respectively. These two parameters were obtained from the model that better fitted experimental sorption data for the temperature range studied. R is the universal gas constant (8.314 kJ/mol·K). The isosteric heat of sorption (Q_{st}, kJ/mol) was calculated by the following equation:

$$Q_{st} = q_{st} + \Delta H_v \quad (5)$$

where, ΔH_v is the latent heat of pure water and was 43.96 kJ/mol at 25°C, which was the average temperature of the tested range from 15°C to 35°C used in the present study.

2.6 Statistical analysis

Data were reported as mean ± standard deviation of triplicate measurements. Significant differences ($p<0.05$) within means were separated by analysis of variance and Tukey's significant difference (HSD) test in the statistical software (SPSS Inc., Chicago, IL, USA).

3 Results and discussion

3.1 Proximate analysis of PKF

Proximate compositions of the PKF are presented in Table 3. Defatted flour samples (PFPKF and TDPKF) showed a higher moisture content than full fat flour sample (FPKF). The protein and carbohydrate were the major components in the defatted flour samples with an average content of about 37-45 g (d.b.) and 37-49/100 g (d.b.), respectively. The protein content of defatted flour samples was approximately 1.8-2.1 fold higher than that of FPKF (~21/100 g, d.b.). Therefore, their sorption behaviors should be different.

Table 3 Proximate compositions (g/100 g d.b.) of the PKF

Composition	FPKF	PDPKF	TDPKF
Moisture	3.35±0.12^{c*}	6.01±0.09^{b}	8.29±0.08^{a}
Protein#	20.97±0.28^{c}	36.99±0.29^{b}	44.95±0.58^{a}
Lipid	51.84±1.39^{a}	21.90±0.32^{b}	0.59±0.07^{c}
Ash	2.61±0.02^{c}	4.50±0.02^{b}	5.75±0.03^{a}
Carbohydrate&	24.58	36.61	48.71

Note: # Protein: N×5.3; & Carbohydrate content was calculated by subtracting other nutrients from the total weight; Means followed by different superscript letters represent significant differences among samples for measured properties ($p \leq 0.05$).

3.2 Moisture sorption isotherm of PKF

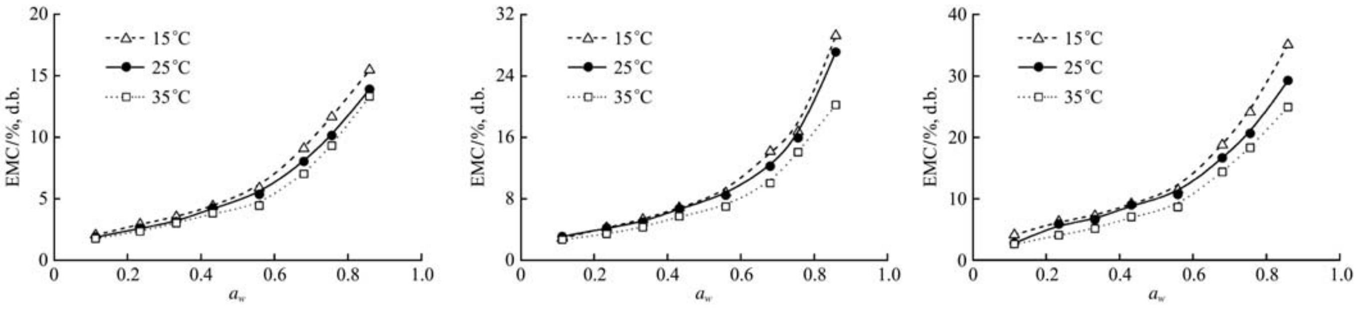
The experimental adsorption and desorption data for three forms of PKF at selected temperatures and a_w are presented in Table 4. The results indicated that the EMC values of PKF increased with the increase of a_w at constant temperatures. This may be due to the fact that vapor pressure of water present in foods increases with that of the surroundings. Also at a selected a_w, the EMC values decreased with increasing temperatures at all levels of a_w. This trend, which is very popular for agricultural products, may be due to a reduction in the total number of active sites for water binding as a result of physical and/or chemical changes in the product induced by temperature[22]. Among all three PKF samples, FPKF exhibited the lowest EMC values than PDPKF and TDPKF with average content of 2.07-16.02 g/100 g (d.b.), which was similar to those of full fat flour obtained from *Amiri* variety pistachio kernels (2.03-13.12 g/100 g d.b. with a_w=0.089-0.853)[10], but significantly lower than those of pistachio paste (1.53-30.21 g/100 g d.b.) under similar experimental conditions[8]. The difference between EMC values among different pistachio products could be due to the variation in chemical composition, especially higher protein and carbohydrate content in defatted PKF and paste samples, respectively.

Table 4 Experimental EMC values (g/100 g, d.b.) at selected temperatures and a_w for PKF in different forms

Temperature/°C	a_w	EMC-adsorption data			EMC-desorption data		
		FPKF	PDPKF	TDPKF	FPKF	PDPKF	TDPKF
15	0.113	2.07±0.01	2.88±0.23	4.15±0.02	2.55±0.07	4.45±0.13	6.33±0.26
	0.234	2.94±0.09	4.26±0.16	6.34±0.19	3.43±0.21	5.58±0.08	7.47±0.20
	0.333	3.54±0.13	5.33±0.56	7.25±0.04	4.26±0.15	6.42±0.08	9.49±1.68
	0.432	4.41±0.04	6.85±0.44	9.22±0.10	5.61±0.30	8.35±0.02	11.36±0.72
	0.559	5.88±0.13	8.78±0.33	11.43±0.25	6.98±0.05	10.23±0.38	13.29±0.46
	0.680	9.09±0.12	14.17±0.63	18.80±0.68	10.34±0.14	15.84±0.63	19.83±0.27
	0.756	11.66±0.19	16.74±0.78	24.13±0.15	11.80±0.25	18.67±0.29	25.40±2.98
	0.859	15.47±0.42	29.27±1.53	35.13±1.88	16.02±0.36	30.18±1.22	38.35±2.38
25	0.113	1.90±0.04	3.11±0.05	2.78±0.17	2.16±0.13	3.69±0.09	5.15±0.24
	0.225	2.61±0.03	4.23±0.06	5.90±0.11	3.01±0.33	5.00±0.15	6.94±0.61
	0.328	3.15±0.03	4.98±0.06	6.62±0.96	3.95±0.32	5.86±0.42	8.18±0.20
	0.432	4.24±0.05	6.75±0.56	9.04±1.21	5.02±0.30	7.93±0.42	10.63±0.30
	0.529	5.35±0.10	8.46±0.29	10.71±0.11	6.14±1.06	9.82±0.34	12.25±0.74
	0.670	8.04±0.18	12.28±0.25	16.70±1.35	8.56±0.12	13.05±0.15	18.15±0.85
	0.753	10.14±0.57	15.94±0.67	20.66±0.23	10.84±0.69	16.51±0.33	22.70±1.47
	0.843	13.61±0.14	27.13±0.90	29.27±1.30	13.95±0.65	28.35±0.27	30.07±0.67
35	0.113	1.78±0.03	2.69±0.18	2.65±0.34	2.01±0.02	3.43±0.04	4.26±0.16
	0.230	2.36±0.06	3.45±0.08	4.12±0.22	2.41±0.12	3.67±0.35	6.02±0.05
	0.321	3.03±0.07	4.33±0.02	5.18±0.15	3.04±0.11	4.56±0.09	7.19±0.23
	0.410	3.84±0.07	5.75±0.05	7.08±0.13	4.38±0.27	6.01±0.76	9.08±0.22
	0.499	4.45±0.07	7.00±0.27	8.66±1.69	5.27±0.26	7.30±0.84	10.28±0.69
	0.670	7.04±0.14	10.05±0.01	14.41±1.86	7.68±0.35	11.50±0.60	16.91±0.01
	0.749	9.31±0.06	14.10±0.17	18.32±1.20	10.10±0.39	15.49±0.14	20.51±0.56
	0.830	13.34±0.27	20.26±0.60	24.95±1.67	13.18±0.32	21.83±0.84	25.60±1.52

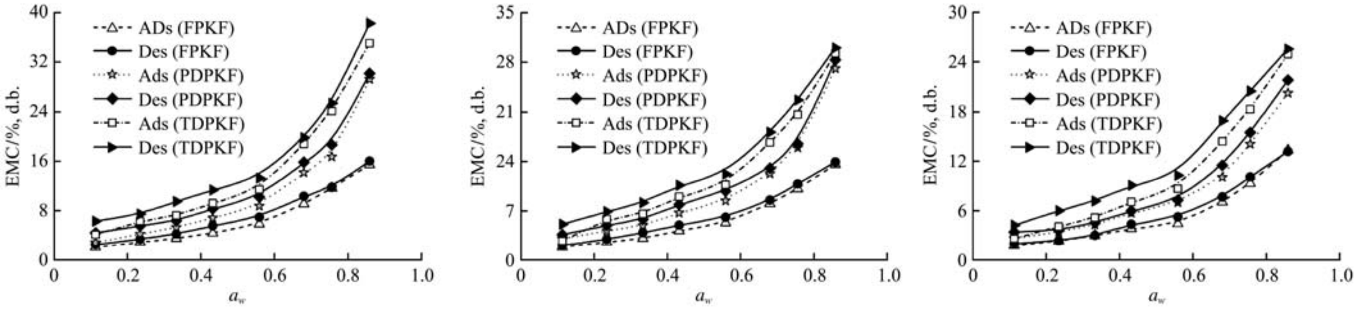
The adsorption isotherms for three forms of PKF at different temperatures are shown in Figure 3. According to the classification of Brunauer et al.[23], all the adsorption isotherm curves of different forms of PKF exhibited the sigmoid shape (type II). A slow increase in EMC values was observed between the a_w values of 0.1 and 0.6 followed by a steep increase beyond 0.6 at all the temperatures. This type of sorption isotherm was the most frequent isotherms for food products with the exception of high-sugar foods. For example, pistachio paste exhibited J shape (type Ⅲ), which absorbed higher amounts of water at higher a_w meanwhile small amount of water at low a_w[9]. Type Ⅱ sorption isotherm can be divided into three regions as reported by Van den Berg and Bruin[18]. The first region corresponding to a_w≤0.234 relates to adsorption of moisture of monolayer water, the second region indicates adsorption of additional layers over this monolayer at a_w of 0.234 to 0.757, and the third region for a_w>0.760 corresponds to condensation of water in pores of the product followed by dissolution of soluble materials.

Figure 4 is a typical comparison between the MSI of FPKF, PDPKF and TDPKF at 15°C, 25°C and 35°C. The results showed that the EMC values of the TDPKF were higher than those of the PDPKF, and in the PDPKF were higher than those of FPKF at any temperature and a_w studied. For instance, at 15°C and a_w of 0.756, the EMC of TDPKF was 24.13 g/100 g (d.b.) whereas that of the PDPKF and FPKF were 16.74 g/100 g (d.b.) and 11.66 g/100 g (d.b.) in the adsorption process (Table 4). This indicates that defatted flour (TDPKF and PDPKF) was more hygroscopic than full fat flour (FPKF). It would therefore indicate that by removing the lipid of PKF, it would become more susceptible to moisture adsorption. The high hygroscopy of defatted flour samples might be due to removal of oil film (residual fat<22 and 1% d.b. for PDPKF and TDPKF, respectively) from flour particles by permitting exposure of large number of hydrophilic parts bound to more water. These results are similar to those found for defatted pumpkin seed flour[24] and dehulled nuts or seeds[25] since they are widely accepted that the lipids and fibers in the seeds or hulls are less hygroscopic than carbohydrates and proteins.



a. FPKF b. PDPKF c. TDPKF

Figure 3 Experimental adsorption sorption isotherms FPKF, PDPKF and TDPKF at 15°C, 25°C and 35°C



a. 15°C b. 25°C c. 35°C

Figure 4 Comparison hysteresis of FPKF, PDPKF and TDPKF at 15°C, 25°C and 35°C

By considerations from the food processing and storage, large values of a_w at the same EMC values may indicate a smaller binding force of water molecules to adsorption sites. A smaller binding force is usually associated with lower dehydration energy requirements, but is associated with faster spoilage because of the availability of more free water for use by various types of spoilage microorganisms[22]. It follows, therefore, that at the same temperatures and a_w values, FPKF is expected to keep longer than that from defatted PKF, due to the former being less hygroscopic. It is recommended that a_w of 0.6 as the upper limit in storage to avoid the mold growth[26]. Therefore, FPKF has to be dried to reduce MC than PDPKF and TDPKF to stay below a_w value of 0.6 during storage at the same temperature.

The adsorption and desorption plots of three forms of PKF at different temperatures, presented in Figure 4 also showed the evidence of moisture sorption hysteresis. The graph clearly showed that EMC for desorption of all three forms of PKF, at a specific a_w and temperature, was higher than the corresponding value of adsorption. Polar site in the molecular structure of the material was almost entirely occupied by adsorbed water in the wet condition. Due to drying and shrinkage, the molecules and their water holding sites were drawn closely to satisfy each other. This reduced the water holding capacity of the material upon subsequent adsorption[27]. The hysteresis cycles for PKF can be classified like Type H3 according to IUPAC classification[28]. These cycles are in the a_w range from 0.10 to 0.90. Foodstuffs, like seeds or nuts, with Type II sorption isotherms usually exhibit hysteresis cycles of Type H3[29]. Type II isotherms are often obtained with aggregates of plate-like particles, which therefore possess non-rigid slit-shaped pores. Because of delayed capillary condensation, multilayer adsorption is able to proceed on the particle surface until high a_w is reached. Once the condensation has occurred, the state of the adsorbate is changed and desorption curve follows a different path until the condensate becomes unstable at a critical value of a_w[29].

3.3 Modeling of the sorption isotherms

Estimated parameters of the models for three types of PKF and R^2, *SEE* and *MRD* are presented in Tables 5 and 6. When all these three criteria are considered for the isotherm data of the three types of PKF at the three temperatures, Smith model gave the best fit to experimental sorption data of FPKF at 15°C to 35°C. This agrees with the results reported by Yazdani et al.[10], who showed that the Smith model adequately represents experimental sorption data of FPKF produced from Amiri variety pistachio kernels in the temperature range of 15°C to 40°C. However, this result does not exactly support the results of Tavakolipour and Mokhtarian[30] who reported that the Caurie model gave the best fit to their data for the FPKF produced from Kerman variety pistachio kernels. For PDPKF, Halsey model was the most appropriate model for fitting well throughout the entire range of a_w and temperature as evidenced by the highest R^2 and lowest *SEE* and *MRD* values both for adsorption and desorption processes. While for TDPKF, Halsey model seemed to be excellent to present the experimental sorption data. There are two exceptions for adsorption data at 15°C and 25°C. R^2 and *SEE* values indicated Halsey model but *MRD* value indicated Oswin model as the best model for adsorption process of TDPKF at 15°C. On the other hand, R^2 value indicated Oswin model, but *MRD* value indicated Halsey and *SEE* value indicated equally Smith and Halsey as the best model for adsorption process of TDPKF at 25°C. Generally, however, Halsey model was by far the best model to represent all the sorption data of TDPKF. Furthermore, from the results given in Tables 5 and 6, the BET model also gave better fits compared to the other models at most temperatures. However, when the applicability range of the models was considered, the Smith and Halsey models, applicable to the whole range, could be more suitable than the BET model (a_w<0.5) for representing the relationship between a_w and EMC of PKF. Although its applicable a_w range is limited, it is still a useful model as it provides the important parameter of MMC, which is vital data for storage of dehydrated food products with minimum quality loss for a maximum period of time.

Table 5 Estimated parameters of different isotherm models fitted to adsorption data of PKF

Model	Parameter	FPKF			PDPKF			TDPKF		
		15°C	25°C	35°C	15°C	25°C	35°C	15°C	25°C	35°C
Smith	R^2	0.993	0.994	0.997	0.959	0.946	0.971	0.979	0.990	0.993
	SEE	0.523	0.337	0.058	1.915	2.009	1.120	1.673	0.849	0.730
	MRD	0.040	0.042	0.011	0.180	0.177	0.110	0.130	0.065	0.085
	A	0.607	0.625	0.357	-0.399	-0.105	0.440	0.526	0.868	0.212
	B	7.511	6.829	6.767	16.684	12.981	10.257	16.790	14.689	13.388
Oswin	R^2	0.989	0.991	0.994	0.993	0.985	0.991	0.992	0.997	0.993
	SEE	0.547	0.454	0.336	0.820	1.053	0.626	1.043	0.510	0.241
	MRD	0.056	0.054	0.075	0.098	0.119	0.076	0.055	0.048	0.049
	A	5.652	5.186	4.708	8.132	7.854	6.989	11.449	10.604	8.939
	B	0.572	0.580	0.642	0.698	0.714	0.655	0.624	0.604	0.650
Henderson	R^2	0.985	0.989	0.974	0.971	0.957	0.969	0.979	0.987	0.993
	SEE	0.626	0.473	0.698	1.605	1.797	1.149	1.669	1.083	0.725
	MRD	0.042	0.104	0.152	0.205	0.214	0.154	0.157	0.103	0.099
	A	0.109	0.114	0.144	0.120	0.119	0.102	0.067	0.058	0.080
	B	1.057	1.078	0.991	0.841	0.850	0.971	0.956	1.035	0.973

Model	Parameter	FPKF			PDPKF			TDPKF		
		15°C	25°C	35°C	15°C	25°C	35°C	15°C	25°C	35°C
Halsey	R^2	0.980	0.992	0.094	0.997	0.996	0.998	0.995	0.992	0.994
	SEE	0.721	0.405	0.084	0.519	0.531	0.314	0.912	0.853	0.234
	MRD	0.095	0.065	0.015	0.028	0.046	0.034	0.064	0.032	0.028
	A	7.544	6.173	4.348	7.830	6.810	6.753	15.725	14.439	9.257
	B	1.403	1.358	1.216	1.168	1.123	1.195	1.294	1.306	1.205
GAB	R^2	0.928	0.934	0.977	0.970	0.975	0.940	0.937	0.849	0.952
	SEE	1.086	0.599	0.162	0.912	0.303	0.336	2.040	0.513	0.906
	MRD	0.056	0.046	0.026	0.036	0.027	0.043	0.054	0.044	0.040
	A	2.924	2.787	2.443	4.301	4.023	3.631	5.746	6.918	5.093
	B	12.069	10.679	12.740	10.804	15.099	12.420	14.189	5.440	6.278
	C	0.974	0.967	0.992	1.001	1.011	0.995	0.944	0.919	0.981
BET	R^2	0.999	0.987	0.991	0.997	0.984	0.976	0.994	0.921	0.982
	SEE	0.014	0.163	0.130	0.118	0.287	0.285	0.230	0.648	0.243
	MRD	0.012	0.034	0.034	0.016	0.037	0.056	0.023	0.071	0.035
	A	2.683	2.571	2.433	4.301	4.039	3.788	5.626	6.320	4.987
	B	16.702	13.206	12.533	10.817	14.837	9.941	15.756	5.800	6.273

Table 6 Estimated parameters of different isotherm models fitted to desorption data of PKF

Model	Parameter	FPKF			PDPKF			TDPKF		
		15°C	25°C	35°C	15°C	25°C	35°C	15°C	25°C	35°C
Smith	R^2	0.996	0.999	0.996	0.968	0.944	0.973	0.970	0.994	0.996
	SEE	0.310	0.148	0.178	1.686	2.084	1.164	2.041	0.751	0.491
	MRD	0.035	0.022	0.055	0.130	0.140	0.124	0.117	0.054	0.039
	A	1.407	1.207	0.678	1.071	0.714	0.529	2.145	2.677	2.258
	B	7.440	6.818	6.823	13.635	13.102	11.129	17.108	14.366	13.086
Oswin	R^2	0.993	0.998	0.996	0.989	0.976	0.991	0.987	0.996	0.995
	SEE	0.424	0.180	0.275	0.994	1.350	0.675	1.345	0.620	0.573
	MRD	0.051	0.025	0.062	0.089	0.121	0.077	0.090	0.050	0.046
	A	6.545	5.882	5.222	9.855	8.929	7.633	13.300	12.432	11.178
	B	0.505	0.521	0.585	0.608	0.655	0.652	0.576	0.525	0.532
Henderson	R^2	0.989	0.991	0.986	0.962	0.942	0.971	0.957	0.980	0.988
	SEE	0.541	0.417	0.504	1.830	2.115	1.206	2.442	1.329	0.909
	MRD	0.084	0.077	0.095	0.175	0.199	0.147	0.174	0.106	0.084
	A	0.066	0.076	0.108	0.070	0.085	0.094	0.044	0.031	0.035
	B	1.230	1.224	1.099	0.993	0.948	0.970	1.060	1.213	1.221
Halsey	R^2	0.982	0.991	0.993	0.997	0.991	0.998	0.997	0.995	0.996
	SEE	0.671	0.432	0.359	0.544	0.855	0.321	0.678	0.648	0.431
	MRD	0.082	0.069	0.069	0.040	0.059	0.045	0.036	0.039	0.016
	A	12.483	9.262	5.877	13.808	9.402	7.654	24.222	27.565	21.560
	B	1.568	1.496	1.326	1.324	1.209	1.203	1.389	1.484	1.449
GAB	R^2	0.912	0.971	0.821	0.962	0.951	0.926	0.968	0.972	0.950
	SEE	0.683	0.311	0.518	0.998	1.065	0.947	0.691	0.694	0.720
	MRD	0.049	0.029	0.076	0.044	0.041	0.065	0.029	0.033	0.028
	A	3.781	3.526	2.846	4.886	4.763	3.585	6.603	6.714	6.189
	B	11.025	9.597	9.852	27.058	16.653	21.279	38.958	16.818	12.361
	C	0.913	0.906	0.965	0.985	0.977	1.023	0.971	0.937	0.936
BET	R^2	0.987	0.996	0.928	0.989	0.984	0.966	0.995	0.994	0.994
	SEE	0.216	0.058	0.352	0.332	0.305	0.474	0.321	0.312	0.264
	MRD	0.040	0.013	0.094	0.035	0.032	0.080	0.025	0.020	0.018
	A	3.404	3.160	2.882	4.823	4.731	3.784	6.687	6.336	5.571
	B	13.029	11.051	8.220	27.649	15.460	15.464	30.247	18.696	16.935

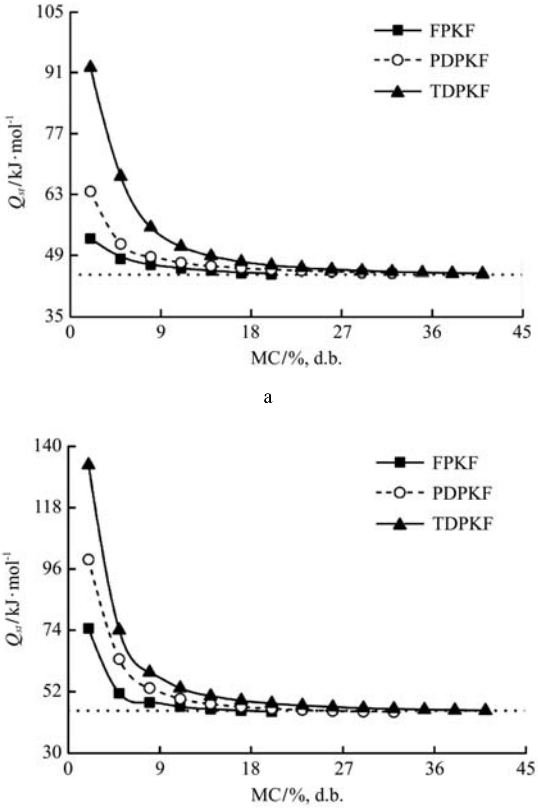
3.4 Monolayer moisture content (MMC)

The MMC of three types of PKF determined by the BET and GAB models at the different temperatures was represented by the parameter A in Tables 5 and 6. In the temperature range of 15°C-35°C, the MMC of FPKF varied from 2.433 g/100 (d.b.) to 3.404 g/100 (d.b.) when the BET model was considered and from 2.443 g/100 (d.b.) to 3.781 g/100 g (d.b.) for the GAB model, which were similar to the value of 1.850 g/100 (d.b.) to 3.110 g/100 g (d.b.) reported for flours obtained from *Amiri* pistachio kernel using GAB model[10]. On the other hand, the corresponding ranges found for the PDPKF and TDPKF using BET and GAB models were 3.784-4.823 g/100 g (d.b.) and 4.987-6.687 g/100 g (d.b.), and 3.585-4.886 g/100 g (d.b.) and 5.093-6.918 g/100 g (d.b.), respectively. As can be noted from these values using both models, MMC showed similar values, although slightly smaller for the BET model, and similar results for the MMC value calculated with BET and GAB models were also observed in macadamia nuts[31]. No matter which model used in their calculation, the MMC was inversely related to temperature, which is an expected result attributed to reduction in the number of sites available for water binding due to physiochemical changes caused by temperature increase. It is also worth noticing in Tables 5 and 6 that the average MMC calculated by the BET model was 2.856 g/100 g (d.b.) for FPKF in the range of tested temperatures, but the corresponding value found for the PDPKF and TDPKF using BET model was 4.244 g/100 g and 5.921 g/100 g (d.b.), respectively. The lower MMC of FPKF might be due to the higher lipid content in FPKF compared to defatted flour samples, which would prevent the FPKF from absorbing more water.

It could be argued that the adsorption branch of hysteresis may be different from those of desorption. It has been shown that the lipids in system on the adsorption branch of the hysteresis loop oxidizes about four to six times slower than the desorption system at the same a_w[32]. The adsorption MMC range obtained from BET model for FPKF, PDPKF and TDPKF at 15°C, 25°C and 35°C was 2.433-2.683, 3.788-4.301 and 4.987-5.626, respectively. These results indicate that the safest storage condition for three types of PKF was corresponding to a_w of 0.181-0.204, 0.205-0.208 and 0.183-0.270, respectively. The microbiological stability would be highly ensured in these water activity ranges. The chemical reactions depending on salvation are also expected to be slow in the monolayer region. On the other hand, during the production of PKF, the drying process should not be conducted to obtain a MC lower than monolayer content to avoid unnecessary power consumption.

3.5 Isosteric heat of sorption

The Q_{st}, obtained from Equations (4) and (5), varied from 74.67 kJ/mol to 44.76 kJ/mol at MCs 2-20% (d.b.) for FPKF, 99.44 kJ/mol to 44.75 kJ/mol at MCs 2-32% (d.b.) for PDPKF and 133.28 kJ/mol to 44.80 kJ/mol at MCs 2-41% (d.b.) for TDPKF. The relationship between Q_{st} of adsorption and desorption process and MC of three types of PKF at average temperature 25°C is plotted in Figures 5a and 5b. It is evident from the Figure 6 that the Q_{st} of PKF shows a strong dependence on MC, indicating that the energy required for sorption in excess of the latent heat associated with the phase change is much higher at low MCs. This reflects the differing strength of water binding, initial occupation of highly active polar sites on the surface (with the greatest interaction energy), followed by the progressive filling of the less available sites with lower bending activation energies[33]. As the MC increased, the Q_{st} of FPKF, PDPKF and TDPKF approached to that of latent heat of pure water beyond the MC of about 11%, 17% and 23% (d.b.), respectively. Furthermore, form Figure 5, it was clearly observed that in the lower MC range (before the Q_{st} approached to that of latent heat of pure water), the Q_{st} of the FPKF was lower than that of PDPKF and further TDPKF at the same MC both for adsorption and desorption processes. During defatting, the flour samples lost their lipids, and the relative contents of carbohydrates and proteins increased, since lipids are less hygroscopic than carbohydrates and proteins. This led to an increase in the number of the water sorption centers in defatted flour samples. Thus, defatted flour sobered higher amounts of moisture, which necessitated high Q_{st} compared to full fat flour. The maximum Q_{st} of desorption process for FPKF (74.67 kJ/mol) calculated in this study is comparable with the value for full fat flours produced from pistachio kernels of Kerman variety (~77 kJ/mol) reported by Tavakolipour and Kalbasi-Ashtari[34], but slightly lower than flours produced from pistachio kernels of Amiri variety (~86 kJ/mol) reported by Yazdani et al.[10]



a

b

Figure 5 Isosteric heats of adsorption (a) and desorption (b) of FPKF, PDPKF and TDPKF at different moisture contents (dotted line represents heat of vaporization of pure water at 25°C)

It is also worth noticing in Figure 5 that the different Q_{st} could be observed at the specific MC between adsorption and desorption processes for all three types of PKF. In this case, taking FPKF as an example showed in Figure 6, the Q_{st} for desorption process was generally larger than that for the adsorption process. The difference between the heat of adsorption and desorption was large at lower MCs, converging as MC increased and practically disappearing above 15% MC (d.b.). This type of behavior has been previously observed for many dehydrated food products[10,15]. It is generally considered that there is no direct relationship between the observed differences and the distribution of hysteresis along the sorption isotherm. These differences are most probably due to structural changes that occur in the product during dehydration, making removal of water easier[35]. The information of Q_{st} at a particular MC provides an indication of the state of the absorbed water and hence, a measure of the physical, chemical and microbiological stability of the food material under given storage conditions. In addition, the variation of Q_{st} with MC provides valuable data for energy consumption, designing of drying equipment, and understanding the water-solid versus water-water interactions.

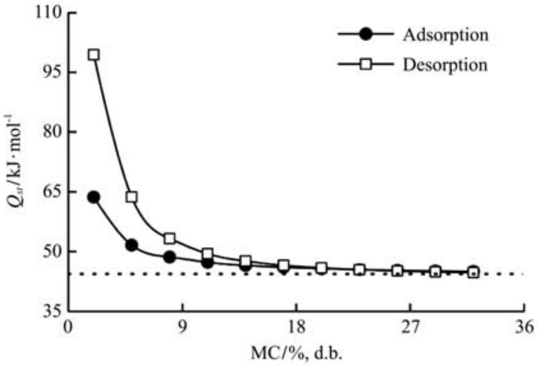


Figure 6 Isosteric heat of PDPKF at different moisture contents (dotted line in the figure represents heat of vaporization of pure water at 25°C)

4 Conclusions

EMC of three types of PKF was obtained at 15°C, 25°C and 35°C by the static gravimetric method. The MSI of all three types of PKF showed a sigmoidal pattern (type II of BET classification), but the EMC values of different PKF samples were significantly different at the same conditions, resulting in various storage and processing conditions. Based on statistical analysis, the Smith model seemed to be the most suitable for describing the sorption isotherms of FPKF, but for PDPKF and TDPKF Halsey model was the best model in the range of investigated temperatures and a_w. MMC of the three products derived from sorption data according to GAB and BET models appeared to be in good agreement. Q_{st} depended exponentially on MC and the values corresponding to water desorption were higher than those evaluated for adsorption. The results of moisture sorption characteristics of PKF would be highly valuable in characterization and optimization of the shelf life and drying process of PKF.

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