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Sorption characteristics of three different food particulates made from potato, beans and peas

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ABSTRACT

Moisture adsorption behavior depends on the properties and shape of the materials in environment. Three dried food materials, potato, beans and peas were selected to represent different properties such as skin, partial skin and skinless food products. How water in the foods behave and resultant moisture in it are important indicators contribute the stability and keeping quality of foods. Laboratory studies were carried out for materials dried at 30^{o} C, 40^{o} C and 50^{o} C and determined moisture which corresponding in several environments corresponding to drying conditions. Material was prepared resembling to different geometrical shapes of parallelepiped from potatoes, cylindrical from cut green beans and sphere from peas. Dried potato (no skin), beans (partial skin) and peas (skin) were used for the experiments. They were kept at constant temperatures of 30^{o}C, 40^{o}C and 50^{o}C with different salt solutions having specific relative humidity values ranging from 11-85% to determine the moisture content which equilibrate with the environment (EMC). Moisture determination was carried out of samples after they reached equilibrium state. Moisture content and relative humidity values of the environment were used for EMC determination. Environmental factors such as physical, chemical and microbiological contribute to deterioration of common food materials due to environmental factors. Study of sorption characteristics are important to expand future export of food products to other parts of the world specially to displaced persons due to wars and people subjected to natural disasters. This manuscript presents results from three important food materials used for human consumption.

Keywords: Sorption, Isotherm, BET, GAB

1. INTRODUCTION

Owing to their unique benefits such as nutrition, low cost and reduce weight, the demand for dried food-plant products ever increases. To cope with this, the development of well-engineered final products and optimized processing conditions are currently being researched in the processing industry. Also, correct and accurate information on sorption isotherms is important in planning storage and importing/exporting conditions of food materials keep its quality to the maximum as water availability in the food determines its self-life and spoilage. The study of sorption characteristics is very important in future preservation of any food material (Labuza, 1968; Rahman and Labuza, 1999; Young, 1967). Adsorption is the mechanism of combining atoms, ions, biomolecular or molecules of gas, liquid or dissolved solids to a material inside and outer. It is usually described through the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. In this case, adsorbent is water, and the materials are dried potato, beans and peas. The relationship between water and resultant final moisture content inside is what was considered in the study.

Potato is important to Australia not only as a consumable eating crop, accounting for more than 40 percent of total vegetable output of local consumption, but also as a staple food in Australians daily life. In Australia and other western countries, most of the overall consumption of vegetable is contributed by potatoes and other forms of foods make from potato.

Beans and peas are a very important source of protein and cholesterol-lowering fiber, especially for people living in Asia and Africa. The high soluble fiber content of beans and peas also prevents one's blood glucose level from increasing sharply after a meal. In addition, dried beans and peas provide large amounts of minerals, B vitamins with virtually no fat. These are also consumed in large quantities in everywhere in the world and shows potential benefits to the health concern people around the world.

For efficient processing and storage of foodstuffs such as potatoes, beans and peas, the control of moisture is crucial as it encourage role in food inside changes which influences keeping quality. Therefore, study of moisture is extremely important way for understanding dehydration process, making appropriate drying equipment, predicting the stability of food's shelf-lives and selecting packaging materials (Gal, 1987). Hence, this study of determine the adsorption behavior of dried potato, beans and peas at 30° C, 40° C and 50° C and determine the moisture equilibrium moisture corresponding to drying conditions is important.

Early research has developed mathematical equations to explain water influence inside foods at several environments. Those are both theoretical and experimental and use for fitting water behaviour in food of food and their products. No equations showed behaviour completely for all humidities of the environment for all kind of foods.

Sorption isotherms

The water participation behavior of a food material is defined as the ratio of vapour pressure of water in the food to the vapour pressure of pure water, at the same temperature.

$$a_w = \frac{p_f}{p_o} = \frac{E.R.H.}{100}$$

Where a_w = water activity, p_f = vapour pressure of the water in the food, p_o = vapour pressure of the pure water and ERH = equilibrium relative humidity

Water activity is highly important for microbial growth, toxin production and enzymatic and non-enzymatic reactions. The action between total moisture content and the corresponding water over wide range at constant temperature result a moisture sorption isotherm.

Models that applied in this kind of experiments for materials were adopted from literature including BET, Guggenheim–Anderson–de Boer (GAB), Halsey, Henderson, Oswin, Peleg and Langmuir. Only BET and GAB model parameters are given as these models are most common models to describe sorption behavior. Empirical constants for the sorption models were determined from experimental data at different temperatures for all three materials. Modeling was carried out using the least square regression and the Microsoft Excel spreadsheet (Microsoft 2003) was used to perform this task using the SOLVER tool based on the Generalized Reduced gradient (GRG) method. The goodness of fit for each model was established using non-linear optimization method where the objective function is to minimize the sum of squares of residuals and thus perform least-square curve fitting. The goodness of fit for each model was evaluated based on statistical parameter coefficient of determination (R^2).

There are many equations available in published data for food (Mc-Laughlin and Magee, 1998). The models namely Henderson, Chung-Pfost, Halsey, Oswin and Guggenheim–Anderson–de Boer (GAB) that is acceptable for sorption isotherms testing which illustrate the relation between activity and content of water at a given temperature. Widely used models are GAB (Guggenheim-Anderson-de Boer) model and BET (Brunauer-Emmett-Teller) models.

$$\text{GAB model:} \quad m = \frac{C^o K^o m_m a_w}{\left[(1 - K^o a_w)(1 - K^o a_w + C^o K^o a_w)\right]}$$

$$\text{BET model:} \quad m = \frac{C^o \ m_m a_w}{\left[(1 - a_w)(1 - a_w + C^o \ a_w)\right]}$$

Where C^o, K^o = constants, a_w = water activity, m = moisture content (kg/kg db) and m_m = monolayer moisture content (kg/kg db)

In the GAB model, the three parameters (C, K and m_m) are associated with the function of temperature and can be obtained by Arrhenius type equation (Maroulis et al., 1988; Moreira et al., 2008).

In general case, the GAB model is the most suitable to apply to sorption activity in whole range. Peng et al., (2007) supported this conclusion that GAB model was regarded as the most versatile sorption model in testing adsorption and desorption isotherms for corn starch powders. What is more, this isotherm has been particularly accurate over the water activities range up to 0.9 while the BET model only fitted for the range of less than 0.60 (Siripatrawan and Jantawat, 2006). According to Mc-Laughlin and Magee, (2007), BET model played a poor fit in sorption isotherms using a standard gravimetric method, in sharp contrast to the models tested the GAB. Also, BET model failed in characterizing water sorption data in multitemperature because of small changes of the isotherm. The hierarchy and the applicability changes advanced to the simplest of the models is GAB> BET (Furmaniak et al., 2007). Nevertheless, there is an assumption put forward by Ayranci and Duman, (2005), in monolayer moisture contents (Mo), BET equations was in good agreement as well as GAB. Moreover, it found to be the best model in all three aspects which are for describing the EMC-ERH data, for desorption as well as for adsorption and mean sorption of water from amaranth (Pagano and Mascheroni, 2005). Finally, GAB-liked isotherms can be divided into three subclasses depending on parameter X4: Classical GAB isotherms (0.1 6 X4 6 0.1), isotherms of type IIb (X4 < 0.1) and isotherms of type IIc (X4 > 0.1) (Wallach et al., 2011). The three-paramerter GAB isotherm was the best when it was considered at each temperature, shows quality agreement, compared with the other isotherms (Pagano and Mascheroni, 2005).

Halsey equation is another widely used model to examine experimental data. Kaymak-Ertekin and Gedik, (2004) pointed out that the Halsey equation was also the best fit to all materials of the experimental sorption data in the range of temperatures and water activities, despite the GAB model appeared to the closest fit. Compared to BET which had the best water activity range for 0.1 ~ 0.5, the Halsey model showed the best for a wide range of water activity in the experimental sorption (Kaymak-Ertekin and Sultanoglu, 2001). However, modified Halsey expressed a poor relationship in predicting desorption moisture isotherms (Iguaz and Virseda, 2007).

Henderson and Chung-Pfost models are similar in the most situations. In the first place, these two equations were proved that it was acceptable for predicting desorption moisture which was a significant contrast to Halsey and Oswin equations (Iguaz and Virseda, 2007). In the second place, for describing the EMC-ERH data, Chung-Pfost and Henderson models were considered next best following the GAB. Also, Henderson and Chung-Pfost model did good fit to absorption of water from amaranth (Pagano and Mascheroni, 2005).

For instance, the Oswin equation, which is regarded as one of five commonly equations in describing sorption isotherms, is quite different from the GAB model. While the GAB model suited for the general cases, Iguaz and Virseda, (2007) put forward that the Oswin model did not fit to desorption moisture isotherms in a drying condition. By looking at different models, it was possible to conclude that the Oswin model is less appropriate for describing the drying process (Guiné, 2009). Despite less satiable in drying process, Oswin model presented the most acceptable to predict equilibrium moisture content when equilibrium moisture content was taken as a dependent variable. It showed that least standard error and least mean relative percent deviation.

There also exists other experimental model for testing sorption isotherms besides the five equations, such as Peleg Model and Langmuir equation. Peleg Model can be assumed in the comparison with the GAB model. Peng et al., (2007) agreed with a view that those models described the experimental data better within the temperature range examined. Sometimes, Peleg's equation may better than the GAB model in the proposed equation (Gondek and Lewicki, 2007). Lastly, Langmuir's equation is the crucial equation among the theoretical models which is based on the forces performing between the product surface and water condensed (Blahovec and Yanniotis, 2009). In addition, the extensions of Langmuir model will convert in the BET and GAB isotherms. Fitting the most appropriate models helps to identify the behavior of foods and components with moisture environment. This knowledge is helping design of processes and equipment, packaging and shelf life of the products.

Thermodynamic properties

It is also important to study thermodynamic aspects and estimate the values of those properties such as heat of sorption, differential enthalpy and entropy. These properties are calculated from the state of water in foods under different physical environments. Heat of sorption informs the release of heat which is an important process requirement. Change of enthalpy provides variations of energy in humid environments and entropy indicates the randomness of the process. But for this study enthalpy and entropy was not considered.

Heat of sorption is the energy release during the water absorbent to food materials and it is an important concept in understanding and interpretation of the scientific background and the underline mechanism of sorption and becoming a valuable tool in designing drying equipment (Bala, 1991; Balaban et al., 1987; Chirife and Igelesias, 1978; Chung and Pfost, 1967). The Clausius-Clapeyron equation given in chemical thermodynamics was used by many researchers to calculate net isosteric heat of sorption using graphical construction of water activity vs inverse Temperature graphs.

2. MATERIALS AND METHODS

Location

Experimental work was performed at the University of Queensland, St Lucia, Australia during doctoral research study research of the Author. The modeling work and manuscript was written at School of Engineering, University of Southern Queensland, Springfield, Australia

Material preparation

Three common food materials used for human consumption were chosen for the experiments. Material selection was based on inside structural arrangement and way the movement of moisture through the complex food material structure and how outer layer envelope which exposed to atmosphere environment facilitates that.

Potato "*Solanum tuberosum*" of the variety Sebago was selected as the material to have an even structural complexity in all three directions, which permits same moisture movement magnitude in all directions. Potato was peeled and made cubes from fleshy inside portion of the dimensions 6.5mm×6.5mm×6.5mm. This prepared a skin less material. Samples were dipped in a sodium metabisulphite solution (0.1% w/w) for 15 min to prevent browning during subsequent drying operation.

Fresh green beans '*Phaseolus vulgaris*' of the variety Labrador was selected and cylinders with length to diameter ratio of 1:1 were made from the middle portion to facilitate higher moisture movement through the edges and less across surface of the skin. Beans of 10±1 mm were selected using vernier calliper with 0.05 mm accuracy.

For a fully skin covered material peas "*Pisum sativum*" of the variety Bounty were selected. To obtain average diameter 10±1 mm was sorted after shelling by hand and graded using a wire mesh. All materials were kept in a plastic container in a cold room at 4°C for more than 24 h before drying experimentation to equilibrate the moisture content.

Experimental design for drying experimentation

Three batches were prepared for all materials at once and used for three drying temperatures. Two replicate batches were prepared for cut beans and diced potato to reduce time of experiments without compromising the quality of the outcome. Three replicate batches were prepared for peas. For beans and potato, a split unit design with two replications corresponding to processing time, with one size per block and three drying temperatures for each block was used. For peas, a randomized complete block design with three replications for each temperature was used.

Equilibrium Moisture Content (EMC) curve determination

Required isotherms were determined using a gravimetric method at temperatures of 30° C, 40° C and 50° C. Samples of dried potato, beans and peas were initially dried at the corresponding drying temperatures to reduce their moisture content below the level of sorption study. Duplicate samples of potato, beans and peas (~ 3 g) were prepared and placed in desiccators containing saturated salt solutions.

Eight laboratory grade salts (Table 1) were used. Saturated salt solutions were prepared by dissolving salt in distilled water to saturation to maintain fixed water activity of the environment.

Each salt solution produced and maintained a specific relative humidity. Desiccators were then placed inside heating cabinets at 30° C, 40° C and 50° C, providing a constant temperature environment. Small glass bottles of toluene were placed inside in the desiccators at the higher relative humidity's to prevent mold growth. Samples were allowed to equilibrate with the environment inside the desiccators until weight change was less than 0.01 mg. The corresponding final moisture contents were then measured plotted against water activity (equilibrium relative humidity) to produce the sorption isotherms. This isotherm curves were used to find the equilibrium moisture contents corresponding to drying conditions.

Table 1 Saturated salt solutions used in sorption experiments and the corresponding relative humidity's produced

Name of the salt	Water activity (a_w)		
	30° C	40° C	50° C
Lithium chloride	0.113	0.112	0.111
Potassium acetate	0.219	0.212	0.205
Magnesium chloride	0.323	0.318	0.314
Potassium carbonate	0.433	0.432	0.431
Magnesium nitrate	0.513	0.487	0.464
Potassium iodide	0.679	0.661	0.644
Ammonium sulfate	0.806	0.799	0.792
Strontium nitrate	0.851	0.850	0.840

Source: Greenspan (1977)

Curve fitting of adsorption data to different sorption equations

Among many models that are commonly applied for vegetable food materials GAB and BET model was selected. Regression procedure was used to obtain empirical constants for the models using experimental data at different temperatures for all three materials. Modelling was carried out using the least square estimation method using the SOLVER tool based on the Generalized Reduced gradient (GRG) method in Microsoft Excel spreadsheet (Microsoft). The goodness of fit for each model evaluation based on statistical parameter "coefficient of determination (R^2)" and "mean absolute error percentage (MAE %)".

Determination of Thermodynamic properties

Amount of moisture that can be held at a given water activity changes with the temperature. These changes provide shape of isotherm and provide valuable information about the response of the material to temperature. The effect of temperature is specific to each product and follows "Clausius-Clapeyron equation" (Iglesias and Chirife, 1976; Rizvi, 1986). Plotting natural log of Aw vs. 1/T, the slope of line provides the value for Qs/R. If Qs is known water activity at any temperature can be found by regression analysis.

$$\left[\frac{\partial\, ln(a_w)}{\partial\left(\frac{1}{T}\right)}\right]_m = -\frac{Q_s}{R}$$

Where A_w – water activity, Q_s –net isosteric heat of sorption (J/mol),
R – Universal gas constant, 8.314J/mol/K, T- absolute temperature (K)

Assuming that net isosteric heat is invariable with temperature for a given EMC (equilibrium moisture content), the integration of the Clausius-Clapeyron equation is expressed as follows: (Nourhene et al., 2008; Ouertani et al., 2014; Wang and Brennan, 1991)

$$\ln(aw) = - qs/RT + constant$$

Application of the "Clausius-Clapeyron equation" to sorption isotherms is a widely used procedure for calculating the isosteric heat of sorption in food systems (Sanchez et al., 1997; Mc-Laughlin and Magee, 1998).

3. RESULTS AND DISCUSSION

Sorption Isotherms

Samples to equilibrate with different hygroscopic environments ranges from one week to one month. Typical moisture adsorption isotherms for the materials are plotted (Figure 1). All the moisture adsorption isotherms obtained showed similar behavior. Graphs show some little deviations of behaviour may be due to the moisture movement through inner structural arrangement and presence of skin or not of the food materials concerned. This type of behaviour is mostly common to the foods reported by various researchers; they are of type II sigmoidal according to the BET classification. Any isotherm curve categorizes and be divided into three regions according to a_w values.

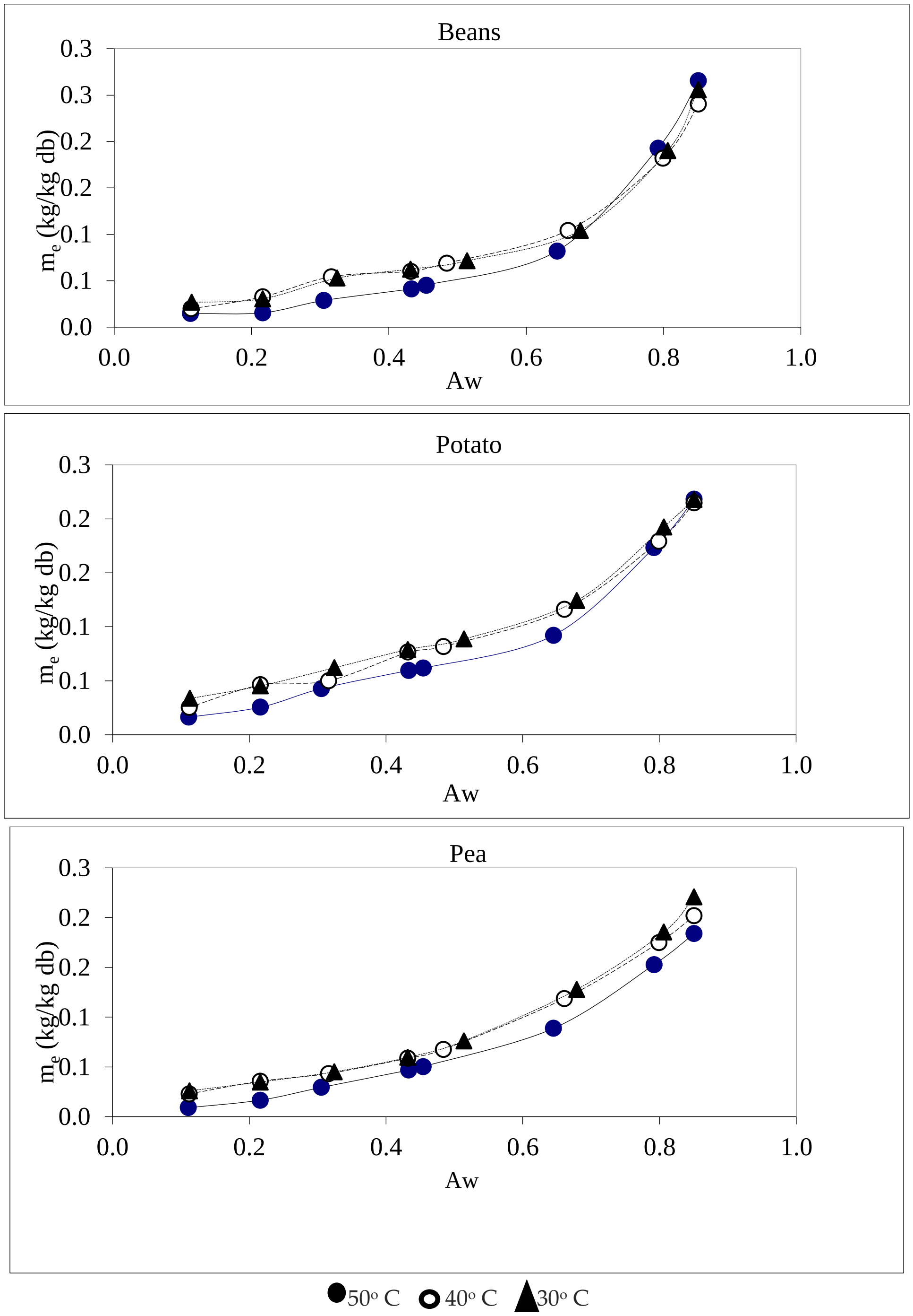

Figure 1 Sorption isotherms of beans, potao and peas

Seen from the graphs revealed (Figure 1) moisture content increases with decrease in temperature, reported by many researchers in the literature (Ayranci and Duman, 2005). This behavior may be attributed to the how water is attached in molecular form to the inner structure of the food materials. At increasing temperatures, force among between tiny water molecules decreases due to increase in kinetic energy of water particles. Therefore, water particles in slow motion bound more easily come to surface at low temperatures (Mc-Laughlin and Magee, 1998).

For all the materials 30°C and 40° C shows similar coincided behavior of moisture changes to water activity. In beans there is an overlap happens between 0.6 and 0.8 water activity this may be due to increase in water from the environment and water movement direction through the sides of the particle dominates water transfer through the outer skin. But for Isotherms at 50°C it shows a behavior moisture influence lower than lower temperatures this may due to increased dryness of the materials.

When looking at the moisture content of different particulates at constant temperature, the decreasing trend observed depend on the constituents of the materials and porosity. Although considered two models shows a very good fitness to the data for the whole region, but actual behavior may be different which dependent on the how water is attracted and bound to the material structure. The monolayer moisture value (m_m) is a very important moisture value designing storage conditions as at this value water is tightly attached to the surface of mono layer of the material. The variation of this value is given in Table 3 for all three materials with respect to the temperatures considered. Constant C is decreasing with increasing of temperature for potato and peas, but this trend is not observed in Beans. This may be due to the reason of hollow structure (cylindrical) of the beans which came from the material preparation stage.

Fitting of sorption models to experimental adsorption data

Among large number of equations reported in literature, only GAB and BET were used to fit the samples. Parameters of the equations are shown (Table 2, 3). In Table 3 adsorption process released heat was introduced as an additional column.

Table 2 Estimated parameters of GAB model

Material	Temperature (° C)	GAB model			R^2
		C^o	K^o	m_m(gH_2O/gsolid)	
Beans	30	4.0852	1.0000	0.0590	0.98
	40	5.6615	0.9553	0.0449	0.99
	50	4.4270	1.0000	0.0289	0.99
Potato	30	9.6469	0.8976	0.0554	0.99
	40	6.8245	0.8866	0.0548	0.99
	50	3.6393	0.9240	0.0482	0.99
Peas	30	7.3177	0.9674	0.0419	0.99
	40	6.7468	0.9785	0.0408	0.99
	50	2.6518	1.0000	0.0372	0.99

Table 3 Estimated parameters of BET model

Material	Temperature (° C)	BET model				
		C^o	m_m(gH_2o/gsolid)	Qs (Cal/moleH_2O)	R^2	MAE%
Beans	30	3.4372	0.0639	3125	0.98	9.1422
	40	6.0159	0.0424	4687	0.99	3.3889
	50	3.9782	0.0305	3725	0.99	9.3545
Potato	30	12.4025	0.0483	6371	0.99	2.690
	40	7.3132	0.0486	5199	0.99	4.7614
	50	3.5806	0.0451	3439	0.99	4.2132
Peas	30	7.2204	0.0407	5002	0.99	2.6285
	40	7.0587	0.0393	5107	0.99	4.6062
	50	2.3356	0.0398	2289	0.99	6.8494

Thermodynamic properties

The net isosteric heat of adsorption can be obtained by the inclination of ln A_w versus 1/T lines at different moisture content values. Figure 2 below shows such a plot for peas.

As seen from the above plot at low moisture contents the net isosteric heat of absorption is higher than that of high moisture content. Similar trend was observed for beans and potatoes indicating strong water surface interactions. As the moisture content increases, there are less available binding sides for water adsorption reported by many authors. Reduced Isosteric heat with increasing moisture is an example of weaker interactions of water and solids.

Below, Table 4 shows variation of Aw with four different moisture values of 0.05, 0.10, 0.15 and 0.20 for materials considered. Due to availability of skin, it shows variation of water activity with respect to temperatures for different moisture contents. This gave us an indication of how the inside structural complexity and resistance of the skin through which water movement to the atmosphere. These properties of the food materials also influence the water activity and moisture availability for any reactions. Also, it determines the shelf-life of materials for further processing and storage requirements.

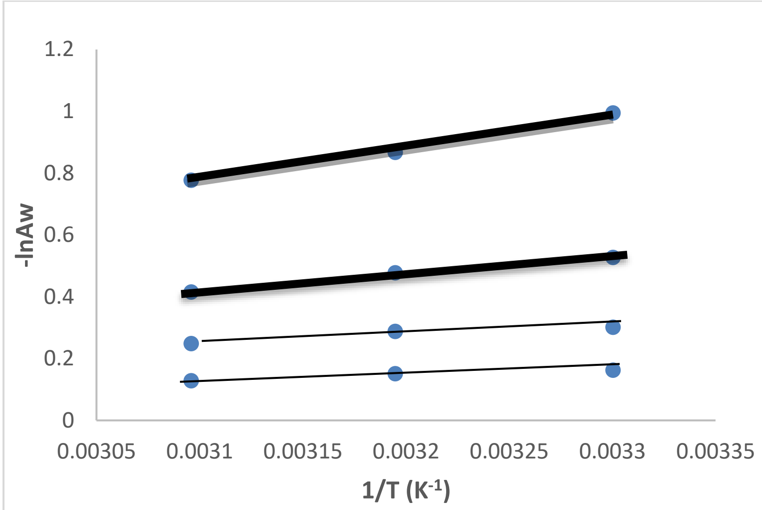

Figure 2 Ln A_w vs. 1/T plot for peas

Table 4 Typical Aw values obtained for constant moisture contents for the materials

Temp	m_e	Peas (skin)	Beans (partial skin)	Potato (no skin)
30	0.05	0.42	0.30	0.25
	0.10	0.62	0.46	0.54
	0.15	0.75	0.60	0.72
	0.20	0.82	0.71	0.82
40	0.05	0.37	0.29	0.30
	0.10	0.59	0.64	0.57
	0.15	0.74	0.74	0.74
	0.20	0.85	0.82	0.82
50	0.05	0.45	0.46	0.35
	0.10	0.66	0.67	0.66
	0.15	0.78	0.74	0.75
	0.20	0.88	0.80	0.84

When consider material like potato which contains similar structural integrity in all three dimensions in space and unavailability of skin tends to get higher values at increasing temperature and moisture values.

4. CONCLUSIONS

The moisture isotherms of three foods, beans, potatoes and peas obtained at three temperatures 30^{o}C, 40^{o}C and 50^{o}C show a typical behavior of food materials. Suitable fits were obtained for GAB and BET models for the experimental moisture adsorption isotherm data of peas, beans and potatoes, for the three temperatures and water activity ranges. They were excellently represented by GAB model. Meanwhile, it was appeared that monolayer moisture content (mo) of the three products derived from treatment of sorption data according to GAB and BET equations was in good agreement and mo values decreasing with increasing temperature for all products. Properties of the structure of material dominate sorption behavior of food materials considered and temperature of the environment they are in. The heat sorption of all materials considered decreases with increasing temperature.

Nomenclature

A_w	Water activity
C, K, m_m	Parameters in GAB model
M_0	Monolayer moisture content
EMC	Equilibrium moisture content
T	Temperature (K)

Ethical issues
Not applicable.

Informed consent
Not applicable.

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Conflict of Interest
The author declares that there are no conflicts of interests.

Data and materials availability
All data associated with this study are present in the paper.

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