



Isotherms and isosteric heat of sorption of two varieties of Peruvian quinoa

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Abstract

The isosteric heats of sorption of two varieties of quinoa (*Chenopodium quinoa* Willd.) grain were determined by the static gravimetric method at four temperatures (40, 50, 60 and 70 °C) and in relative humidity environments provided by six saturated salt solutions. Six mathematical equations were used to model the experimental data: GAB, Oswin, Henderson, Peleg, Smith and Halsey. The isosteric heat of sorption was determined using the parameters of the GAB model. All the equations were shown to be appropriate by the coefficients of determination (R^2) and the mean absolute error (MA%E). The influence of temperature was observed because the adsorption of water by the grains was lower at higher temperatures. The equilibrium moisture contents for security of storage, for long periods of time at water activity lower than 0.65, were 12 - 13%. The effect of temperature on the parameters of the GAB model was analysed using the exponential Arrhenius equation. The isosteric heats of sorption were determined by applying the Clausius-Clapeyron equation as a function of humidity. The isosteric heat at 5% moisture for grains of the Blanca de Juli variety was 3663 kJ/kg and for the Pasankalla variety it was 3393 kJ/kg. The experimental data for isosteric heat as a function of humidity were satisfactorily modelled using three mathematical equations.

Keywords: Quinoa grains; moisture security; sorption isotherms; isosteric heat of sorption; mathematical models.

1. Introduction

Quinoa (*Chenopodium quinoa* Willdenow) is considered to be one of the most complete foods in the world; it is rich in nutrients, with a unique pattern of amino acids and a high content of polyunsaturated fatty acids and minerals (Bojanic, 2011). For this reason, the United Nations, through the auspices of the FAO, declared 2013 as the "International Year of Quinoa". Peru is one of the leading manufacturers and exporters of quinoa worldwide. In 2015, exports reached 142.2

million US dollars at an average value of U.S. \$ 3.46/kg of quinoa. The USA is the main destination for these exports followed by the United Kingdom, Netherlands and Canada (AGRODATA, 2016).

In Peru, 80% of quinoa is grown in the highland region located at an altitude of 2500-4000 m. The air at these altitudes contains saturation pressures, densities, moisture and temperatures that are lower than in the Amazonian and coastal regions. This causes the grains to naturally contain between 9 and 10% moisture at harvesting

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time. However, the regions where quinoa is exported from are located at an altitude of less than 1500 m. Under these conditions, if the quinoa grains are not properly stored they can absorb water up to levels that are not permitted by law, causing microbial deterioration and other adverse reactions.

Knowledge about the gain or loss of water in foods due to relative humidity is of vital importance in various stages of the consumption chain. This characteristic is specific to each type of food and can be checked experimentally. The water activity (a_w) of a food is a characteristic that is temperature dependent, because above certain limits, chemical, enzymatic and microbiological reactions occur that are capable of causing it to deteriorate. The main cause of deterioration, apart from production, transportation, trade and consumption, is deterioration due to excess water absorbed from the environment. Sorption isotherms can be determined experimentally and can be adjusted to facilitate mathematical models that determine storage conditions and types of packaging. Various studies have been conducted to determine the sorption isotherms of dried foods and to adjust data to mathematical models (de Oliveira *et al.*, 2014; Polachini *et al.*, 2016; Rosa *et al.*, 2015; Villa-Vélez *et al.*, 2015).

Every aspect of the sorption or desorption of water involves energy. According to Aguerre and Viollaz (1989), this phenomenon occurs in the gas/solid interface of foods but it is the thermodynamic properties of water that regulate this phenomenon. The isosteric heat of sorption is a measure of the energy required for the evaporation or condensation of water from foods. This energy is variable in foods, due to the chemical bonding that the water molecules form with components such as fats, proteins, carbohydrates, etc. One way to understand more about this heat is through the study of sorption isotherms. There have been several studies about isotherms and isosteric heats of sorption in grains such as quinoa, rice, orange peels,

orange seeds, beans and soybeans (Aviara *et al.*, 2004; Miranda *et al.*, 2011; de Oliveira *et al.*, 2014; Resende *et al.*, 2006; Rosa *et al.*, 2013; Villa-Vélez *et al.*, 2015). Taking into consideration the importance of greater knowledge of the isotherms and energies involved in the process of water sorption, the objectives of this study were the following: to obtain the isothermic curves of two varieties of quinoa; to determine the models that best represented the experimental data; and to verify the sorption heat involved in the process.

2. Materials and methods

The experimental tests were conducted in the process laboratory at the Institute of Biosciences, Letters and Exact Sciences of the State University of São Paulo, SP, Brazil and the materials microscopy laboratory at the State University of Ponta Grossa, PR, Brazil. Quinoa grains of the Blanca de Juli and Pasankalla varieties, and of the seed type, from the 2009-10 crop, were obtained from the National Institute of Agrarian Investigation (INIA), Puno, Peru.

2.1 Physical properties

The grains were selected, placed in plastic bags, identified and stored in a cold room at 5 °C. The initial moisture was determined by the standard oven method (105 °C/24 h) and the physical properties (geometric mean diameter, real density, apparent density, unit mass, porosity and sphericity) were determined according to the methodology of (Vilche *et al.*, 2003). The surface of the grains was observed using a scanning electron microscope (SEM); the grains were previously coated in gold.

2.2 Water sorption isotherms

The saturated solutions of six salts ($MgCl_2$, K_2CO_3 , NaBr, $NaNO_2$, NaCl and KCl) were used to determine the sorption isotherms. The saturated solutions provided water activity (a_w) values from 0.278 to 0.823 for temperatures of 40, 50, 60 and

70 °C. Approximately two grams of quinoa were placed in each container and then placed in a BOD, model SP-500, incubator chamber. Constant mass was reached between 20 and 25 days and was quantified by the standard oven (105 °C/24 h) method. The tests were performed in triplicate for both varieties.

2.3 Modeling of sorption isotherms

Six mathematical models used to fit experimental data are collected in Table 1 (Eqs. 1, 5 and 9). These were used to adjust the experimental data and to determine the model that gave the best fit for the experimental data.

Table 1

Mathematical models applied to the experimental sorption data for quinoa grains of two varieties

Models	Equations
GAB (Van den Berg and Bruin, 1981)	$X_e = \frac{X_m C k A_w}{(1 - k A_w)(1 - k A_w + C k A_w)}$ (1)
Moisture monolayer	$X_m = X_0 \exp\left(\frac{\Delta X_m}{RT}\right)$ (2)
Constant monolayer	$C = C_0 \exp\left(\frac{H_m - H_n}{RT}\right)$ (3)
Constant multilayer	$K = K_0 \exp\left(\frac{\lambda - H_n}{RT}\right)$ (4)
Peleg (Peleg, 1993)	$X_e = k_1 a_w^{n_1} + k_2 a_w^{n_2}$ (5)
Oswin (Oswin, 1946)	$X_e = A \left(\frac{a_w}{1 - a_w}\right)^B$ (6)
Henderson (Henderson, 1952)	$X_e = \left(\frac{-\ln(1 - a_w)}{A}\right)^{1/B}$ (7)
Halsey (Halsey, 1948)	$X_e = \left(\frac{-A}{\ln a_w}\right)^{1/B}$ (8)
Smith (Smith, 1947)	$X_e = A + B \ln(1 - a_w)$ (9)

In the equations shown in Table 1, X_e is the equilibrium moisture content in % dry basis. In the GAB model the constants X_m , C and K are dependent on the temperature; X_m represents the moisture of the molecular monolayer on the inner surface (Blahovec, 2004), C is the constant related to the heat of sorption of the monolayer and K is the heat of sorption of the multilayer compared to pure water (Moreira *et al.*, 2008). In Table 1 (Eqs. 2, 3 and 4) the constants X_0 , C_0 and K_0 are the parameters of the entropic character and

ΔH , H_o , H_m and H_L (kJ/kg) are the heats of sorption of water in X_e , in the monolayer, in the multilayer, and in pure water, respectively (Martín-Santos *et al.*, 2012; Moreira *et al.*, 2008; Polachini *et al.*, 2016; Rosa *et al.*, 2013; Villa-Vélez *et al.*, 2015). In the Peleg model, K_1 , K_2 , n_1 and n_2 are constants and have the restrictions that $n_1 < 1$ and $n_2 > 1$. In the Oswin, Henderson, Halsey and Smith models, A , B , C are constants and T is the absolute temperature. The adjustments to the models were made using SOLVER from the Excel® programme of Windows® 2010.

2.4 Determination of the isosteric heat of sorption

The isosteric heat of sorption, Q_s , (Eq. 10), or heat of sorption, is the energy required to remove water from a solid matrix. This corresponds to the enthalpy of the vaporisation of water from a food, which is always greater than pure water. In seeds, such as quinoa grains, water molecules are distributed in the intercellular and extracellular spaces in such a way that they are linked to molecules of starch, fat, protein and other components. Q_s represents the sum of the net isosteric heat, q_s , and the enthalpy of vaporisation of pure water, H_L .

$$Q_s = q_s + H_L \tag{10}$$

The enthalpy of vaporisation or condensation of pure water can be calculated using Eq. (11):

$$H_L = 2501 - 2.361 T \quad (R^2 = 0.998) \tag{11}$$

The q_s can be calculated by using the Clausius-Clapeyron graphical Eq. (12) on a given X_e (Martín-Santos *et al.*, 2012; Miranda *et al.*, 2011; Thys *et al.*, 2010) and by the integrated method of Eq. (13) (Chen, 2006; Thys *et al.*, 2010):

$$(\ln a_w)_{X_e} = -\frac{q_s}{RT} + \frac{S_d}{R} \tag{12}$$

$$q_s = R \left(\frac{T_1 T_2}{T_2 - T_1}\right) \ln\left(\frac{a_{w2}}{a_{w1}}\right) \tag{13}$$

Where R is the general gas constant (0.462 kJ/kg K) and T is the absolute temperature in degrees Kelvin. Plotting $\ln a_w$ vs $1/T$ (Eq. 12) for different equilibrium moisture contents and adjusting to a straight, the slope (q_s/R) is obtained. In Eq. (13), the water activities correspond to temperatures

of 40 (T₁) and 70 °C (T₂). Both methods showed no significant differences in the calculated values (Mulet *et al.*, 1999), which were obtained using Eq. (13).

The (a_w) for each X_e were determined by the constants of the GAB model, X_m , C and K , according to the methodology used by (Villa-Vélez *et al.*, 2012). In order to obtain the expressions for predicting the Q_s of the quinoa grain, the following Eqs. (14 to 16) were used (Chen, 2006; Mulet *et al.*, 1999; Tsami, 1991):

$$Q_s = q_0 \exp\left(-\frac{x_g}{x_0}\right) + H_L \quad (14)$$

$$Q_s = q_0 \exp(-K_1 X_e) + H_L \quad (15)$$

$$Q_s = q_0 \exp(-K_2 X_e) X_e^{K_3} + H_L \quad (16)$$

Where q_0 is the heat of sorption of the monolayer, X_0 is the initial moisture of the product; K_1 , K_2 and K_3 are constants.

The moisture equilibriums and heats of sorption calculated by the models in relation to the experimental values were evaluated by the coefficient of determination, R^2 and the mean absolute error (MA%E) (Chen, 2006; Miranda *et al.*, 2011; Silva *et al.*, 2010; Tolaba *et al.*, 2004), defined as:

$$MA\%E = \frac{100}{N} \sum_{n=1}^{\infty} \frac{|X_g - X_C|}{X_g} \quad (17)$$

3. Results and discussion

3.1 Physical properties

The moisture content (% dry basis), geometric mean diameter (mm), unit mass (mg), real density (kg/m³), apparent density (kg/m³), porosity (%) and sphericity (%) of the grains at the beginning of the tests were 11.81 ±0.07 and 11.16% ±0.06; 1.66 ±0.04 and 1.73 ±0.15 mm; 2.92 ±0.05 and 3.55 ±0.15; 1213.1 ±36.8 and 1277.6 ±22.9; 661.7 ±2.9 and 681.6 ±2.6; 45.45 and 46.64%; 85 ±7 and 86 ±6 for the Blanca de Juli quinoa and the Pasankalla quinoa, respectively. Similar diameters and densities were determined for Ecuadorian and Argentinian quinoa (Alvarado, 2012; Vilche *et al.*, 2003).

Figure 1 shows a quinoa grain magnified by 30x and Figure 2 shows a grain

magnified by 270x. The grain is a seed type, untreated for the removal of saponin, which is a characteristic of commercial grains. It can be seen that the surface roughness is well organised, which contributes to the increase in the surface area for adsorption or desorption. According to Sukhorukov and Zhang (2013) this is a typical characteristic of seeds from the Chenopodioideae family.

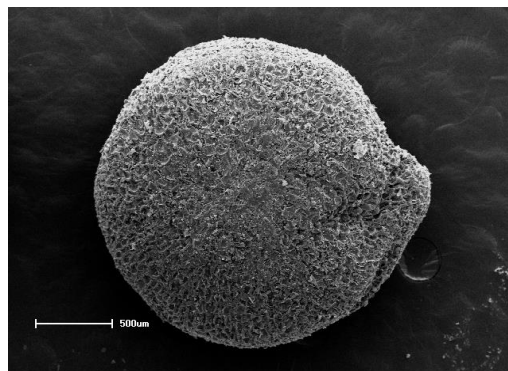


Figure 1. Scanning electron microphotographs of grain quinoa at 30x magnification.

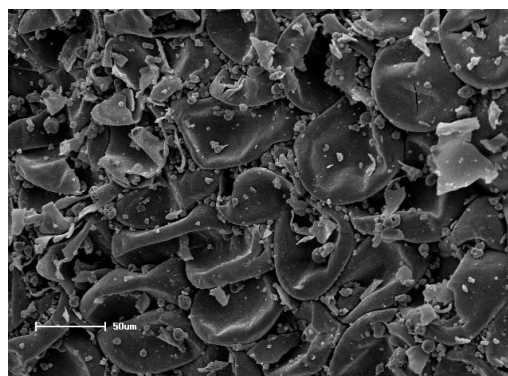


Figure 2. Scanning electron microphotographs of grain quinoa surface at 270x magnification.

3.2 Water sorption isotherms

The data for water activity and moisture equilibrium for the four temperatures are shown in Table 2. Figure 3 shows the effect of temperature on the isotherms of both varieties of quinoa. An inverse relationship between X_e and temperature was observed. Foods with water activity less than 0.65 can be stored for long periods without risk of mould growth.

Table 2

Equilibrium moisture content (X_e , % d.b.) obtained by adsorption at different water activity and temperatures for quinoa grains of two varieties

Salts	Blanca de Juli							
	40 °C		50 °C		60 °C		70 °C	
	a_w	X_{eq}	a_w	X_{eq}	a_w	X_{eq}	a_w	X_{eq}
MgCl ₂	0,316	8,95	0,3054	7,27	0,2926	5,49	0,278	4,73
K ₂ CO ₃	0,4	10,10	0,381	9,14	0,362	6,87	0,343	6,41
NaBr	0,5317	12,19	0,5093	10,20	0,4966	8,55	0,497	8,26
NaNO ₂	0,615	12,85	0,599	10,79	0,59	9,73	0,587	8,95
NaCl	0,7468	14,66	0,7443	14,08	0,745	12,66	0,751	11,85
KCl	0,8232	17,03	0,812	15,74	0,8025	13,70	0,795	12,36
Pasankalla								
MgCl ₂	0,316	7,13	0,3054	6,35	0,2926	5,44	0,278	5,06
K ₂ CO ₃	0,4	8,38	0,381	7,33	0,362	6,68	0,343	6,19
NaBr	0,5317	9,88	0,5093	9,25	0,4966	8,32	0,497	8,04
NaNO ₂	0,615	11,46	0,599	10,13	0,59	9,19	0,587	9,07
NaCl	0,7468	15,69	0,7443	14,46	0,745	12,88	0,751	12,62
KCl	0,8232	18,51	0,812	17,24	0,8025	14,42	0,795	13,73

In the present study, in terms of water activity, the quinoa grains that showed values of 0.615 reached moisture contents of 12.85 and 11.46% at 40 °C for the Blanca de Juli and Pasankalla varieties, respectively. Similar behaviour has been determined in grains of different varieties of quinoa (Alvarado, 2012; Miranda *et al.*, 2011; Tolaba *et al.*, 2004).

The maximum experimental equilibrium moisture contents, with water activities from 0.80 to 0.82 at the four experimental temperatures, were 17.03 - 12.36% and 18.51 - 13.73% for the Blanca de Juli and Pasankalla varieties, respectively. The Pasankalla variety absorbed more water than the Blanca de Juli variety, with water activities greater than 0.8 at the four temperatures.

Table 3 shows the values of the regression parameters for the adjustments of data for X_e versus a_w in terms of the mathematical models for the two varieties of quinoa.

All the models had good fits, with R^2 greater than 0.977 and MA%E less than 8.48%. The mean MA%E for the four temperatures was less than 5.7%. The constants of the GAB model (X_m , C and K) varied with temperature, confirming behaviour found by other authors (Blahovec, 2004; Moreira *et al.*, 2008). According to Blahovec (2004), the constant C decreases and K increases with increasing temperature. This observation was confirmed in the present study. On the other hand, the constant C was greater than 2.0, and the constant K was less than 1.0, so the isotherms were classified as Type II (Brunauer *et al.*, 1940). This behaviour has also been observed for several varieties of yellow corn and quinoa (Alvarado, 2012; Miranda *et al.*, 2011; Samapundo *et al.*, 2007; Tolaba *et al.*, 2004).

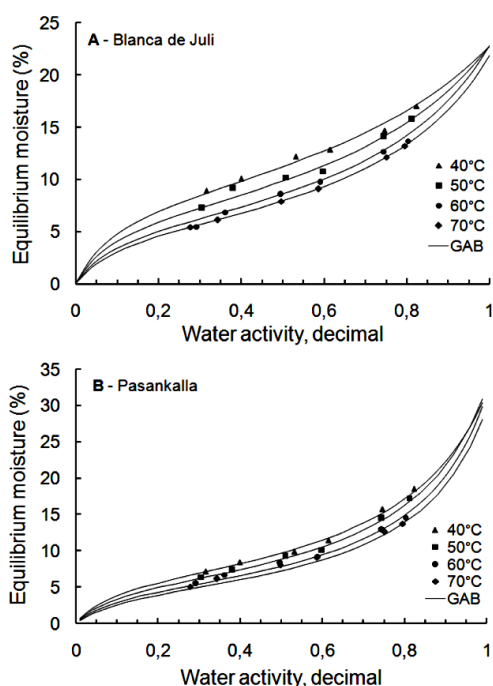


Figure 3. Experimental data of equilibrium moisture contents for quinoa grains of varieties Blanca de Juli (A) and Pasankalla (B). Lines correspond to the GAB model (Eq. 1).

Table 3

Estimated values of coefficients models; determination coefficient (R^2) and mean relative error (MR%E) for quinoa grains of two varieties

Model	Constant	Blanca de Juli				Pasankalla			
		40°C	50°C	60°C	70°C	40°C	50°C	60°C	70°C
GAB	X_m	8,77	7,30	6,09	5,62	6,43	5,73	5,08	4,71
	C	15,39	14,45	13,60	12,50	13,68	12,83	11,55	10,65
	K	0,63	0,69	0,74	0,75	0,80	0,83	0,84	0,84
	R^2	0,99	0,98	0,99	0,98	0,996	0,996	0,995	0,995
	MA%E	2,83	2,93	3,31	5,79	2,3	2,7	3,8	6,8
OSWIN	A	11,26	10,09	8,50	8,03	9,81	9,07	8,34	8,01
	B	0,27	0,30	0,37	0,35	0,41	0,44	0,39	0,40
	R^2	0,98	0,98	0,99	0,98	0,995	0,996	0,996	0,998
	MA%E	1,66	3,24	2,91	5,19	2,0	1,3	2,5	2,0
HENDERSON	K	0,002	0,007	0,007	0,010	0,018	0,019	0,012	0,011
	N	2,35	1,97	2,16	2,02	1,58	1,60	1,86	1,90
	R^2	0,988	0,977	0,998	0,988	0,984	0,982	0,990	0,994
	MA%E	1,71	2,82	5,18	4,38	3,7	3,8	6,5	7,5
PELEG	K_1	14,48	13,52	9,81	10,97	10,17	13,11	11,41	10,31
	n_1	3,84	4,33	1,90	2,68	3,87	5,64	3,68	3,55
	K_2	7,81	8,83	7,71	4,96	19,08	18,44	10,42	10,33
	n_2	0,42	0,51	0,59	0,54	0,34	0,61	0,49	0,52
	R^2	0,980	0,982	0,996	0,988	0,998	0,997	0,995	0,998
MA%E	1,66	2,89	1,46	4,24	1,2	1,1	2,4	1,8	
SMITH	A	7,20	5,48	4,04	4,12	3,87	3,23	2,35	3,45
	B	5,67	6,14	6,31	5,46	8,45	8,23	7,70	6,49
	R^2	0,982	0,981	0,986	0,968	0,995	0,994	0,995	0,997
	MA%E	2,37	3,65	3,41	5,65	2,12	2,20	5,37	2,37
HALSEY	A	874,08	359,36	235,63	323,15	64,41	61,74	46,67	43,80
	B	2,97	2,70	2,68	2,65	2,00	2,00	2,00	2,00
	R^2	0,981	0,981	0,983	0,965	0,996	0,997	0,992	0,993
	MA%E	2,41	3,77	8,12	8,48	2,43	5,75	3,68	3,85

The GAB model is often used to determine energies related to adsorption sites in the monolayer and multilayer and the thermodynamic properties of water in foods (Martín-Santos *et al.*, 2012; Miranda *et al.*, 2011; Moreira *et al.*, 2008; Thys *et al.*, 2010; Tolaba *et al.*, 2004; Villa-Vélez *et al.*, 2015). Figure 2 shows the adjustments to the GAB model for the experimental points of moisture equilibrium and the a_w of the two varieties of quinoa at the four tested temperatures.

The activation energy (Table 4), ΔH , obtained for the moisture of the monolayer, X_m , represents the energy required to

break or bind water molecules to the solid water system in this position (Martín-Santos *et al.*, 2012). The values for this energy were 943.25 and 523.38 kJ/kg for the Blanca de Juli and Pasankalla varieties, respectively (Table 4). This shows that the Pasankalla grains absorbed water faster than the Blanca de Juli grains. The heats of sorption of the monolayer and multilayer of Blanca de Juli quinoa (2413 and 2074 kJ/kg, respectively) were lower than the heats of sorption for the Pasankalla quinoa (2705 and 2282 kJ/kg, respectively) (Table 4).

Table 4

Estimated values of coefficients models GAB; determination coefficient (R^2) and mean relative error (MR%E) for quinoa grains of two varieties

Variety	ΔH kJ/kg	R^2 -	H_o, H_m kJ/kg	R^2 -	H_L, H_m kJ/kg	R^2 -	H_o	H_m	H_L
Blanca de Juli	943,25	0,981	338,78	0,989	297,17	0,932	2413	2074	2371
Pasankalla	523,38	0,995	423,84	0,989	89,66	0,905	2705	2282	2371

When these figures are compared to the heats of sorption of the monolayer of two varieties of Ecuadorian quinoa (between 2667 and 2946 kJ/kg) and the heats of sorption of the multilayer (2483 to 2544 kJ/kg) at temperatures of 20, 25 and 30 °C (Alvarado, 2012), it can be seen that the energy value of the monolayer in the Ecuadorian quinoa was higher, due to the water being more strongly bound to the substrate at lower temperatures.

3.3 Isosteric heat of sorption

The dependency of Q_s with X_e for the two varieties of quinoa is shown in Figure 4. The graph in Figure 4 shows that the grains of Pasankalla quinoa showed lower heats of sorption than the Blanca de Juli grains; they were in the range of 5 - 17% moisture. This demonstrates that the grains of Pasankalla quinoa absorbed and/or lost more water than the Blanca de Juli grains. When moisture levels were over 20%, the sorption heats were similar for both varieties of quinoa; there was a tendency for similar values for the enthalpy of vaporisation of pure water (H_L); 2371 kJ/kg at an average temperature of 55 °C. Thus, it was confirmed that the Q_s increased with decreasing moisture in the grains. Similar results were observed in the desorption isotherms obtained by using Eq. (14) (Miranda *et al.*, 2011; Tolaba *et al.*, 2004).

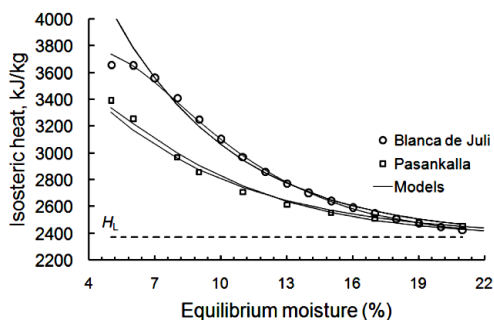


Figure 4. Effect of moisture content on the isosteric heat of sorption for quinoa grains of varieties Blanca de Juli and Pasankalla. Lines correspond to the models and heat of vaporization of water, H_L .

At 5% moisture levels, the Blanca de Juli variety had a sorption heat of 3663 kJ/kg and the value for the Pasankalla variety was 3393 kJ/kg, confirming that the Pasankalla grains absorbed more water than the Blanca de Juli grains. Quinoa grains of the Real variety from Bolivia needed between 4,000 - 5,000 kJ/kg of energy for moisture between 2 - 5% at temperatures of 20, 30 and 40 °C (Tolaba *et al.*, 2004). Quinoa grains from Chile showed values of 3,400 - 3,880 kJ/kg for moisture levels below 4% at temperatures of 20, 40 and 60 °C (Miranda *et al.*, 2011). Two Ecuadorian varieties of quinoa had values of between 3,600-3,900 kJ/kg at 6% moisture and temperatures of 20, 25 and 30 °C (Alvarado, 2012).

Table 5 shows the constants of the adjustment models for the experimental data for sorption heat. The three equations represented the experimental data very well. However, Eq. (17), with three parameters, showed a better R^2 and a MA%E of 0.997 and 0.991; and 0.338 and 1.115% for the Blanca de Juli and Pasankalla varieties, respectively.

Table 5

Estimated values of coefficients models Eqs. (14 to 16) for determination isosteric heats of sorption

Model	Constant	Blanca de Juli	Pasankalla
Tsami (Eq. 14)	q_0 (kJ/kg)	4192,200	2000,647
	X_0 (%bs)	5,555	6,558
	R^2	0,959	0,977
	MA%E	1,396	1,054
Tsami (Eq. 15)	K_1 (kJ/kg)	4167,860	2001,887
	K_2	0,180	0,153
	R^2	0,959	0,977
	MA%E	1,399	1,055
Mulet (Eq. 16)	K_1 (kJ/kg)	761,066	1310,405
	K_2	0,309	0,220
	K_3	1,326	0,495
	R^2	0,997	0,991
	MA%E	0,338	1,115

4. Conclusions

Sorption curves were determined for two quinoa grain varieties at temperatures of 40 - 70 °C and water activity from 0.28 - 0.82.

The moisture safety values for long storage periods were approximately 12 - 13% for both varieties. At high relative humidities ($a_w > 0.74$), the Pasankalla variety had a higher equilibrium moisture content than the Blanca de Juli variety. Of the six mathematical models that were tested, five models showed a MA%E of less than 3.9%; the most successful model was Peleg. The sigmoid type isotherms were classified as type II. The moisture contents for safe storage using the X_m constant in the GAB model were 8.77 - 5.62%, and 6.43 - 4.71% for the Blanca de Juli and Pasankalla varieties, respectively at the studied temperature range. The energy required for water absorption (activation energy), the heats of sorption of the monolayer and multilayer, and the isosteric heat, were higher for the Blanca de Juli variety compared to the Pasankalla variety. The Pasankalla variety tended to gain water faster than the grains of the Blanca de Juli variety. The three presented models can be used to determine the isosteric heat as a function of grain moisture.

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References

- AGRODATA. 2016. Exportaciones de quinua peruana. Available in: <http://www.agrodataperu.com/category/quinua-exportacion>
- Aguerre, R.J.; Viollaz, P.E. 1989. Swelling and Pore Structure in Starchy Materials. *Journal of Food Engineering* 9: 71–80.
- Alvarado, J. de D. 2012. Propiedades termodinámicas relacionadas con el agua constitutiva de alimentos. (Grafitext, Ed.) (1st ed.). Ambato, Ecuador. Retrieved from http://fcial.uta.edu.ec/images/stories/docs/libros/jdda_ptrceacda.pdf
- Aviara, N.A.; Ajibola, O.O.; Oni, S.A. 2004. Sorption Equilibrium and Thermodynamic Characteristics of Soya Bean. *Biosystems Engineering* 87: 179–190.
- Blahovec, J. 2004. Sorption isotherms in materials of biological origin mathematical and physical approach. *Journal of Food Engineering* 65(4): 489–495.
- Bojanic, A. 2011. La quinua: Cultivo milenario para contribuir a la seguridad alimentaria mundial. Available in: http://www.fao.org/fileadmin/templates/aiq2013/res/es/cultivo_quinua_es.pdf
- Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. 1940. On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society* 62: 1723–1732.
- Chen, C. 2006. Obtaining the isosteric sorption heat directly by sorption isotherm equations. *Journal of Food Engineering* 74(2): 178–185.
- de Oliveira, D.E.C.; Resende, O.; Campos, R.C.; Donadon, J. R. 2014. Obtenção e modelagem das isothermas de dessecção e do calor isostérico para sementes de arroz em casca. *Científica* 42(3): 203–210.
- Halsey, G. 1948. Physical adsorption on non-uniform surfaces. *Journal of Chemical Physics* 16: 931–937.
- Henderson, S. M. 1952. A basic concept of equilibrium moisture. *Agricultural Engineering* 33: 29–32.
- Martín-Santos, J.; Vioque, M.; Gómez, R. 2012. Thermodynamic properties of moisture adsorption of whole wheat flour. Calculation of net isosteric heat. *International Journal of Food Science & Technology* 47(7): 1487–1495.
- Miranda, M.; Vega-Gálvez, A.; Sanders, M.; López, J.; Lemus-Mondaca, R.; Martínez, E.; Scala, K. 2011. Modelling the Water Sorption Isotherms of Quinoa Seeds (*Chenopodium quinoa* Willd.) and Determination of Sorption Heats. *Food and Bioprocess Technology* 5(5): 1686–1693.
- Moreira, R.; Chenlo, F.; Torres, M.D.; Vallejo, N. 2008. Thermodynamic analysis of experimental sorption isotherms of loquat and quince fruits. *Journal of Food Engineering* 88(4): 514–521.
- Mulet, A.; Sanjuán, R.; Bon, J. 1999. Sorption Isotherm Heat Determination by Thermal Analysis and Sorption Isotherms. *Journal of Food Science* 64(1): 64–68.
- Oswin, C.R. 1946. The kinetics of package life III. The isotherm. *Journal of Chemical Industry* 65: 419–421.
- Peleg, M. 1993. Assessment of a semi-empirical four parameter general model for sigmoid moisture sorption isotherms. *Journal of Food Process Engineering* 16: 21–37.
- Polachini, T.C.; Bietol, L.F.L.; Lopes-Filho, J.F.; Telis-Romero, J. 2016. Water adsorption isotherms and thermodynamic properties of cassava bagasse. *Thermochimica Acta* 632: 79–85.
- Resende, O.; Corrêa, P. C.; Goneli, L.A.D.; Ribeiro, D.M. 2006. Isothermas e Calor Isostérico de Sorção do Feijão. *Ciência Tecnologia Alimentaria* 26(3): 626–631.
- Rosa, D.P.; Luna-solano, G.; Polachini, T.C.; Telis-Romero, J. 2015. Modelagem matemática da cinética de secagem de semente de laranja. *Ciência Agrotecnologia Lavras* 39(3): 291–300.
- Rosa, D.P.; Villa-vélez, H.A.; Telis-Romero, J. 2013. Study of the enthalpy-entropy mechanism from water sorption of orange seeds (*C. sinensis* cv. Brazilian) for the use of agro-industrial residues as a possible source of vegetable oil production. *Ciência E Tecnologia de Alimentos* 33: 95–101.
- Samapundo, S.; Devlieghere, F.; Meulenaer, B. De; Atukwase, A.; Lamboni, Y.; Debevere, J. M. 2007. Sorption isotherms and isosteric heats of sorption of whole yellow dent corn. *Journal of Food Engineering* 79: 168–175.
- Silva, S.A.; de Almeida, C.F.; Alves, N.M.C.; Melo, D.S.C.; Gomes, J.P. 2010. Hygroscopic and thermos-

- dynamic features of dehydrated coriander. *Ciência Agronômica* 41(2): 237–244.
- Smith, S.E. 1947. The sorption of water vapour by high polymers. *Journal of the American Chemical Society* 69: 646.
- Sukhorukov, A.P.; Zhang, M. 2013. Fruit and seed anatomy of *Chenopodium* and related genera (Chenopodioideae, Chenopodiaceae/ Amaranthaceae): Implications for evolution and taxonomy. *Plos One* 8(4): 1–18.
- Thys, R.C.S.; Noreña, C.P.Z.; Marczak, L.D.F.; Aires, A.G.; Cladera-Olivera, F. 2010. Adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) starch and thermodynamic analysis. *Journal of Food Engineering* 100(3): 468–473.
- Tolaba, M.P.; Peltzer, M.; Enriquez, N.; Lucia-Pollio, M. 2004. Grain sorption equilibria of quinoa grains. *Journal of Food Engineering* 61(3): 365–371.
- Tsami, E. 1991. Heat of sorption of water in dried fruits. *International Journal of Food Science and Technology* 25(3): 350–359.
- Van den Berg, C.; Bruin, S. 1981. Water activity and its estimation in food systems: theoretical aspects. In *Water Activity: Influences on Food Quality* (pp. 1–61). New York: Academic Press.
- Vilche, C.; Gely, M.; Santalla, E. 2003. Physical properties of quinoa seeds. *Biosystems Engineering* 86(1): 59–65.
- Villa-Vélez, H.A.; de Souza, S.J.F.; Pumacahua-Ramos, A.; Polachini, T.; Telis-Romero, J. 2015. Thermodynamic properties of water adsorption from orange peels. *Journal of Bioenergy and Food Science* 2(2): 72–81.
- Villa-Vélez, H.; Váquiro, H.; Bon, J.; Telis-Romero, J. 2012. Modelling Thermodynamic Properties of Banana Waste by Analytical Derivation of Desorption Isotherms. *International Journal of Food Engineering* 8(1): 1–19.