Biotecnología y Ciencias Agropecuarias / Biotechnology and Agricultural Sciences

Rev. Colomb.investig.agroindustriales. 2016 p-23- 33

ISSN 2422-0582 e-ISSN 2422-4456

Hydration kinetics of four quinoa (***Chenopodium quinoa*** Willd.) varieties

Cinética de hidratación de cuatro variedades de quinua (***Chenopodium quinoa*** Willd.)

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DOI: http://dx.doi.org/10.23850/24220582.348

Recibido: 13.08.2016 Aceptado: 23.10.2016

Abstract

The effect of time, temperature and varieties were analyzed during kinetics hydration of quinoa grains and some physical properties were determined. Quinoa grain varieties Kancolla, Salcedo Inia, Blanca de Juli and Pasankalla were used in the study. The hydration was performed in triplicate with 25 g of grain immersed into a solution with 0.55% lactic acid and 0.2% SO_2, three temperatures (30, 40 and 50°C) at seven time intervals from 0 to 6 hours were considered to determine moisture of the grains. Moisture data were adjusted to empiric model of Peleg and to the diffusion model based on the Fick's second law. Effective diffusivity as well as activation energy of the water absorption was also determined. The data were submitted to analyses of variance (ANOVA) and Tukey's means difference test at 5% probability. Models adjustments were evaluated through determination coefficient (R2) and mean quadratic error (RMSE). Physical properties of Pasankalla variety shown different values compared with white varieties. Peleg's model constants K1 ranged from 28 to 65.8 (s/%) and K2 from 0.004 to 0.008 (1/%). The effective diffusivity ranged from 2.594 x 10-11 to 8.180 x 10-11 m2.s^{-1} and activation energy from 210.5 to 1648.5 kJ.k^{-1}.

Keywords: Quinoa grain; Moisture; Peleg; Fick's second law; Activation energy.

Resumen

Fueron determinados el efecto del tiempo, temperatura y variedades, en la cinética de hidratación, además de algunas propiedades físicas en los granos de quinua. Para el estudio se utilizaron granos de quinua de las variedades Kancolla, Salcedo Inia, Blanca de Juli y Pasankalla. La hidratación se realizó por triplicado, de 25g de quinua, inmersos en solución de 0,55% de ácido láctico y 0,2% de SO_2; tres temperaturas (30, 40 y 50°C) y siete intervalos de tiempo, 0 a 6 h. Los datos de contenido de agua fueron ajustados al modelo empírico de Peleg y al modelo difusivo basado en la segunda ley de Fick. Se determinaron la difusividad efectiva, así como la energía de activación. Los datos fueron evaluados mediante el análisis de varianza (ANOVA) y los promedios por la prueba de Tukey con un 5% de probabilidad. Los resultados del ajuste a los modelos fueron evaluados a través del coeficiente de determinación (R2) y el error medio cuadrático (RMSE). Las propiedades físicas de la variedad Pasankalla mostraron ser diferentes a las demás variedades. Las constantes, K1 del modelo de Peleg se encuentran entre 28 a 65,8 (s/%) y K2 de 0,004 a 0,008 (1/%). La difusividad efectiva fue entre 2,594 x 10^{-11} a 8.180 x 10-11 m2.s^{-1} y la energía de activación entre 210,5 a 1648,5 kJ.k^{-1}.

Palabras clave: Granos de quinua; humedad; Peleg; segunda ley de Fick; energía de activación.

INTRODUCTION

Quinoa (*Chenopodium quinoa* Willd.), is an Andean grain rich in carbohydrates (61.0%), protein (14.6%), fats (5.6%), fiber (3.4%) and minerals (3.4%) (Repo-Carrasco, Espinoza, & Jacobsen, 2003). These compounds are essentials for human nutrition and quinoa is considerate one of the most complete food in the world. There are many varieties of quinoa grouped into white and colored varieties. The white varieties are the main marketed worldwide as whole grain, flours and flakes. Pasankalla (PA), a colorful variety, is marketed from an expanded product.

In order to aggregate value at quinoa and to disposal each components separately it is necessary to mill the grains and recovery their fractions. Wet milling is a process to separate the main components of grains with high amount of starch, protein, lipids and fiber (Lopes Filho *et al*., 2006). During hydration step, the grains can reach between 50 to 60% moisture, which is fundamental to facilitate mechanical operations to separate the components with high yields. Therefore, the knowledge of water absorption kinetics as function of time, temperature and grain variety are essential to optimize the wet milling process. The methodology to study hydration kinetics has been investigated for other grains as yellow corn. Studies were done immersing corn and amaranth grains into a solution of 0.2% SO_2 and 0.55% lactic acid for different times and temperatures to determine the influence of these variables on the water absorption rate and increases in yield of starch (Lopes Filho *et al*., 2006; Manzoni, Kronka, & Lopes Filho, 2002).

Sulfur dioxide (SO_2) and slightly elevated steeping temperatures are used to control the growth of putrefactive microorganisms and aid the degradation of kernel structure to enhance milling. Besides, SO_2 cleaves disulfite bonds of proteins that encapsulate starch granules in the endosperm of the grain which enhance starch release (Manzoni *et al*., 2002). During corn hydration for wet milling, warm temperatures help the dispersion of protein and accelerated hydration rate, which reduced steeping time.

Lactic acid is usually formed by bacterial fermentation in commercial steeps and is often added to steep water used in laboratory batch steeping (Shandera, Parkhurst, & Jackson, 1995). The role of lactic acid is not completely understood. Cox *et al*. (1944) reported that lactic acid softened the kernel and increased the effectiveness of SO_2. However (Shandera *et al*., 1995) studied interactions between lactic acid, SO_2 and temperature in steep solutions and reported that excessive use of lactic acid (lowering the pH of steep solution below ≈ 2.5) decreases the overall mill ability of the steeped corn kernel.

Hydration is a mass transfer phenomenon that utilizes mathematical models to preview and simulate changes in the food as it is immersed into water solution. These models should represent the water kinetic diffusion into the material. There are several mathematical models empirical as well as theoretical. The two most considered and utilized are the diffusive model (Crank, 1975) and Peleg equation (Peleg, 1988). The first is known as the Fick's second law applied for transient regime in different geometry: plate, cylinder and sphere and consider the variables of time, temperature, characteristic dimension and effective diffusivity. Peleg equation is empirical and relates the variables of moisture and time with two constants. Kinetics of hydration using these models were studied for grains, corn, amaranth, bean, Cicer arietinum, wheat and sesame (Khazaei & Mohammadi, 2009; Lopes Filho et al., 2006; Maskan, 2002; Piergiovanni, 2011; Prasad, Vairagar, & Bera, 2010; Resio, Aguerre, & Suarez, 2006; Solomon, 2009).

To perform analyses of hydration kinetics some physical properties are necessary: geometric mean diameter, average mass, real and bulk densities, sphericity, and porosity. Physical properties have been determined to study kinetics hydration of Sesamum indicum L. (Khazaei & Mohammadi, 2009) and quinoa (Alvarado, 2012; Vilche *et al*., 2003).

The present study had the following objectives: assess and evaluate the curves of the water absorption of the grains of quinoa of four varieties under the influence of time (0 to 6 hours) and temperature (30, 40 and 50 ° C). Evaluate both mathematical models of their adequacy to describe the water absorption and determining the activation energy.

MATERIALS AND METHOD

Sample preparation. Four varieties of quinoa (KA, SI, BJ and PA) harvested in 2009/10 were obtained from Instituto Nacional de Investigación Agraria (INIA – Puno – Perú). The research was performed at Food Science and Technology laboratory (Cytal) of Universidad Peruana Unión and at the Wet Milling laboratory of Universidade Estadual Paulista, Brazil. Small grains and foreign materials were separated by sieve the 0.8 mm opening. Broken grains and those of different color were removed manually with the aid of woods pointed. After selecting and cleaning, 5 kg of each variety were placed into plastic bags and stored in dried environment.

Physical properties. Physical properties were determined in the four varieties of quinoa. For true density of the grains determination, liquid displacement method was used. Two grams of quinoa were placed inside an essay tube of 10 ml containing 5 ml of toluene. True density was calculated by the ratio between grain mass and volume displaced. For bulk density the mass of grains with 604 cm^3 was measured in analytical balance. Twelve replications were done for each determination. Diameters were measured by grains images submitted to the computational program of Windows™ 2010.

Grains were fixed by transparent adhesive tape with larger and minor face set upward. The image was digitalized and amplified by ten times of the original size. Using diameters values, the Geometric mean diameter, D_g, was calculated by Equation. (1), sphericity by Equation. (2) and porosity determined using true and bulk density in Equation. (3). The mass of one grain was determined by the ratio between 0.5 g of grains weighed in an analytical balance (precision of 0.00001 g) and the number of the grains. The 1000 mass was estimated by extrapolation of the results. (Equations 1, 2, and 3). The external and internal structures of the grain were observed through a Scanning Microscopy Electronic prior coated with gold.

$$D_g = (a\,b\,c)^{1/3} \qquad \text{Equation 1}$$

$$\emptyset = \frac{(abc)^{1/3}}{a} \qquad \text{Equation 2}$$

$$\varepsilon = \left(1\text{-}\frac{\rho_a}{\rho_r}\right) x100 \qquad \text{Equation 3}$$

Soaking of grains. Soaking was performed under agitation in a water bath with controlled temperature. Samples of 25 g of quinoa were placed into glass vessels with lid containing 75 mL of 0.2% SO_2 and 0.55% lactic acid solution according to Lopes Filho *et al*. (2006). Soaking time was 6 h at temperatures of 30, 40, and 50 ^{0}C under agitation of 60 rpm. Each hour one recipient was removed, cooled in tap water and the solution drained to determine the moisture of the grains. Before determination, the grains were placed over a towel paper to remove superficial water. Samples of 10 g were placed inside an oven at 105^{0}C for 24 h (AACC, 2000). As the grains increase volume because water absorption, for each steeping time (0 to 6 h) it was calculated their mean diameter and an arithmetic mean of seven values were considered for the diffusive model.

Kinetics of water absorption

Peleg model. Empirical Model – Moisture data were adjusted to a Peleg model of Equation 4. (Peleg, 1988).

$$M_t = M_0 + \frac{t}{K_1 + K_2 * t} \qquad \text{Equation 4}$$

Where M_t is moisture content at time t (%), M_o is initial moisture content (%), K_1 is the Peleg rate constant (s/%), and K_2 is the Peleg capacity constant (1/%).

For an infinite time the grain will absorb the maximum water reaching the equilibrium moisture (Equation 5):

$$M_\infty = M_0 + \frac{1}{K_2} \qquad \text{Equation 5}$$

The constants K_1 and K_2 are function of temperature thus, substituting the constants by respective equations it obtains a simple equation that permits calculates moisture as function of temperature and time.

Diffusion model. The diffusion of water as a function of time and the radius of the grain may be represented by Fick's second law in transient state for spherical coordinates (Crank, 1975). (Equation 6)

$$\frac{\partial M}{\partial t} = D_{ef}\left(\frac{\partial^2 M}{\partial r^2} + \frac{2}{r}\frac{\partial M}{\partial r}\right) \qquad \text{Equation 6}$$

Where, D_{ef} is the effective diffusivity, M is the moisture at any time, r is the radial coordinate and t is the time.

The solution to this partial differential equation is (Prasad *et al.,* 2010) (Equation 7)

$$\frac{M_t - M_\infty}{M_0 - M_\infty} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\,\mathrm{Exp}\left(-\frac{n^2\pi^2 D_{ef} t}{r^2}\right) \qquad \text{Equation 7}$$

The following hypotheses were considered to apply the diffusion model:

At zero time, the surface of the grain was at equilibrium with the environment. Grains composition is homogeneous related to the diffusivity. Quinoa grains reach equilibrium at the end of soaking. Water properties remain constant during soaking process. The diffusion process only considers water transport into the grains. Temperature is constant along the process. Water diffusion is in radial orientation. Negligible change in volume during soaking. Quinoa grains had same characteristics for all treatments.

The Equation 7, is a solution in series from 1 → ∞. One way to know if it can be truncated at some term is through the number of Fourier Mass Flow (Equation 8).

$$F_{OM} = D_{ef}t/r^2 \qquad F_{OM} \geq 0.2 \qquad \text{Equation 8}$$

The parameters of Peleg models and Fick's second law were estimated by non-linear least squares fitting using software Excel© the Windows 2010© and Solver tool (GRG nonlinear).

Activation energy. If there is effect of temperature on some parameter as the effective diffusivity, this can be expressed using the Arrhenius relationship (Equation 9).

$$D_{ef} = D_0 \mathrm{Exp}(-\frac{E_a}{RT}) \qquad \text{Equation 9}$$

Where D_o is the pre-exponential factor, E_a is the activation energy, R is the water gas constant and T the absolute temperature. Activation energy is the energy needed to water molecules diffuses into porous solid.

Applying log at both sides of the equation it becomes a linear. Plotting ln D_{ef} *versus* an inverse of absolute temperature (1/K), the slope of the straight line is E_a/R, where *R*= 0.462 kJ.kg.K^{-1} thus activation energy value can be obtained.

Selection of model. The variables considered in the water absorption process were soaking temperatures (30, 40 and 50 ^{0}C), seven times (from 0 to 6 h), and four varieties. Moisture data were submitted to analyses of variance (ANOVA) and mean differences by Tukey test at 5% probability using the software STATISTICA 8.0 (North Melbourne – Victoria, Australia 3051). The goodness of fit between the experimental and predicted amounts of water absorbed was determined using the models adjustments were evaluated by coefficient of determination (R^2), root mean square error (RMSE) and by the mean absolute percentage error (MA%E) (Equations 10 and 11).

$$\mathrm{RMSE} = \left[\left(\sum_{i=1}^{7}(X_{exp} - X_{cal})^2\right)/N\right]^{1/2} \qquad \text{Equation 10}$$

$$\mathrm{MA\%E} = \frac{100}{N}\sum_{n=1}^{\infty}\frac{|X_{exp} - X_C|}{X_{exp}} \qquad \text{Equation11}$$

RESULTS AND DISCUSSION

Physical properties. Table 1 presents the results of physical properties determination of the four quinoa grains.

Initial moisture contents ranged from 10.20 to 10.99 (%) d. b. accounting for a difference of 0.79 points percent. This initial difference of moisture content as well as temperature affected equilibrium moisture at the end of soaking.

The D_g of the four varieties (1.73 to 1.88 mm with approximately 10% moisture) was relatively larger than other varieties published. PA variety had 1.88 mm, greater between 5 and 8.6%, compared to the other varieties. Alvarado, (2012) reported D_g for three varieties of Ecuadorian quinoa with moisture between 20.8 and 31.0% from 1.44 to 1.62 mm. Vilche *et al.,* (2003) presented values of D_g for Argentina quinoa with 15% moisture between 1.40 to 1.56 mm. The D_g of quinoa grains are much larger than grains of *Amaranthus cruentus* (10.5% moisture) reported as 0.9 mm (Resio *et al*., 2003). The unitary mass was 3.03, 2.97, 2.92 and 3.55 mg for KA, SI, BJ and PA varieties, respectively.

The unitary mass of PA was 16.9 to 21.3% higher than the others. Unit mass of Argentina quinoa grains ranged from 2.49 to 3.12 mg (Vilche *et al*., 2003), and for Sesame grains was 2.94 mg (Khazaei & Mohammadi, 2009). True density of the four varieties ranged between 1169.4 and 1277.6 k.m^{-3} with PA value being 4.2 to 9.3% higher than the others. Contrarily, the apparent density of quinoa SI (687.2 k.m^{-3}) was greater about 0.8 to 3.9% among the others. Porosity of quinoa PA was 46.64%, higher 2.6 to 8.5% than the others. Also, sphericity of quinoa PA (81.44%) was greater about 3.8 to 8.9% than the others. Reported true densities of three varieties of Ecuadorian quinoa varied from 1211 to 1250 k.m^{-3}, bulk density from 719 and 732 k.m^{-3} and porosity from 40.6 and 41.4% (Alvarado, 2012). These physical properties are of the great importance to develop operations of cleaning, storing, transportation and hydration of the grains.

Scanning Electron Micrograph presented in Figure 1, shows that quinoa grains have roughened surface with cavities like "flower petals", which would allow the grain to absorb more water. This surface is characteristic

Table 1. Mean values of physical properties of the four quinoa varieties grains.

Physical properties	Quinoa varieties			
	Kancolla	**Salcedo Inia**	**Blanca de Juli**	**Pasankalla**
Initial moisture content (%) d. b.	10.56 ±0.07	10.20 ±0.03	10.99 ±0.02	10.43 ±0.04
Equilibrium moisture content (%) d. b.	128.6 ^{A}	131.7 ^{A}	150.5 ^{A}	137.5 ^{A}
	138.1 ^{B}	144.1 ^{B}	206.8 ^{B}	143.0 ^{B}
	163.9 ^{C}	176.5 ^{C}	264.5 ^{C}	152.2 ^{C}
Average radio, mm	0.92 ^{A}	0.98 ^{A}	0.95 ^{A}	1.00 ^{A}
	0.94 ^{B}	1.00 ^{B}	0.98 ^{B}	1.11 ^{B}
	1.07 ^{C}	1.14 ^{C}	1.01 ^{C}	1.41 ^{C}
Length, mm	2.18 ±0.21	2.24 ±0.18	2.28 ±0.06	2.31 ±0.13
Width, mm	1.99 ±0.14	1.89 ±0.22	2.11 ±0.13	2.25 ±0.16
Thickness, mm	1.21 ±0.07	1.24 ±0.09	1.19 ±0.03	1.28 ±0.13
Geometric mean diameter, mm	1.73 ±0.08	1.73 ±0.09	1.79 ±0.04	1.88 ±0.14
Unit mass, mg	3.03 ±0.26	2.97 ±0.04	2.92 ±0.05	3.55 ±0.15
True density, kg/m^3	1169.4 ±30.4	1226.4 ±34.5	1213.1 ±30.1	1277.6 ±18.7
Bulk density, kg/m^3	666.7 ±2.1	687.2 ±3.8	661.7 ±2.9	681.6 ±2.6
Porosity, %	42.98	43.96	45.45	46.64
Spherecity, %	80.03 ±6.3	77.61 ±3.9	78.41 ±2.4	81.44 ±2.0

The superscripts A, B and C corresponds to 30, 40 and 50 °C respectively.

of seeds of *Chenopodiacea* family as reported by Sukhorukov & Zhang (2013). The germ forms a ring around the endosperm which is abundant in starch granules. In the soaking or steeping process, water will diffuse toward the center of the grain to reach humidity between 50-60%. Under these conditions the components can be mechanically separated and recovered at high purity level.

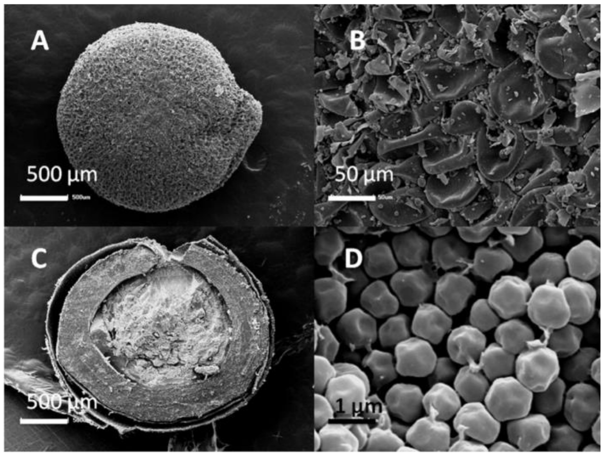

Figure 1. Scanning electron microscope photomicrographs of quinoa grain: (A) whole grain 30x, (B) the roughened surface 270x, (C) half grain 30x, and (D) starch granules from endosperm 10 kx.

Soaking of grains. Results of grains humidity as a function of time and temperature for the quinoa varieties are shown in Table 2. It is observed an influence of soaking time on the average moisture of the grains for BJ and KA varieties. At 50°C, there were no significant differences between the fifth and sixth hours for *SI* variety and between sixth and seventh hours at 30 to 40°C and in third and fourth hours at 50°C for PA variety.

It can be observed the moisture contents are different for BJ and KA at six hours of hydration. Moisture of SI shown no statistical difference at 50°C between 5 and 6 h, while PA shown no difference at 30 and 40^{o}C between 6 and 7 h and at 50°C between 3 and 4 h. The greatest density of PA variety is a barrier of water diffusion, which demanded higher times to reach larger moisture content. As the density of the PA is 9.4% more than the other varieties, its cellular structure is more compact. Studies of rehydration of various dry foods showed that very compact structures rehydrate at a slower rate than less compact structures (Marabi & Saguy, 2004).

The influence of temperature on water absorption shown significant difference for KA, SI and BJ varieties. For PA variety there was no significant difference at temperatures of 40 and 50°C in the second and fifth hours. As stated before, water absorption is more difficult in the PA due to its higher density.

Table 2. Moisture content (%) d. b. as a function of time and temperature for the four quinoa varieties.

Time, hours	Kancolla			Salcedo Inia		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
0	$10,56^{Ga\beta}$	$10,56^{Ga\beta}$	$10,56^{Ga\beta}$	$10,20^{Ga\gamma}$	$10,20^{Fa\gamma}$	$10,20^{Fa\gamma}$
1	$56,90^{Fc\beta}$	$67,08^{Fb\beta}$	$70,43^{Fa\gamma}$	$68,68^{Fc\alpha}$	$79,61^{Eb\alpha}$	$92,26^{Ea\alpha}$
2	$68,14^{Ec\beta}$	$81,20^{Eb\beta}$	$86,40^{Ea\beta}$	$85,86^{Ec\alpha}$	$95,25^{Db\alpha}$	$104,78^{Da\alpha}$
3	$82,61^{Dc\gamma}$	$92,33^{Db\beta}$	$99,30^{Da\gamma}$	$95,64^{Dc\beta}$	$106,83^{Cb\alpha}$	$118,06^{Ca\beta}$
4	$89,85^{Cc\delta}$	$96,64^{Cb\gamma}$	$107,94^{Ca\gamma}$	$101,48^{Cc\alpha}$	$111,57^{Bb\beta}$	$129,51^{Ba\beta}$
5	$95,92^{Bc\gamma}$	$105,03^{Bb\gamma}$	$119,42^{Ba\gamma}$	$108,37^{Bc\alpha}$	$115,94^{Bb\beta}$	$139,67^{Aa\beta}$
6	$101,78^{Ac\delta}$	$111,13^{Ab\delta}$	$135,76^{Aa\gamma}$	$114,08^{Ac\alpha}$	$117,98^{Ab\beta}$	$151,49^{Aa\beta}$
	Blanca de Juli			Pasankalla		
	30 °C	40 °C	50 °C	30 °C	40 °C	50 °C
0	$10,99^{Ga\alpha}$	$10,99^{Ga\alpha}$	$10,99^{Ga\alpha}$	$10,43^{Fa\beta}$	$10,43^{Fa\beta}$	$10,43^{Fa\beta}$
1	$51,38^{Fc\gamma}$	$66,65^{Fb\beta}$	$77,93^{Fa\beta}$	$58,97^{Ec\beta}$	$65,38^{Ea\beta}$	$65,58^{Ea\delta}$
2	$65,12^{Ec\gamma}$	$84,66^{Eb\beta}$	$105,68^{Ea\alpha}$	$64,51^{Dc\gamma}$	$73,96^{Db\gamma}$	$77,80^{Da\gamma}$
3	$86,15^{Dc\beta}$	$105,00^{Db\alpha}$	$133,03^{Da\alpha}$	$75,06^{Cb\alpha}$	$88,03^{Ca\gamma}$	$90,07^{Ca\delta}$
4	$98,18^{Cc\beta}$	$120,83^{Cb\alpha}$	$150,46^{Ca\alpha}$	$94,90^{Bc\gamma}$	$97,00^{Bb\gamma}$	$102,22^{Ca\delta}$
5	$106,07^{Bc\alpha}$	$127,42^{Bb\alpha}$	$169,86^{Ba\alpha}$	$101,27^{Ac\beta}$	$106,97^{Ab\gamma}$	$112,89^{Ba\delta}$
6	$110,42^{Ac\beta}$	$141,54^{Ab\alpha}$	$175,77^{Aa\alpha}$	$106,23^{Ac\gamma}$	$114,91^{Ab\gamma}$	$125,40^{Aa\delta}$

A In the superscripts of each column (Capital letters), the differences between means followed by a same letter were not significant.
a In the superscripts of each row (Lowercase letters), the differences between means followed by a same letter were not significant.
α In the superscripts (Greek letters), the differences between means followed by a same letter were not significant in the varieties of quinoa. (Tukey's test P=0.05).

To verify the influence of varieties in water absorption and the last three hours of soaking were compared. In the first three hours at 30°C SI variety absorbed more water than the others. For temperatures of 40 and 50 °C, the water absorption was higher for SI, followed by BJ, KA and PA varieties, respectively. SI variety had higher water absorption during the last three hours of soaking at 30°C followed by BJ, PA and KA varieties, respectively. At 40 and 50°C BJ absorbed more water than SI, PA and KA varieties. In general, SI and BJ absorbed more water than KA and PA varieties. It suggests that in the last three hours the grains showed more potential to absorb water. The true density of 1277 k.m^{-3} of quinoa PA may explain the difficulty of water absorption compared to the other varieties because it is more compact with higher mass in the same volume, as compared with the others. This provides a greater mass diffusion resistance.

Kinetics of water absorption. The kinetics of water up taking in quinoa grains at the three temperatures is shown in Figures 2 and 3. In addition, can be observed that moisture content increase exponentially as a function of time with tendency to stabilize during the last hours. High absorption occurs at the beginning of soaking with average moisture content above 30% in the first hour for all varieties. High absorptions at the beginning of hydration are typical for vegetal products (Khazaei & Mohammadi, 2009), which can mainly be attributed to the two situations. The first is that the water initially fills the empty spaces of the surface of the grain and the interior of the pericarp and endosperm. Following, the water diffuses into the germ and endosperm slower. The second is due to the higher moisture gradient between the grain and its surrounding areas at the beginning of the process. Studies of hydration in amaranth grain showed that after 80 minutes, moisture reached close to 50% (Resio *et al.*, 2003) and for the present study, quinoa grains took more than two hours to reach similar results.

Peleg model. Figure 2 shows the adjustments of the data by Peleg's model. Table 3, shows the constants of the model with their respective R^2 and RMSE. It is observed tha the values of constant rate, K$_1$ and constant capacity K$_2$ decreased as temperature increased for all varieties. This trend was also observed in hydration of bean, lupine, wheat, chickpeas, soybeans, sesame and other (Khazaei & Mohammadi, 2009; Maskan, 2002; Piergiovanni, 2011; Prasad *et al.*, 2010; Resende & Corrêa, 2007; Solomon, 2009).

The inverse constant rate of BJ variety was 2.78x10^{-2} %/s at 50°C, more than twice of PA variety at 30°C (1.11 x10^{-2} %/s). Constant K$_2$ is an indicator of how much water the grain absorbs during soaking time. The results show that BJ variety absorbed more water (63.72%) at 50°C and KA less water (46.30%) at 30°C. The R^2 values are close to unity and RMSE values are lower than 0.0224, confirming that Peleg's model represents satisfactorily moisture up taking as a function of time in the temperature range considered.

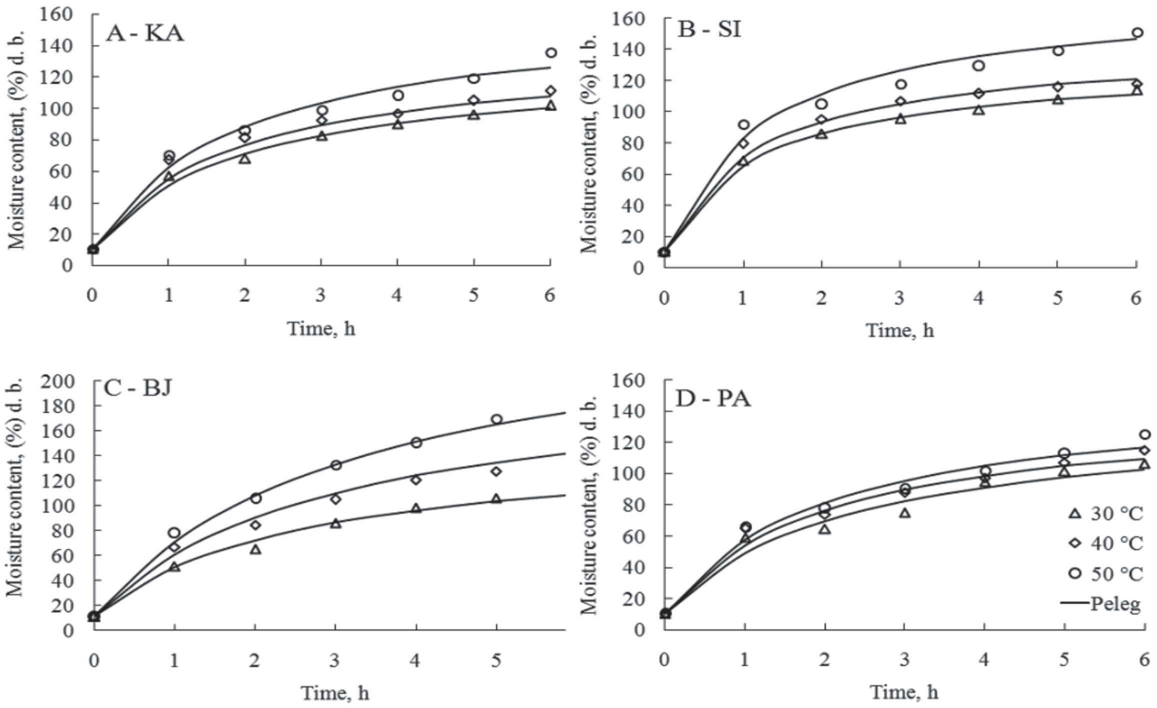

Figure 2. Fitting data to Peleg equation of quinoa KA (A), quinoa SI (B), quinoa BJ (C) and quinoa PA (D).

Table 3. Values of constant K1, K2 of Peleg's equation, constant rate, 1/K1, constant capacity 1/K2, and statistics parameters of data fitting.

Variety	Soaking temperature	K_1	K_2	K_1^{-1}	K_2^{-1}	R^2	RMSE	MA%E
	°C	s/%	1/%	%/s (10^{-2})	%	-	% (d. b.)	%
Kancolla	30	58,4	0,008	1,71	118,08	0,993	0,0253	2,37
	40	53,0	0,008	1,89	127,54	0,984	0,0533	4,75
	50	46,0	0,007	2,18	153,36	0,980	0,0545	4,39
Salcedo Inia	30	36,0	0,008	2,78	121,52	0,997	0,0193	1,60
	40	33,0	0,007	3,03	133,89	0,990	0,0395	2,96
	50	28,0	0,006	3,57	166,25	0,982	0,0619	4,75
Blanca de Juli	30	65,8	0,007	1,52	139,54	0,992	0,0308	2,76
	40	53,8	0,005	1,86	195,77	0,993	0,0472	4,21
	50	45,9	0,004	2,18	253,49	0,997	0,0336	2,07
Pasankalla	30	65,0	0,008	1,54	127,08	0,968	0,0564	6,56
	40	55,0	0,008	1,82	132,61	0,981	0,0488	4,30
	50	51,0	0,007	1,96	141,74	0,979	0,0519	4,73

As the constants K_1 and K_2 showed a linear correlation with temperature, they can be included in Equation 4, obtaining the Equations 12, 13, 14 and 15.

$$M_t = M_0 + \frac{t}{(99.6\text{-}T)+(0.026\text{-}1\times10^{-4}T)t} \quad \text{Equation12}$$

$$M_t = M_0 + \frac{t}{(50.7-0.25T)+(0.025-1\times10^{-4}T)t} \quad \text{Equation13}$$

$$M_t = M_0 + \frac{t}{(128.8-1.475T)+(0.025-4\times10^{-4}T)t} \quad \text{Equation14}$$

$$M_t = M_0 + \frac{t}{(128.8-1.475T)+(0.025-4\times10^{-4}T)t} \quad \text{Equation15}$$

Equations 12, 13, 14 and 15, are for the quinoa grains varieties KA, SI, BJ and PA, respectively.

Diffusion model. The adjustments for the diffusion model (Figure. 3) allowed determine D_{ef} of the water in grains quinoa in the four varieties (Table 4). For proper adjustment, 25 terms of the series were peformed, if only one term is considered, the absolute error of the initial moisture is higher. PA and KA varieties have a Mass Fourier Number (F_{OM}) higher than 0.2 after five hour of soaking whereas for SI it took four hours and for BJ, six hours. Therefore, the series can be truncated at the first term after 5 hours of soaking.

The water D_{ef} in foods is a very important property in mass transfer studies. It was found the diffusion coefficient increases with temperature (30 at 50°C) varying from 3.913 to 5.327 x 10^{-12} $m^2.s^{-1}$, 6.420 to 7.500 x 10^{-12} $m^2.s^{-1}$, 2.594 to 2.846 x 10^{-12} $m^2.s^{-1}$ and 3.941 to 8.180 x 10^{-12} $m^2.s^{-1}$ for varieties KA, SI, BJ and PA, respectively. This model is more laborious in predicting moisture, unlike the Peleg equation.

It permits the introduction of the average grains radius. For all varieties, R^2 are greater than 0,964 indicating a good fit, the RMSE between 0.01121 and 0.03204 and MA%E are considered acceptable for this type of experiments. Resio et al. (2003) determined the effective diffusivities between 3.84 x10^{-12} and 8.25 x 10^{-12} $m^2.s^{-1}$, for hydration of amaranth, lower than the values for quinoa. Lopes Filho *et al*. (2006), used diffusion model to determine the D_{ef} during yellow corn hydration, The values are in the order of 10^{-12} $m^2.s^{-1}$. Effective coefficients of water in grains "chickpeas" during two hours soaking at 40, 50 and 60°C were 1.92 x 10^{-9}, 2.86 x 10^{-9} and 3.24 x 10^{-9} $m^2.s^{-1}$, respectively (Prasad *et al*., 2010)Weibull e modelos exponenciais foram ajustados aos dados da amostra encharcadas.

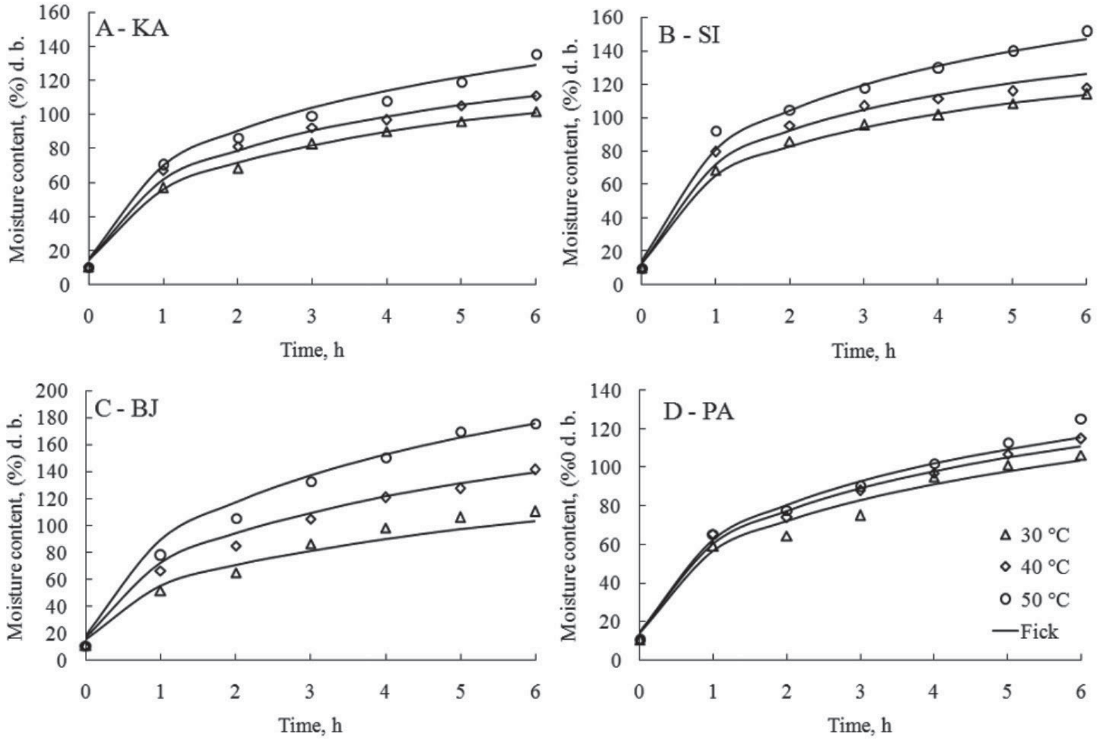

Figure 3. Fitting data to Flick's second law model of quinoa KA (A), quinoa SI (B), quinoa BJ (C) and quinoa PA (D).

Table 4. Values of constant effective diffusivity of Fick equation and statistics parameters of data fitting.

Variety	**Temperature**	**D_{ef} x10^{-11}**	**R^2**	**RMSE**	**MA%E**
	°C	**$m^2.s^{-1}$**	**-**	**% (d. b.)**	**%**
Kancolla	30	3.913	0.998	1.933	6.11
	40	4.452	0.992	2.962	7.72
	50	5.327	0.989	4.608	9.38
Salcedo Inia	30	6.420	0.996	2.209	5.93
	40	7.000	0.982	4.953	8.36
	50	7.500	0.988	5.003	9.22
Blanca de Juli	30	2.594	0.989	6.420	11.96
	40	2.729	0.995	5.217	11.30
	50	2.846	0.994	7.172	14.00
Pasankalla	30	3.941	0.978	5.004	10.60
	40	5.357	0.992	3.321	8.52
	50	8.180	0.990	4.630	8.91

Adequa\u00e7\u00e3o dos modelos foi determinada por meio do coeficiente de determina\u00e7\u00e3o (R2, being higher than that for quinoa grains. Khazaei & Mohammadi (2009), determined the effective diffusivity of water in sesame seeds (*Sesamum indicum* L.) at 27, 40, 50, 60°C, and found values of 4.16 x 10^{-11}, 5.14 x 10^{-11}, 6.12 x 10^{-11} and 6.97 x 10^{-11} m^2/s, respectively.

Activation energy. The activation energies calculated by the diffusion coefficients using the Equation 10, are shown in Table 5.

The activation energies of diffusion were 1036.3, 582.4, 659.0, and 1964.9 $kJ.k^{-1}$ for KA, SI, BJ and PA varieties, respectively (Table 4).

Table 5. Parameters of Arrhenius equation, constant diffusivity, Do, activation energies, Ea, and statistics parameters of data fitting for quinoa grains hydration.

Variety	**D_o**	**E_a**	**R^2**	**RMSE**	**MA%E**
	$m^2.s^{-1}$	**$kJ.k^{-1}$**	**-**	**$kJ.k^{-1}$**	**%**
Kancolla	5.62x10^{-10}	696.1	0.9878	1.51	0.044744
Salcedo Inia	7.99x10^{-11}	352.1	0.9978	0.61	0.020676
Blanca de Juli	1.17x10^{-11}	210.5	0.9986	0.38	0.013112
Pasankalla	5.04x10^{-07}	1648.5	0.9893	3.41	0.108285

The activation energies of PA variety are more than two times of values for the other varieties. This confirms that because it is harder than the others, water diffusion has more resistance. Among white varieties, BJ has the lowest E_a and greater absorption of water, more than 60% of the others under the same conditions of time and temperature (Figure 3-C). As BJ quinoa requires less time to hydrate, low energy is necessary for water diffusion. Activation energies of hydration for many grains are reported in literature: 500 to 1333 $kJ.k^{-1}$ for wheat (Maskan, 2002), 1139 $kJ.k^{-1}$ for chickpea (Prasad *et al.,* 2010)Weibull e modelos exponenciais foram ajustados aos dados da amostra encharcadas. Adequa\u00e7\u00e3o dos modelos foi determinada por meio do coeficiente de determina\u00e7\u00e3o (R2, 1878 $kJ.k^{-1}$ for yellow corn (Lopes Filho *et al*., 2006), 409 $kJ.k^{-1}$ for sesame seed (Khazaei & Mohammadi, 2009), and 1783 $kJ.k^{-1}$ for amaranth grains. The results of the present work (Table 4) are within the range of wheat, chickpea and sesame grains. The activation energy of PA quinoa is similar to amaranth and yellow corn grains. All coefficients of determination (R^2) of the linear fit is greater than 0.94 and the RMSE below 10% for all varieties, which gives confidence to the results presented. With E_a and D_0 values, D_{ef} , was calculated as a function of temperature for each variety (Equations 16, 17, 18 and 19).

$$D_{ef} = 7.3x10^{-6}Exp\left[-\frac{1.036,3\ kJ/kg}{0,462\ kJ/kgK}\left(\frac{1}{T}\right)\right] \qquad \text{Equation16}$$

$$D_{ef} = 1.42x10^{-8}Exp\left[-\frac{582,4\ kJ/kg}{0,462\ kJ/kgK}\left(\frac{1}{T}\right)\right] \qquad \text{Equation17}$$

$$D_{ef} = 7.06x10^{-10}Exp\left[-\frac{659,0\ kJ/kg}{0,462\ kJ/kgK}\left(\frac{1}{T}\right)\right] \qquad \text{Equation18}$$

$$D_{ef} = 7.31x10^{-10}Exp\left[-\frac{1.964,9\ kJ/kg}{0,462\ kJ/kgK}\left(\frac{1}{T}\right)\right] \qquad \text{Equation19}$$

Equations 16,17, 18 and 19 are for the quinoa grains varieties KA, SI, BJ and PA, respectively. Knowing the values of D_{ef}, average radius, and the initial and equilibrium moistures, it is possible to calculate the moisture content and time required for hydration of the quinoa grains using Equation 7.

CONCLUSIONS

The absorption curves of quinoa grain soaked in water solution (0.2% SO_2 and 0.55% lactic acid) were estimated and evaluated at temperatures of 30, 40 and 50°C. All varieties showed high uptake in the first three hours and constant absorption over the last three hours. Water absorption was more rapid at higher temperatures and varieties of SI and BJ absorbed faster than the PA and KA varieties. Constants from Peleg's equation and Fick's second law, were temperature dependent for all four varieties. The activation energy as function of D_{ef} was determined, being higher for the colorful variety PA. Both models (Peleg and Diffusion) adjusted very well to the experimental data with coefficients of determination (R^2) higher than 0.96 and RMSE less than 0.032%.

ACKNOWLEDGEMENTS

The authors acknowledge the Universidad Peruana Unión (UPeU), the Consejo Nacional de Ciencia, Tecnología e Innovación (CONCYTEC) and the Instituto de Biociências, Letras e Ciências Exatas (IBILCE) for financial support (N° 324-2010-CONCYTEC-OAJ).

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