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Extraction Kinetics of Saponins from Quinoa Seed (*Chenopodium quinoa* Willd)

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Abstract

Quinoa has higher protein content (11-16% m/m) and better amino acid profile than cereals and represents a valuable resource for healthy nutrition. The aim of this work was to study the saponins extraction kinetics during washing of soaked quinoa. The experimental curves of saponins content as a function of time was measured at water temperatures of 20, 40, 60, and 70^{o}C. A spectrophotometric method was proposed to determine total saponins content, while an unsteady state diffusional model was applied to this extraction problem, assuming strict internal control to the mass transfer rate. As a first analysis, the complete analytical solution for constant diffusion coefficient (D_{eff}) using the initial radius (R_0) provided an accurate predicted curve at each temperature. The diffusion coefficients (around 10^{-10} m^{2}s^{-1}), were correlated with temperature using an Arrhenius-type relationship to obtain an activation energy E_a of 16.9 kJ mol^{-1}. The preliminary values of E_a and preexponential factor (D_0) thus obtained were used as initial values of a second, more robust fitting where the whole dataset of saponins concentrations as a function of time for all temperatures. The Arrhenius equation was directly inserted into the diffusional solution. The following parameters were obtained: E_a= 17.2 kJ mol^{-1} and, D_0= 3.232×10^{7}m^2 s^{-1}, respectively with an overall r^2=0.985. Saponins content agreed well with experimental values. As the equation is capable of predicting saponin extraction times for various operating conditions, it can be used within equipment design schemes.

Keywords: Quinoa; Saponins; Diffusive model; Spectrophotometric method

1 Introduction

The quinoa (*Chenopodium quinoa* Willd) is an ancient crop of the Andean region of South America. It is considered a pseudo-cereal with high levels of protein and a good balance of essential amino acids (Food and Agriculture Organization, 2011; Escuredo, Martin, Moncada, Fischer, & Hierro, 2014; Navruz-Varli & Sanlier, 2016). In addition, the lipid fraction is rich in essential fatty acids, such as linoleic and α-linolenic acids (Navruz-Varli & Sanlier, 2016; Peiretti, Gai, & Tassone, 2013) and, besides, quinoa has a high minerals content particularly calcium, magnesium, potassium, phosphorus and manganese, with high amounts of iron as well (Vega-Galvez et al., 2010). Having no gluten, quinoa is a food of choice for celiacs (Ridout, Price, Dupont, Parker, & Fenwick, 1991). On these grounds, in recent years, quinoa seeds have become important to an extent that FAO declared 2013 as the International Year of Quinoa (Food and Agriculture

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Nomenclature

D_{eff}	Effective diffusive coefficient, $m^2\ s^{-1}$
D_0	Pre-exponential factor, $m^2\ s^{-1}$
E_a	Activation energy, kJ mol^{-1}
n	Number of data points
r	radial position, m
R_g	Universal gas constant, 8.314 x 10^{-3} kJ $mol^{-1}K^{-1}$
R_0	Initial particle radius, m
S	saponins content, kg 100 kg dry $matter^{-1}$
t	Washing process time, s
T_w	Water temperature, in ^oC
T_k	Water absolute temperature, K
Greek symbols	
π	Dimensionless number
Subscripts	
0	Initial
e	Equilibrium
w	Water
m	average
d	Dimensionless
exp	Experimental
pred	Predicted

Organization, 2013).
However, these seeds have saponins, triterpenoid glycosides concentrated in the seed coat, that affect the taste of quinoa and protein digestibility, so they must be removed before consumption (Kozioł, 1992; Francis, Kerem, Makkar, & Becker, 2002). Traditionally, the saponins are removed by a solid-liquid extraction usually carried out domestically washing the seeds under running water with which saponins develop foam; as foam formation vanishes, washing is considered complete (Ridout et al., 1991). However, the saponins content that a human can consume in quinoa is still a topic of discussion in terms of its bitterness and negative biological effects (Chauhan, Eskin, & Tkachuk, 1992; Quispe-Fuentes et al., 2013). Recently, a standard was issued by the Codex alimentarius which establish a value of 0.12% m/m as a maximum limit to be considered convenient for consumption in quinoa with a moisture content of 13.5% w.b. which represents a 0.14% (m/m) in dry basis units (Codex Alimentarius, 2017).
Regarding the methodology for measuring the amount of saponins, Koziol (1991) developed a method based on measuring the foam height formed by adding quinoa seeds to water in a tube, which was agitated for a period of time. However, this method has some drawbacks because the production and stability of foam are dependent on the chemical structure and surfactant capacity of the saponins, presence of salts, pH and agitation method. Other authors, as San Martin and Briones (2000) and Quispe-Fuentes et al. (2013) utilized successfully the reversed-phase high performance liquid chromatography (RP-HPLC) to determine saponins. This is a well-established method in the pharmaceutical industry due to its high accuracy and precision. However, suitable standards of saponins are necessary for correct identification of the components and their quantitative determination (Ruales & Nair, 1993). On the other hand, Nickel, Spanier, Botelho, Gularte, and Helbig (2016) studied the effect of different types of processing (i.e.: washing, cooking and toasting) on the saponins content of quinoa and applied a spectrophotometric method to determine the total saponins content with good results. The basic principle of this method is the reaction of oxidized triterpene saponins with vanillin. Sulfuric acid is used as oxidant and the distinctive colour of the reaction is purple (Hostettmann & Marston, 1995). This method is simple, fast and inexpensive to

operate. However, some factors as the selection of standards and the optimum wavelength should be considered before applying this technique (Cheok, Salman, & Sulaiman, 2014).
Authors such as Ridout et al. (1991), Koziol (1991) and Nickel et al. (2016) investigated the effect of different treatments on the saponins content from quinoa using one of methods referred previously; nevertheless the information was limited only to the initial and final values for this compound. With respect to the saponin extraction kinetics few works were found in literature. Quispe-Fuentes et al. (2013) developed a diffusive model, considering spherical geometry, for the kinetics of saponins extraction in quinoa seeds during washing, obtaining accurate predictions. These authors utilized a chromatographic method for saponins quantification. It is possible that products experience swelling and thus structural modifications during washing (or soaking). From the technological point of view (for instance to develop equations of use in automatic control algorithms) simplified models as the analytical solutions of the unsteady state diffusion equation can be tested to represent the phenomenon (Torrez Irigoyen & Giner, 2014). Although information on the nutritional potential of quinoa has been published (Kozioł, 1992; Vega-Galvez et al., 2010; Navruz-Varli & Sanlier, 2016), only limited information is available on the kinetics of saponins extraction.
Therefore, the objective of this work is to study saponins extraction kinetics applying analytical solutions of the diffusion equation. Saponins were experimentally determined by a spectrophotometric technique. Knowledge of the kinetic behaviour may contribute to improve the understanding of the extraction mechanism and is useful for design purposes, since the diffusional model can be employed for estimating the extraction time to reach a safe saponins content for human consumption.

2 Materials and Methods

2.1 Material

Quinoa grains of the CICA variety, provided by the INTA EEA Famaillá, Provincia de Tucumán Argentina (Famaillá Experimental Station of the National Institute of Agricultural Technology, Province of Tucumán) were utilized. Moisture content at reception was 0.111 kg water kg dry matter^{-1}. The experimental work carried out can be described by the flow sheet shown in Fig. 1.

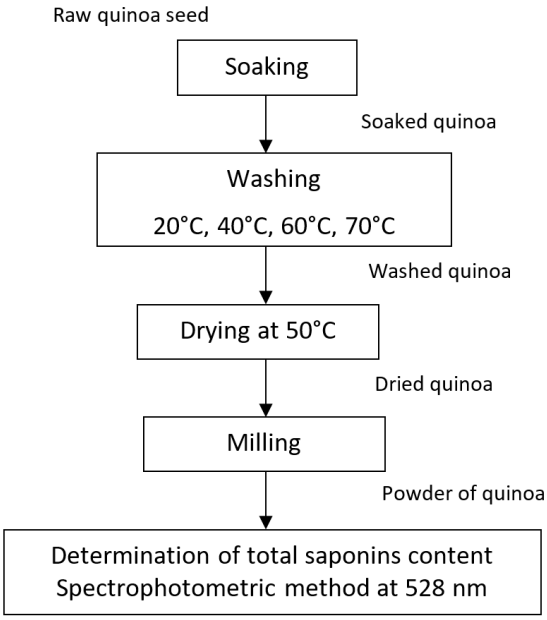

Figure 1: Flowsheet representing the experimental plan followed in this work

2.2 Soaking

Seeds were visually inspected to remove foreign materials and then immersed in distilled water, using a water-to-quinoa mass ratio of 5:1, and allowed to soak for 120 min. Figure 2 shows the characteristics dimensions for soaked quinoa seed measured by a digital caliber.

2.3 Washing

Experimental curves of quinoa moisture and total saponins content as a function of time were measured in a shaking water bath at 20, 40, 60 and 70°C. The grains were loaded in a steel bas-

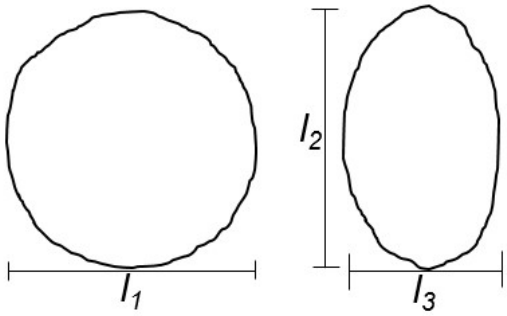

Figure 2: Drawing of front view and plan view of the quinoa seed and their axis measured utilizing a digital caliber. $l1$: 2.301 ± 0.113 mm, $l2$: 2.198 ± 0.077 mm and $l3$: 1.371 ± 0.408 mm

ket (initial mass of seeds: 60 ± 0.4 g) and immersed in the water bath. Samples were removed at various times between 5 and 70 min for moisture content and total saponins determination.

2.4 Drying

In order to obtain powder suitable for saponins content determination a thin layer of soaked and washed quinoa was dried by placing the seeds in a tray inside a mechanical convection oven set at 50^{o}C until reaching a final moisture content of 0.117 ± 0.001 kg water kg dry matter^{-1}. Moderate temperatures were considered for the drying step in order to avoid undesirable reactions such as Maillard (Brožková et al., 2018).

2.5 Determination of moisture content

Moisture content was determined in triplicate by the AOCS Ac 2-41 whole grain method (130^{o}C, atmospheric pressure, 3 h) in a mechanical convection oven (air velocity, 0.25 m s^{-1}) Sanjor Model SL30SDB, Argentina.

2.6 Milling

The dried samples were milled for three minutes in a grinder (Peabody, Pe-mc9100, China) and reduced to a powder sieved with a mesh size of 80 which correspond to a particle size of 0.177 mm.

2.7 Determination of saponins content by spectrophotometric analysis

For extraction of saponins, 2.5 g of sample was added to 25 mL of 50%(v/v) ethanol and left for 30 min at room temperature. Subsequently, the extracts were filtered through qualitative filter paper (grammage 80 g m^{-2}) into 25 ml glass volumetric flask and topped up to volume with 50% Ethanol. The analysis was carried out by adding 1 mL of the diluted extract (1:20 dilution) to 3.5 mL of the Lieberman-Buchard reagent (16.7% of acetic anhydride in concentrated sulfuric acid). The solution was vortexed and left to stand in the dark for 30 min at room temperature, before being placed in a spectrophotometer set at 528 nm. Quantification was performed with a standard of saponins provided by Biopack Chemical products. The calibration curve was performed at 50 – 350 μg mL^{-1} and the results were expressed as kg saponins per 100 kg dry matter (Gianna, Manuel Montes, Luis Calandri, & Alberto Guzman, 2012; Nickel et al., 2016). All measurements were carried out three times.

3 Mathematical modeling of saponins extraction

3.1 Microscopic mass balance with diffusional transport of mass

In general, taking the grain volume as a system and assuming mass transport by molecular diffusion, the microscopic mass balance can be expressed in the following way for constant volume of seed (Crank, 1975)

$$\frac{\partial S_I}{\partial t} = \nabla(D_{eff}\nabla S_I) \tag{1}$$

where D_{eff} is the effective diffusion coefficient of saponins relative to the dry matter. For radial water flux in spherical geometry, consider-

ing diffusion coefficient independent of saponins content, Eq. 1 can be developed to give (Pabis, Jayas, & Cenkowski, 1998).

$$\frac{\partial S_I}{\partial t} = D_{eff}\left(\frac{\partial^2 S_I}{\partial r^2} + \frac{2}{r}\frac{\partial S_I}{\partial r}\right) \quad (2)$$

This equation holds true for each internal point of the solid, and gives the local value of the diffusing component S_l kg saponins 100 kg dry matter^{-1} s^{-1} as a function of time t in seconds and the radial coordinate r in m, whose axis is always normal to the surface and whose origin is placed at the center of symmetry.

Initial and boundary conditions in mass transfer

The initial and boundary conditions to solve the partial differential equation Eq. 2, are the following: *Initial condition*:

$$t = 0 \ ; \ S_L = S_0 \ ; \ 0 \leq r \leq R_0 \quad (3)$$

where S_0 is the initial saponins content and R_0 is the initial seed radius (average value of 214 1.652 $\times$ 10^{-3} m). *Boundary condition in the particle centre*: The water flux is zero by symmetry

$$r = 0 \ ; \ \frac{\partial S_L}{\partial r} = 0 \ ; \ t > 0 \quad (4)$$

Boundary condition at the surface The surface boundary condition can be represented as follows:

$$r = R_0 \ ; \ S_s = S_e \ ; \ t > 0 \quad (5)$$

where S_s is the particular value of S_l at the surface. This represents that during washing the external resistance may be considered negligible compared to the internal, so a prescribed boundary condition could be proposed which means a strict internal control for mass transfer (Quispe-Fuentes et al., 2013).

Analytical solution of the diffusion equation

The unsteady state diffusion equation for spheres (Eq. 2), with the initial condition given by Eq. 3 and boundary conditions provided by equations 4 and 5, can be analytically solved after integration in the sphere volume to give the average saponins content S_m as a function of time (Quispe-Fuentes et al., 2013).

$$S_d = \frac{S_m - S_e}{S_0 - S_e} = \frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}e^{-n^2\pi^2\frac{D_{eff}t}{R_0^2}} \quad (6)$$

where S_d is the dimensionless saponins content, S_e equilibrium saponins content in kg saponins 100 kg dry matter^{-1} and n number of data points. To implement the analysis, Eq. 6 was solved for S_m

$$S_m = S_e + (S_0 - S_e)\frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}e^{-n^2\pi^2\frac{D_{eff}t}{R_0^2}} \quad (7)$$

With the purpose to determine the effective diffusion coefficient ten terms of the series was applied to fit the experimental data.

Dependence of the diffusion coefficient with temperature

With the aim of estimating the effect of temperature on D_{eff} the natural logarithms of the experimental diffusion coefficients were plotted as a function of the reciprocal of the water bath absolute temperature by means of an Arrhenius-type equation, as proposed in (Eq. 8)

$$LnD_{eff} = LnD_0 - \frac{E_a}{R_g T_k} \quad (8)$$

Where T_k stands for the absolute water temperature in K. Symbol D_0 represents the pre exponential factor in m^2 s^{-1}, while E_a is the activation energy in kJ mol^{-1}, being R_g the gas constant, 8.314 x10^{-3} kJ mol^{-1} K^{-1}.

3.2 Statistical analysis

Triplicate experiments were carried out for each determination, measuring saponins content. Different conditions were compared by the Tukey's test (Montgomery, 1991), at a confidence level of 95%. The goodness of fit was evaluated by two indicators, to have prediction errors expressed in the same units as the fitted variable, the root

mean square error ($RMSE$).

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(Y_{pred,i} - Y_{exp,i})^2}{N}} \quad (9)$$

Where $y_{exp,i}$ stands for an experimental value and $y_{pred,i}$ represents the corresponding predicted number. The other statistical indicator is the coefficient of determination r^2, which was computed by using the following equation:

$$r^2 = 1 - \frac{\sum_{i=1}^{N}(Y_{exp,i} - Y_{pred,i})^2}{\sum_{i=1}^{N}(Y_{exp,i} - Y_m)^2} \quad (10)$$

Where y_m is the average value of the experimental data.

4 Results and discussion

4.1 Experimental saponins extraction curves

The Tukey's test of that three determination of the experimental saponins content did not present significant differences at a confidence level of 95% in all cases. Experimental extraction curves showing the average seed saponins content (S_m) as a function of time, in kg Saponins 100 kg dry matter^{-1} are presented in Fig. 2. The initial saponins content determined by the spectrophotometric method was 0.179 % (m/m) which correspond with the bitter variety of this seed, saponins content > 0.11 % m/m (Nickel et al., 2016). However, after the soaking process a value of 0.156 % (m/m) was measured. For sake of clarity, henceforth the values will be expressed in dry basis units, in this manner the 0.156% (m/m) becomes to 0.311% d.b. In this work this last value was considered as initial saponins content.

As observed in Fig. 3, saponins content falls with time in all cases with decreasing slope. This suggests an internal control for mass transfer as well as a gradual approach towards equilibrium values. As is shown in Fig. 3 the saponins content decrease faster during the first 5 min of process. From this time and until 40 min is observed a gradual decrease in the content reaching an equilibrium saponins content above this last process time. Besides, this decrease is faster at higher temperatures. Quispe-Fuentes et al. (2013) have reported a similar behavior during saponins extraction from quinoa seeds in a comparable temperature range. At the final process time the saponins content values are lower than the 0.140 % expressed in dry matter units proposed by the Codex Alimentarius (2017).

However, the scarce literature found agrees in that the effectiveness of saponins elimination can be expressed as a percentage of total extraction (Erramouspe, Armada, & Molina, 2013; Cheok et al., 2014). In this work, the final value for saponins content represents, in all experiments, an extraction percentage higher than 80% against the initial content ($S_{finalcontent}$/ $S_{initialvalue}$ *100). Nickel et al. (2016) used the spectrophotometric method and found a percentage of 17 % (p/p) for quinoa seeds washed during 15 min. On the other hand, authors as Ridout et al. (1991) and Ruales and Nair (1993) who analyzed the saponins content after different treatments have reported similar extraction percentages. However, these authors used the gas chromatography and HPLC methods, respectively for saponins quantification. It is difficult to compare the saponins content between different works because no official method exists so far (Codex Alimentarius, 2017).

The amount of elimination of saponins content obtained by different methods can be comparable. However, the absence of an official method to quantify these compounds in products intended for human consumption is not yet available, except for the recent standard established by the Codex Alimentarius.

4.2 Analytical series solution of diffusion

Table 1 lists the parameters resulting from the fitting of ten terms of the analytical series solution model (Eq. 7) to the data of Fig. 3 by a nonlinear least squares quasi newton method (Systat version 12, 2007). The table also includes statistical indices of goodness of fit. Values of r^2 and $RMSE$ are highly satisfactory.

Parameters of goodness of fit, r^2 and RMSE in Table reftable:1 indicate that the model (Eq. 7)

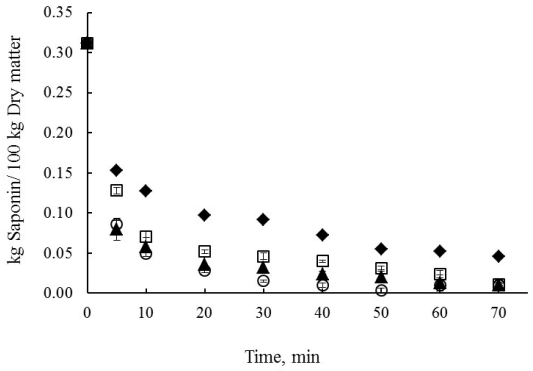

Figure 3: Experimental curves of quinoa saponins content as a function of time, at different water temperatures: (⧫) 20˚C, (□) 40˚C, (▲) 60˚C and (○) 70˚C

provides an adequate description of the experimental behavior (Eq. 7). The values for Effective diffusivity coefficient are in agreement with those presented by Abdelkader (1992) who studied the loss of glucose from potatoes and Varzakas, Leach, Israilides, and Arapoglou (2005) who developed a research on the theoretical and experimental approaches for the determination of solute effective diffusivities in foods. Figure 4 shows the predictions of Eq. 7 with the parameters of Table reftable:1 together with the experimental data.

The Fig. 4 shows a reasonably good prediction for all cases. The agreement between the experimental data and predicted values were obtained in spite of the assumptions made of constant diffusion coefficient and negligible shrinkage which are required to obtain the analytical solution (Eq. 7). The rapid elimination of saponins from quinoa seeds was favored by the previous stage of soaking, which is recommended by several authors with the purpose of facilitating the saponins extraction. Authors as Chauhan et al. (1992) and Nickel et al. (2016) attribute this effect to the hydration of particles, which allows water to penetrate in the particle, thus facilitating the release of saponins by diffusion. Secondly, the presence of saponins on the seed coat may also contribute to an easier removal of these compounds (Koziol, 1991; Vega-Galvez et al., 2010).

As the temperature increased, extraction of saponins was faster. However, for 60 and 70^{o}C, at the end of the process, the appearance of seeds became altered losing the seed coat and germ. Even when proteins and carbohydrates experience a high degree of hydration during washing. However, the total content of protein in quinoa seed varied between 10 and 13 % d.b. while the starch content in this product is five times as large, in the range of 58-66% d.b. (Kozioł, 1992; Food and Agriculture Organization, 2011; Srichuwong et al., 2017). From this point of view, it is possible to ascribe the loss of structure more to starch gelatinization than to protein denaturation. Authors as Kashaninejad, Maghsoudlou, Rafiee, and Khomeiri (2007) who investigated the hydration kinetics of a starchy grain as rice at different temperatures, suggested that soaking must be conducted at temperatures below that of starch gelatinization (65 -70^{o}C) to preserve kernel structure. For this reason, it is considered that a temperature of 50^{o}C should not be exceeded during the process (Jan, Panesar, Rana, & Singh, 2017; Li & Zhu, 2017). Besides, authors as Mota et al. (2016) who studied the loss of soluble solids (some proteins, minerals, some vitamins) during soaking in water at several temperatures for different seeds suggested that long periods of time in hot water may contribute to a higher reduction of water-soluble nutritional compounds in quinoa seeds.

4.3 Dependence of the diffusion coefficient with temperature

An Arrhenius-type Equation was fitted to data of the natural logarithm of the experimental diffusion coefficients (Ln D_{eff}) as a function of the reciprocal of the water absolute temperature of $1/T_k$, that is, (1/ (Tw+273.15)), by means of an Arrhenius-type equation (Eq. 7). The symbol T_w stands for the water temperature in ^{o}C. The E_a is a measure of the effect of temperature on the diffusion coefficient.

Predictions shown in Fig. 5 are in good agreement with the experimental coefficients. Results

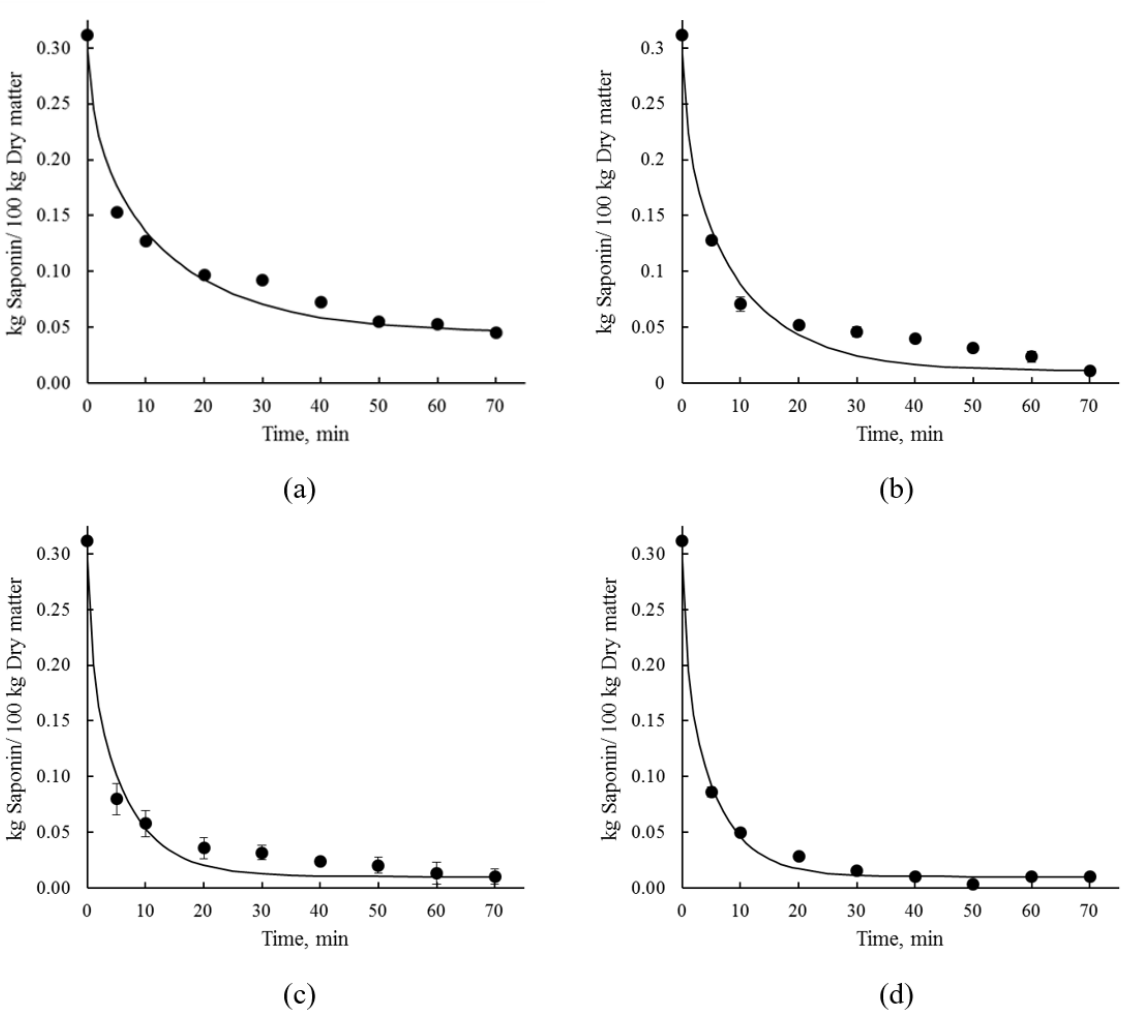

Figure 4: Saponins content curves from soaked quinoa during washing treatment. Experimental data (symbols), and predicted values (-) by f the analytical solution (Eq.6), for water temperatures of: (a) 20^{o}C, (b) 40^{o}C, (c) 60^{o}C and (d) 70^{o}C

Table 1: Effective diffusion coefficients of saponins in quinoa determined by fitting the Eq. 6 to experimental data and their Asymptotic Standard Estimation (S)

$T\ ^oC$	$D_{eff}\ \times\ 10^{-10}\ m^2/s$	$S(D_{eff})\ \times\ 10^{-11}$	r^2	$RMSE$
20	2.848	1.962	0.983	0.013
40	4.012	3.115	0.978	0.016
60	6.665	5.837	0.979	0.014
70	7.538	4.088	0.995	0.008

from the fitting of Eq.7 were: $E_a = 16.9$ kJ mol^{-1} and D_0 =2.875 × 10^{-7} m^2 s^{-1}, with a high coefficient of determination, r^2=0.987. The activation energy for saponins extraction was comparable to that obtained in a similar temperature range by Quispe-Fuentes et al. (2013) during saponins extraction and Chi et al. (2006) who studied the leaching of flavonoids from vegetables.

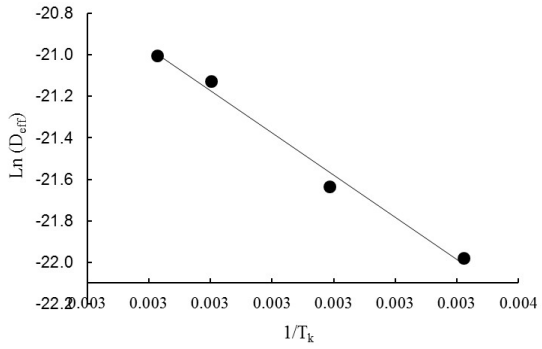

Figure 5: Dependency of the experimental diffusion coefficient with water temperature (symbols) together with predictions by an Arrhenius-type equation fitted to them (solid line)

4.4 A more accurate method to calculate the activation energy for saponins extraction process

In this section, a second method of fitting the analytical solution to whole dataset was tested to obtain an activation energy (E_a) that can be determined with more degrees of freedom. With this purposes the Eq.7 was rewritten in the following way:

$$S_m = S_e + (S_0 - S_e)\frac{6}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}\cdot e^{-n^2\pi^2\frac{(D_0 e^{\frac{E_a}{8.314}\frac{1}{(T_w+273.15)}}t)}{R_0^2}} \quad (11)$$

The effective diffusion coefficient was replaced directly by the Arrhenius equation, Eq. 8 to find an overall activation energy (E_a)) and a pre-exponential factor (D_0). This equation was solved by a nonlinear least squares quasi newton method for whole dataset, using as initial values for E_a and D_0, those obtained previously in section 4.3.

An overall activation energy (E_a) of 17.2 (2.6) kJ mol^{-1} and a pre-exponential factor equal to 3.232×10^{-7} (3.234×10^{-9}) m^2 s^{-1} were estimated with a global coefficient of determination of 0.985 (Systat 12, 2007), which is higher than the average coefficient of determination of the fittings shown in Table reftable:1. The values presented between brackets correspond to the asymptotic standard error of the parameters.

The consideration of more degrees of freedom in a single fitting stage allows a more accurate determination of the activation energy and then a more reliable influence of temperature on for the process. Some authors as van Boekel (2008) who works about the estimation of kinetics parameters on some quality food process recommend the use of all data available in order to estimate the activation parameters with more precision.

The predictions obtained by this second fitting procedure were satisfactory and the figures obtained, between predicted and experimental data, were almost coincident to those shown in Figure (4). Therefore, to avoid repetition, it was considered that it was more than sufficient to inform the statistical parameters of the second fitting procedure, the overall coefficient of determination (r^2=0.985) and the asymptotic standard error (between brackets) for each parameter E_a=17.2 (2.6) kJ mol^{-1} and D_0= 3.232×10^{-7} (3.234×10^{-9}) m^2 s^{-1}.

In order to study the rate of the extraction process, Eq.12 was derived with respect to time, and the following equation was obtained:

$$\frac{dS_m}{dt} = -(S_0 - S_e)\frac{6}{R_0^2}D_0 e^{-\frac{E_a}{R_g T_k}}\cdot \sum_{n=1}^{n=\infty} e^{-\frac{1}{n^2}\pi^2 D_0 e^{-\frac{E_a}{R_g T_k}}\frac{t}{R_0^2}} \quad (12)$$

Figure 6 show the saponins extraction rates estimated from experimental saponins contents, and the predicted values a fair agreement is achieved.

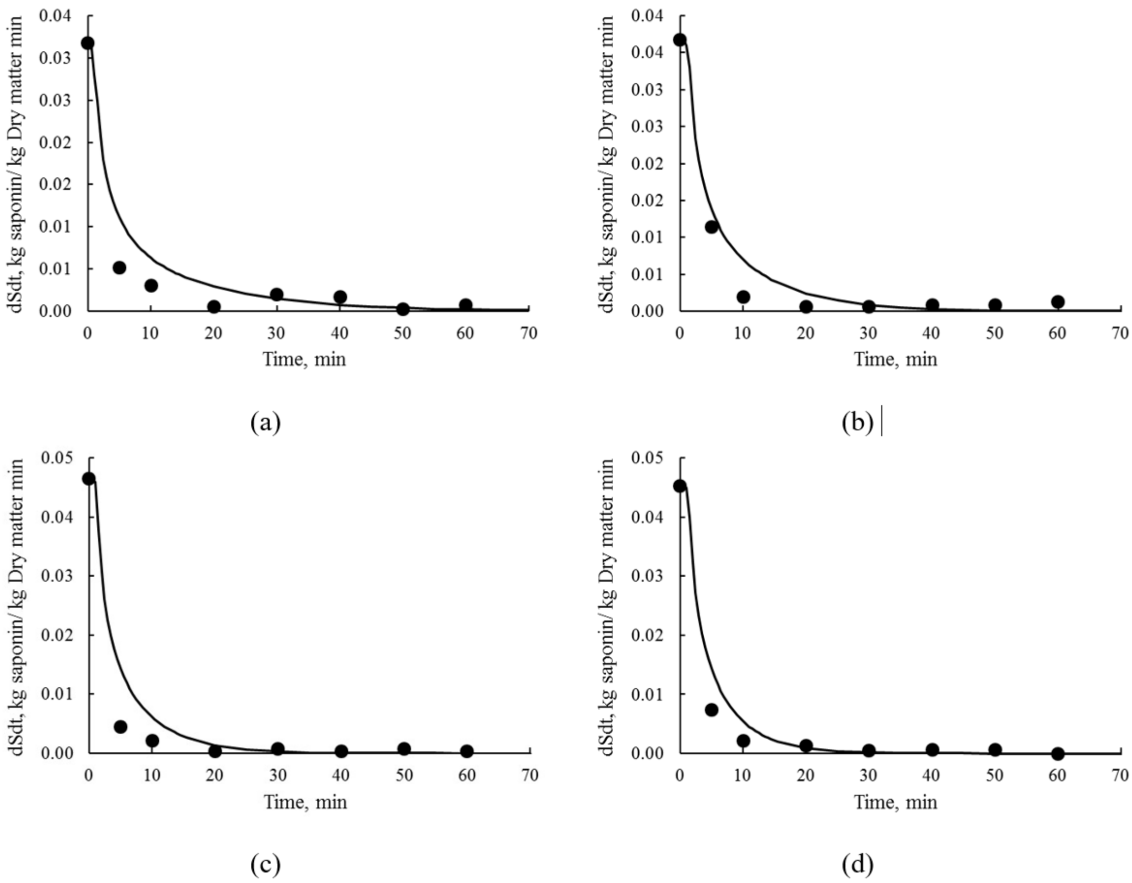

Figure 6: Saponins extraction rate ($-dS_m/dt$), kg saponins / kg dry matter min, obtained from (symbols) values obtained from experimental measurement and (solid line) predicted by the derivative of the diffusive model with respect to time for various water temperatures

The deviation observed at the beginning may be due to the error involved in calculating the experimental derivatives, which are approximated by two point forward finite differences.

Figure 6 shows that the saponins extraction rate is faster between in the first part of the process, which is then followed by a phase of much slower transfer rate. Lucas, Le Ray, and Mariette (2007) and Machado, Oliveira, and Cunha (1999) who studied the water absorption and solute leaching during soaking of different breakfast cereals reports a similar behavior.

5 Conclusions

In this work, the experimental extraction kinetics of saponins from quinoa seeds was studied at various water temperatures to improve the understanding of this process.

The spectrophotometric method was adequate to determine the total saponins content. From this study, the treatment carried out at 40^{o}C for 6 min, can be considered optimum to reach a safe level of saponins for human consumption without visible damage to the seed.

An unsteady state diffusional model was proposed with strict internal control to the mass transfer rate, assuming constant diffusion coef-

ficient and using the initial particle size during the process. The complete analytical solution of the diffusion equation provided reasonably accurate predictions of the experimental curves.

The experimental diffusion coefficients determined in this work were correlated as a function of water temperature by means of an Arrhenius-type equation. Both the values of the diffusion coefficient (around 10^{-10}m^2 s^{-1}) and the activation energy (about 16.9 kJ mol^{-1}) are within the ranges expected for similar processes.

A second, more general method for fitting the diffusional model to the entire set of data involved the inclusion of the Arrhenius equation inside the diffusional model to directly fit an overall activation energy (E_a) of 17.2 kJ mol^{-1} and a pre-exponential factor equal to 3.232×107 m^2 s^{-1}. A slightly more accurate prediction was obtained compared with the first fitting method.

In future work, a model similar to that developed here will be combined with another model for water diffusion into the grain. In addition, leaching of minerals will be measured to know the extent of this possible phenomenon. Such a model, combined with mass balances that include the water increase content, will be useful for equipment design, by predicting saponins extraction times for different operating conditions.

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