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Numerical modeling of chickpea (*Cicer arietinum*) hydration: The effects of temperature and low pressure

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ABSTRACT

Chickpea is a leguminous that can be consumed both fresh and baked, and must be hydrated in both cases. The objective of this study was to discuss mathematical and numerical models, and also experimentally evaluate the process of water uptake in chickpea (*Cicer arietinum*) under different temperatures and pressures, determining the diffusion coefficient of water in the grains and the activation energy of the hydration process. The values for the diffusion coefficient ranged from 7.38×10^{-11} to 5.21×10^{-10} m^2 s^{-1}. The activation energy was determined at 36.040 kJ mol^{-1}, the activation volume at -7.724×10^3 cm^3 mol^{-1} and the constant value was 2.185×10^{-4}. By comparing the experimental results with those obtained from the analytical solution of the theoretical model, there was a satisfactory fit of the model to the experimental data, and the hydration curves were plotted. A good adjustment of the numerical model, the model of Abu-Ghannam and the Peleg model was made to the experimental data. The Arrhenius–Eyring type equation was used to explain the dependency of the diffusion coefficient with the temperature and pressure in the hydration process.

1. Introduction

The largest producers and exporters of chickpeas are India, Australia, Turkey, Ethiopia and Myanmar. India is in 1st place in the global rankings in the production of chickpea and its production in 2012 reached 7.7 million tonnes, representing approximately 66.7% of world production (FAO, 2012). It is one of the oldest and most consumed legume in the world, traditional to some countries of the Middle East as a source of proteins, carbohydrates, minerals, vitamins and fiber. It differs from other legumes due to their high digestibility, low content of anti-nutritional substances, besides better availability of iron (Singh et al., 1991).

Vegetables are sources of essential amino acids such as lysine, B vitamins, as well as phytosterols, which has been associated with the prevention of breast cancer, obesity and diabetes (Bazzano et al., 2001). Despite their significant nutritional value, their nutritional characteristics are often lost in inadequate preparation or they are replaced by other foods, because they usually require a long hydration and cooking time, which is a drawback for many consumers (Gowen et al., 2007b). They are a major source of protein after meat and eggs, and their main advantage over these two foods is its lower cost. Fabaceas widely used in food such as lentils, chickpeas, soybeans and beans are perishable and must be dried to ensure its quality during storage, preventing its dehydrated consumption due to its hardness (Naviglio et al., 2013). These grains are considered to be "hard-to-cook" and require pretreatment rehydration before baking or canning, because the hydration promotes a reduction in cooking time, in the starch gelatinization, in the maintenance of nutritional quality and improvement of the proteins digestibility (El-Hady and Habiba, 2003; Pirhayati et al., 2011; Zanella-Díaz et al., 2014; Naviglio et al., 2013).

The water absorption is a phenomenon that can be explained by models based on concepts of chemical kinetics, as developed by Peleg (1988), and by analytic expressions derived from Fick's second law of diffusion, as in the work of Hsu (1983), who has assessed the hydration process in legumes considering the diffusion coefficient dependent on water concentration. Processes such as the water absorption are explained by physical or empirical modeling. As discussed by Saguy et al. (2005), in the first approach, a mathematical formulation is derived from the physical aspects of the phenomenon, which requires sufficient understanding of the mechanisms involved in the problem to establish accurate

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Nomenclature

α	scale parameter of the Weibull equation (h)
β	shape parameter of the Weibull equation
C	concentration (kg m^{-3})
d.b.	dry basis
D	diffusion coefficient (m^2 s^{-1})
D_0	constant parameter in Table 5 (s^{-1})
D_T	Arrhenius temperature dependent constant (s^{-1})
D_P	Eyring pressure dependent constant (s^{-1})
E_a	activation energy (kJ mol^{-1})
ER	relative error
ER_{sph}	relative error for spherical geometry
ER_{nsph}	relative error for non spherical geometry
ER_{an}	relative error for analytical solution
k	absorption rate constant (min^{-1})
k_0	absorption constant (min^{-1})
k_1	absorption rate Peleg ($d.b.^{-1}$ h)
k_2	absorption capacity Peleg ($d.b.^{-1}$)
k_v	pseudo-second-order kinetic constant ($d.b.^{-1}$ h^{-1})
P	pressure (MPa)
r, a	average grain radius (m)
R	universal gas constant (8.314 kJ mol^{-1} K^{-1})
R^2	determination coefficient
RMSE	root mean square error
$M(t)$	moisture content at time t (d.b.)
M_o	initial moisture content (d.b.)
M_{eq}	equilibrium moisture content (d.b.)
M_{exp}	experimental moisture content (d.b.)
M_{sph}	moisture content for spherical geometry (d.b.)
M_{nsph}	moisture content for non spherical geometry (d.b.)
M_{an}	moisture content for analytical solution (d.b.)
T	temperature (K, °C)
t	time (s, min, h)
V	volume (m^3)
ΔV	volume activation (cm^3 mol^{-1})
X_{ex}	experimental values
X_{aj}	adjusted values
$W_s(t)$	sample mass at time t (g)
W_{dm}	dry mass (g)

estimates of the physical reality. On the other hand, the empirical model involves less effort in this respect, since it is designed from correlations between parameters variations of the quantities involved. It has the advantage of bypassing phenomenological modeling inaccuracies arising from uncertainties and inadequacies of the assumptions made.

Some studies on the absorption process of water in agricultural products are presented by Clemente et al. (1998) and Hung et al. (1993). The hydration of products that exhibit a lag phase at the beginning of the hydration process because of the formation of the coating layer, such as adzuki beans, were studied using suitable models as the sigmoidal model for the correct representation of the water absorption kinetics (Kaptso et al., 2008; Oliveira et al., 2013). Gowen et al. (2007b) evaluated the effects of blanching in the water uptake and Turhan et al. (2002) have adjusted hydration curves to the Peleg model to study the effects of different hydration temperatures and their influence on water absorption. Recently, Ghafoor et al. (2014) evaluated the effect of hydration aided by ultrasound in navy beans and described the kinetics of hydration through the second Fick's law and models of Peleg, Weibull and first-order kinetics. Yildirim et al. (2011) have assessed the effects of ultrasound in the hydration process, along with different temperatures. In addition to studies on hydration, Sayar et al. (2001) evaluated starch–water reactions during hydration and Alajaji and El-Adawy (2006) have reported the effects of cooking chickpeas traditionally and using a microwave, with regard to loss of nutrients, vitamins and minerals.

Ibarz et al. (2004) have examined in their work the effects of hydration pre-treatments using high pressure (above 275 MPa) on reduced chickpea cooking time. Prasad et al. (2010) have conducted a detailed study on temperature dependency on hydration kinetics in chickpea, comparing the theoretical model to other developed models, such as the model of Peleg, Weibull and Exponential, to experimental data, obtaining a best fit to the hydration model of Peleg (1988). Naviglio et al. (2013) presented a device (Extractor Naviglio) for hydration and flavoring of cannellini beans to the cyclical low pressures, achieving a significant reduction in the time required to reach the grain moisture balance. Another approach was explored by Zanella-Díaz et al. (2014) that sought to obtain rapid hydration in tepary and pinto beans employing pressure gradients through the vacuum impregnation technique, and adjusting the Peleg model to the data obtained experimentally.

Although several studies used combined pressure and temperature to accelerate the hydration process, denaturation of proteins or enzymatic inactivation are relevant, few works present models that correlate the dependence of the diffusion coefficient with these two variables simultaneously. Ahromrit et al. (2007) examined in his work the influence of temperature and pressure on starch gelatinization during hydration of Thai glutinous rice, using the equation of Arrhenius–Eyring to express the dependence of this phenomenon with the proposed treatments. Another work that applies the combined formulation of these variables is described by Ramos et al. (2009), who studied the inactivation of harmful microorganisms and enzymes to foods, prolonging their shelf life and maintaining or enhancing their nutritional qualities.

Despite the process of cooking food on microwaves is highly promising, cooking based on increased temperature and pressure is widely used in many regions and deserves attention in studies aiming to analyze the balance among cooking time, power consumption and reduction of the loss of nutrients. Rocca-Poliméni et al. (2011) have developed a model for the study of heat and mass transfer inside a commercial pressure cooker and the model proved to be able to predict the evolution of the thermodynamic variables involved in the process of cooking.

The mentioned methods for evaluating the kinetics of grain water uptake, typically employ the analytical fit to the experimental data or phenomenological models, which requires certain simplifications, regarding the experimental conditions and the material used, and require a high time and cost to obtaining results (Montanuci et al., 2014). An alternative or complementary approach to these methods is the numerical–computational modeling, also discussed by Naviglio et al. (2013) which can be advantageous not only to estimate the parameters involved, but also to validate them in relation to the experimental data, which in turn can be used for similar processes without the need of further experiments.

The water absorption process is an important stage in the preparation of food, and in this work it is studied under the effects of temperature and low pressure. Experimental parameters were determined for the analytical and numerical study on the combined effects of temperature and pressure in chickpea water absorption, and a comparison was made between the experimental data obtained and results from the use of existing models for water uptake. The objectives of this work were to apply mathematical models to predict grain water uptake by using temperature and pressure and to apply the kinetic constants to quantify the effects of temperature and low pressure in the hydration process using the Eyring and Arrhenius equations, respectively. Furthermore, to investigate the influence of the combined effects of temperature and low pressure in the diffusion coefficient using an equation such as the Arrhenius–Eyring. In this study we have showed the potential of numerical simulation and understanding the hydration process, in order to indicate how the moisture diffusion inside the grain during the process of water absorption occurs.

2. Materials and methods

2.1. Sample preparation

Chickpea (*Cicer arietinum*) used for the experiment was bought in local market, and the grains were sorted to avoid impurities and broken grains. In the process of hydration, samples of approximately 30 g of chickpeas were used, soaked in 250 ml distilled water at temperatures of 10, 25 and 40 °C using a refrigerated incubator B.O.D. (Technal) until reaching moisture balance, with three replications for each treatment. The use of temperature at 10 °C to hydration of chickpea is explained by the possible hydration of the product when stored in a commercial refrigerator and the reduced growth of microorganisms during the process. Additionally for the pressurized treatments, we used a cylinder assembly in aluminum and manometer, which allowed us to assess pressure and keep it constant throughout the hydration process, and pressure was determined by adding compressed air to the cylinder with the aid of a compressor. The pressure inside the cylinder was obtained with the aid of compressed air in order to investigate the combination of pressure and temperature in the hydration process and not in the cooking chickpea. The use of low pressures (from 0.10 to 0.30 MPa) is due to the fact that this is the pressure range supported by the developed equipment.

Initial moisture content on dry basis was determined using the standard method, which included a stove with forced circulation and three homogenized samples with 10 g of material, at temperature of 105 ± 1 °C for 24 h.

2.2. Determination of water absorption and moisture content

During water uptake, the samples were periodically weighed on a digital scale with an accuracy of 0.001 g until two consecutive readings were made with no significant mass gain, indicating the equilibrium moisture content. The first reading was made in the first 30 min and the following readings were made at 1 h intervals. To make the weighing of the product easier, the grains were placed in PVC net during hydration. Before weighing, the samples were left on paper towels to remove excess water, and were returned to immersion after the checking of mass gain. These procedures are based on the works of Sayar et al. (2001) and Haladjian et al. (2002).

Regardless of the periodic removal of the product for assessment of mass gain occurs in a short period of time (about 2 min), the hydration process may suffer some influence of the compression and decompression. However, this influence has been ignored because the total time of hydration is much greater than the time of withdrawal.

Moisture content was determined for plotting the hydration curves for each treatment from the beginning of the hydration process until the product reaches the equilibrium moisture content; it was measured on a dry basis using the traditional expression presented in Brooker et al. (1992):

$$M(t) = \frac{W_s(t) - W_{dm}}{W_{dm}} \tag{1}$$

where $M(t)$ is the moisture content in decimal dry basis at time $t, W_s(t)$ is the mass of the sample at time t and W_{dm} is the dry mass for their treatment.

The use of a B.O.D. refrigerated incubator (Technal) to maintain hydration temperature constant throughout the hydration process precluded the practical use of the shaking table available. However, the process of removal and return of the product in beakers with distilled water, after weighing, modifies the placement of the grains so that they periodically change their surfaces of contact with water and other grains.

2.3. Determination of initial radius

In spite of the possibility of developing models of the equivalent radius variation of the product studied here, considering a comparison with the known analytical solution (Crank, 1975), that chickpeas material is homogeneous, isotropic and does not occur variation of its volume. This characterization is relevant to problems of lumped or distributed parameters model which does not explicitly the volumetric variation of the product, and under the assumption that the sorption kinetics of the product is not changed, as performed by Gastón et al. (2002, 2004). The methodology used to determine grain mean radius is in accordance with the work of Sayar et al. (2001), where the initial volume of the grain is assumed to be constant and the grain is assumed to have spherical conformation. Then, 50 grains were placed in graduated cylinder with 50 ml of distilled water and the displaced volume of water was set equal to $V = 50\frac{4\pi r^3}{3}$ and the mean radius r of each grain was determined.

2.4. Comparison of experimental, analytical, and numerical results

Unlike the analytical solution, and the experimental results that express values of moisture content for each point at each period of time, the numerical solution obtained with the pde toolbox returns the moisture content to each node belonging to the domain of interest over time. To find the value of moisture content within the polygons, we considered the centroid of each finite element, and the moisture content of this centroid was estimated by the traditional array of shape functions for the linear interpolation of nodal values of moisture. The average moisture content value in the entire domain was found by an arithmetic mean of moisture contents obtained in the centroids of each polygon with intervals of 30 min, in a similar approach to that performed by Haghighi and Segerlind (1998). These values were then compared to the experimental results and to the other results.

To assess the quality of approximation of the analytical, numerical, and empirical models to the experimental data, we used two metrics consisting of the determination coefficient (R^2), the root mean square error (RMSE) and the relative error (ER) which equations are, respectively:

$$R^2 = 1 - \frac{n\sum_{i=1}^{n}(X_{ex} - X_{aj})^2}{n\sum_{i=1}^{n}X_{ex}^2 - \left(\sum_{i=1}^{n}X_{ex}\right)^2} \quad \text{and}$$

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(X_{ex} - X_{aj})^2}{n}} \quad \text{and} \quad \text{ER} = \frac{|X_{ex} - X_{aj}|}{|X_{ex}|}100$$

where X_{ex} is the experimental values, X_{aj} is the adjusted values, and n the number of observed data.

3. Theoretical considerations

3.1. Partial differential equation model – analytic model

Regarding the study of product mass transfer by hydration, we can considered that this phenomenon is described in Fick's second law, assuming that diffusion is solely radial and that the diffusion coefficient is constant (Crank, 1975). In this case, moisture content variation can be represented by a partial differential equation as a function of hydration time, assuming homogeneous, isotropic, and one-dimensional media, as:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{c}{r}\frac{\partial C}{\partial r}\right) \tag{2}$$

where C is the substance concentration, D is the diffusion coefficient ($\mathrm{m}^2\ \mathrm{s}^{-1}$), t is time (s), r the radial distance (m) and the parameter $c = 0$ for plane bodies, $c = 1$ for cylindrical bodies and $c = 2$ for spherical bodies. By employing the same arguments of Crank (1975), we can write the Eq. (2) as:

$$\frac{1}{D}\frac{\partial M}{\partial t} = \frac{1}{r}\frac{\partial^2 Mr}{\partial r^2} \tag{3}$$

since the diffusion coefficient $D > 0$ and it is constant with respect to r and t. Thus, a mathematical formulation for the physical problem of the one-dimensional radial diffusion for homogeneous and isotropic media, with diffusion coefficient spatio-temporally constant in terms of moisture content M, is given by:

$$\begin{cases} \frac{1}{D}\frac{\partial M}{\partial t}(r,t) = \frac{1}{r}\frac{\partial^2 Mr}{\partial r^2}(r,t), & (r,t) \in (0,a) \times (0,t) \\ \frac{\partial M}{\partial r}(0,t) = 0, & r = 0,\ t \geqslant 0 \\ M(a,t) = M_{eq}, & r = a,\ t \geqslant 0 \\ M(r,0) = M_0, & 0 < r < a,\ t = 0 \end{cases} \tag{4}$$

where $M(t)$ is the moisture content in dry basis at time t, M_{eq} the equilibrium moisture content, M_0 the initial moisture content of the product, D the diffusion coefficient, t the time of hydration, and a is the radius of the product. The solution of Eq. (4) presented in Crank (1975) and Ghafoor et al. (2014) is as:

$$\frac{M(t) - M_{eq}}{M_0 - M_{eq}} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{n^2\pi^2}{a^2}Dt} \tag{5}$$

The expression (5) is truncated to the first 8 terms to be effectively used in determining the diffusion coefficient. Obtaining the coefficient of liquid diffusion for grain and seed consists of a nonlinear regression adjustment of the analytical solution of Fick's second law, given in the form of a infinite series, as expressed by (5), to the experimental data of moisture content as a function of time of hydration. In this study we used the first eight terms of the series, and the estimate of diffusion coefficient D was made using the Statistica 10 software, by Gauss–Newton method, with the residue estimated by the least squares method (Statsoft, 2004).

3.2. Ordinary differential equation model – Abu-Ghannam model

This is a model expressed in ordinary differential equation to estimate the change rate of moisture content over time. It can be obtained when considering the hypothesis that the moisture content M depends only on time, i.e., $M = M(t)$, also that the final moisture content M_{eq} is constant over time, and that the body is homogeneous and isotropic. Furthermore, the change rate of moisture content $M(t)$ at time t is proportional to the difference between the moisture in any time t and the final moisture M_{eq}. Thus, a mathematical model for this phenomenon can be written as in Abu-Ghannam and McKenna (1997b):

$$\frac{dM(t)}{dt} = -k\left(M(t) - M_{eq}\right) \tag{6}$$

where coefficient $k > 0$ is specified for hydration or drying processes by an Arrhenius type of equation, $M(t)$ is the moisture content in time t and M_{eq} is the final moisture content. The minus sign in (6) is used to maintenance the consistency between the mathematic formulation and the physics formulation of the problem and shows that this equation describes water uptake phenomena.

To calculate such rate of change over time, we must specify an initial condition for (6). Then, taking as initial condition $M(0) \equiv M_0$ at $t = 0$, a mathematical formulation in terms of an initial value problem (IVP) is such as:

$$\begin{cases} \frac{dM(t)}{dt} = -k\left(M(t) - M_{eq}\right), & k > 0 \text{ and } t > 0 \\ M(0) \equiv M_0, & t = 0 \end{cases} \tag{7}$$

which solution is given by

$$M(t) = (M_0 - M_{eq})e^{-kt} + M_{eq} \tag{8}$$

where $k = k_0\, e^{-\frac{E_a 1}{R\,T}}$ is the rate constant of the hydration expressed as min^{-1}.

3.3. Peleg model

This work also applied the model developed by Peleg (1988) as empirical model and whose constants, k_1 and k_2 were fitted to experimental data and compared to those found in the literature. Although this have been done here, Kumar et al. (2011) discussed a theorical fundamentals for this model based on the Kinetic Theory, which was shown to be equivalent to that of kinetic processes of pseudo-second order, as described by Ho and McKay (1999), and they presented the Peleg constants like $k_1 = 1/k_v M_{eq}^2$, and k_v a kinetic constant of pseudo-second order and M_{eq} moisture in balance, and $k_2 = 1/M_q$, thus, kinetic constant functions and capacity of water absorption at equilibrium.

Once this model presents a good adjustment to experimental data, it is widely used to study water uptake in farm products, and its solution shows moisture content as a function of time, allowing for its estimate after certain periods of time, based on experimental data related to both parameters, k_1 and k_2. This model has been used to study absorption and desorption processes on several products, by the transferring of water, as seen in Turhan et al. (2002), Mercali (2009), Prasad et al. (2010), Ghafoor et al. (2014) and Oliveira et al. (2013). The Peleg model is traditionally presented as:

$$M(t) = M_0 + \frac{t}{k_1 + k_2 t} \tag{9}$$

where $M(t)$ is the moisture content of the product at a given instant of time, and M_o is the initial moisture content of the product, t is time, and the plus sign is used to model water uptake. The k_1 and k_2 parameters are the constants of Peleg, which are associated with the initial rate of water transfer and with the concentrations of water in equilibrium conditions.

3.4. The combined effect of pressure and temperature on the rate constant

The dependence of temperature, T, in the water absorption can be evaluated by calculating the variation of the diffusion coefficient D with temperature, using the Arrhenius equation, given by:

$$\ln D = \ln D_T - \frac{E_a}{RT} \tag{10}$$

where D_T is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. Constants values of D_T and activation energy E_a were determined from a linear regression fit of the diffusion coefficients as a function of the inverse of temperature expressed in (10) with the Statistica 10 software (Statsoft, 2004).

The dependence of pressure, P, in the water absorption can be evaluated by calculating the variation of the rate constant D the reaction with pressure using an equation based on the Eyring equation determined by:

$$\ln D = \ln D_P - \left(\frac{\Delta V}{RT}\right)P \tag{11}$$

where D_P is the pre-exponential factor, ΔV is the activation volume, R is the universal gas constant, T is the temperature and P is the pressure. Values of D_P constant and the activation volume ΔV were determined from a set of linear regression of the diffusion coefficients as a function of pressure as described by Eq. (11) with the Statistica 10 software (Statsoft, 2004).

In order to obtain an expression relating the constant k with pressure P and the temperature T, it follows the approach presented in Ahromrit et al. (2007), which showed that such wording is as:

$$\ln D = \ln D_0 - \frac{E_a}{RT} - \left(\frac{\Delta V}{RT}\right)P \tag{12}$$

where $\ln D_0$ is a constant. After estimating the value of the diffusion coefficient for the respective treatments, the Arrhenius–Eyring type equation, (12), was used to examine the dependency between the diffusion coefficient, temperature and pressure of hydration. The Statitisca 10 software was used to estimate the values of the constant D_0, activation energy E_a and volume activation ΔV values were found using multiple linear regression of the Arrhenius–Eyring type equation to the diffusion coefficients adjusted for each treatment.

It can be noticed that the diffusion coefficient D, does not appear explicitly in the models of concentrated parameters or in empirical models in this paper (Abu-Ghannam and Peleg models), but in the distributed parameter equations. In traditional approaches, the diffusion coefficient is determined by a nonlinear fitting expression (5) truncated to the first terms, to the experimental values of the moisture content for each treatment performed, as done for Kader (1995), Naviglio et al. (2013) and Ghafoor et al. (2014), or by combining the influence of temperature and pressure in the process, like in Indrawati et al. (2000), Ahromrit et al. (2007) and Ramos et al. (2009). After its determination, the diffusion coefficients found for each treatment are explained as to their individual or combined effects, by using the Arrhenius, Eyring and Arrhenius–Eyring equations, as detailed in expressions (10)–(12). In this work, the dependence of the diffusion of moisture in the product in relation to temperature, pressure and concentration, as shown in Luikov (1966), was implied in the diffusion coefficient D, which added such contributions as in the usual diffusion model derived from the Fick's second law, relating the product properties, the mechanisms involved and the contribution from the surrounding environment, which in turn to facilitate the mathematical modeling of the process and its resolution. However, as pointed by Saguy et al. (2005), this approach covering up the actual mechanisms involved in water transfer, resulting, sometimes, unsatisfactory solutions when compared with the experimental results.

3.5. Numerical solution and discretization for the domain

The numerical solution of the space–time diffusion of moisture was obtained by using the setting *pde toolbox*, available on Matalb 2011, which enables a solution of an initial value problem and boundary analogous to the problem (4), specifying the diffusion coefficient D, the boundary conditions of Neumann $\frac{\partial M(0,t)}{\partial r} = 0$ and Dirichlet $M(a,t) = M_{eq}$ and the initial condition, $M(r,0) = M_0$. The package *pde toolbox* makes use of unstructured grids for discretization of the domain and the finite element method (FEM) for solving differential equations, in addition to provide resources for visualization of the results (Mathworks, 2012).

It is important to point out the numerical results in this type of problem can be sensitive to the type of variables positioning in the nodes or centroids of mesh elements used. By ignoring this characteristic, the numerical values obtained may not be consistent with the experimental ones, since the arrangement of variables to calculate the nodal values of the components of the calculation overestimates the moisture content, since the boundary condition of equilibrium artificially induces more rapid transport of moisture to the interior of the grain, compared with the experimental data. The origin of this inconsistency results partly from the specification of the Dirichlet boundary condition, M_{eq}, to the equilibrium moisture content in the interface with the surrounding fluid. This condition imposes an immediate saturation of the most concentrated area for the less concentrated area, near the border, due to the unrealistic and instantaneous water absorption, as identified by Hsu (1983). This problem was solved by specifying a sufficient level of refinement to the domain discretization and placing the variables in the centroids of the elements, considering the different contributions of the calculated values, not artificially increasing the rate of water absorption.

The numerical solution of problem with initial value and boundary similar to (4) was obtained by parametrizing the parabolic differential equation specified in the *pde toolbox* environment:

$$d\frac{\partial u}{\partial t} - c\nabla u + bu = f \tag{13}$$

Considering $u = M(r,t), d = 1, b = 0, f = 0$ and $c = D > 0$, in the expression (13), is possible to achieve the solution of the problem (4), since in this work product water mass is equal to the moisture content, since the moisture content is expressed on dry basis and dry matter is considered constant throughout the water uptake process.

The diffusion coefficient, D, was inserted in the *pde toolbox* environment after being found with Statistica 10, and the M_0 and M_{eq} values were inserted according to the values of the initial moisture content of the product and the equilibrium moisture content found for each treatment in practice.

It should be emphasized that the analytical solution of Fick's second law can provide the grain moisture value at each reading. However the physical–mathematical assumptions specified in the mathematical model do not consider the actual geometric shape of the product. A better representation of the geometrical shape of the product studied is shown in Fig. 1. In this case, the theoretical approach to the solution is impracticable, requiring the use of a numerical solution to the solution of the physical problem.

Fig. 1 illustrates a two-dimensional domain consisting of 892 nodes and 1668 triangular elements, enabling a more appropriate geometric representation of chickpeas. The mesh was created by the Matlab 2011 software through the *pde toolbox* environment (Mathworks, 2012).

3.6. Weibull analysis

The assumptions of the product homogeneity and direction of water flow used in this work, although necessary to obtain the analytical solution of the Fick's second law, can obscure the

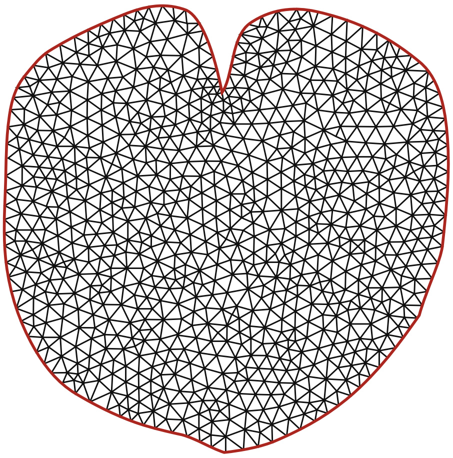


Fig. 1. Domain discretization using unstructured mesh – cross grain.

understanding of the contributions of water conduction mechanisms involved in the hydration process. As described by Bewley and Black (1978) and verified by Pietrzak et al. (2002), in fact, some pulses have a greater water uptake rate through the micropyle than the rest of the grain's coating layer. However, even if the regions have preferred absorption of water, it is important to characterize if the absorption is preferably a diffusive phenomena, especially when modeling based on Fick's second law are used.

An approach, in this case, is the Weibull distribution as shown in Waezi-Zadeh et al. (2011), Marabi et al. (2003) and Kliger et al. (2011), who used it to analyze if the mechanism involved in the sorption is by diffusion, convection or relaxation, with an expression defined as:

$$\frac{M(t) - M_0}{M_{eq} - M_0} = 1 - \exp\left(-\left(\frac{t}{\alpha}\right)^{\beta}\right) \tag{14}$$

where $M_0, M(t)$ and M_{eq} are the initial moisture content, at the time t and at the equilibrium point, α is the scale parameter in hours and $\beta$is the shape parameter. A non-linear fit to expression (14) was used to estimate the parameters α and β, since, as discussed by Saguy et al. (2005), the scale parameter defines the reciprocal of the kinetic absorption rate and it represents the time necessary to reach approximately 63% of the hydration process. Different values of β lead to changes in hydration curves, and they are related to the mechanisms involved in the transfer of water, such as the diffusion, convective or of relaxation ones.

4. Results and discussion

Samples of chickpea showed increased moisture content in relation to hydration time for all treatments. As the hydration process was not interrupted until it reached equilibrium moisture content, except for weightings, the rate of water uptake decreased throughout the hydration process due to the saturation of water in free capillary spaces, as reported by Abu-Ghannam and McKenna (1997a).

Based on the results observed by Evranuz and Gürtas (1992), where the loss of soluble solids during the hydration of chickpeas at 40 °C for 18 h was estimated to be about 1%of the mass of original grain, in this work the loss of solids compared to the initial mass of the product and with product water uptake was not significant. Abu-Ghannam and McKenna (1997b), based on reducing trend of the moisture content equilibrium with increasing temperature, also did not consider the loss of soluble solids when calculating the moisture content of the grain. The initial moisture content of the product used for analytical and numerical solution, to problems (4) and (13), respectively, was $M_0 = 0.11$ (decimal d.b.) and the initial radius of the product was estimated in 4.978 mm, considered constant throughout the hydration process.

The values found for experimental equilibrium moisture content, diffusion coefficients, constants of Abu-Ghannam and Peleg, along with the results of metrics used to assess the quality of the adjustments of the models to experimental data are described in Table 1.

When analyzing the results of the hydration process, considering that the diffusion coefficient and the initial radius of the product are constant, one can see that the values found for the diffusion coefficient in the treatments ranged from 7.38×10^{-11} to 5.21×10^{-10} m^2 s^{-1}. It can be noticed a greater rate of water uptake at the beginning of the hydration process and an increase of the diffusion coefficient following the increase of temperature and pressure. These values agree with those found by other researchers as Montanuci et al. (2014). Naviglio et al. (2013) presented values of D from 2.17×10^{-9} to 4.70×10^{-7} m^2 s^{-1} for the operating condition of cyclic pressure (between 0 and 10 bar) in the hydration of cannellini beans. Yildirim et al. (2011), when studying the effects of temperature and ultrasound in the process of water diffusion in chickpeas, found values of D from 1.40×10^{-10} to 7.72×10^{-10} m^2 s^{-1}, for temperatures from 20 °C to 97 °C. Seyhan-Gürtas et al. (2001), also for chickpeas, have determined diffusion coefficients from 9.71×10^{-11} to 5.98×10^{-10} m^2 s^{-1}. Pramiu et al. (2011), have also found similar values from 5.67×10^{-11} to 2.67×10^{-10} m^2 s^{-1} for the diffusion coefficient in treatments submitted to different temperature and 0.30 MPa pressure for the same legumes studied here. When analyzing the phenomenon of water transfer in chickpeas, Sayar et al. (2001) have reported diffusion coefficient values from 2.43×10^{-10} to 11.68×10^{-10} m^2 s^{-1}, in temperatures from 20 °C to 45 °C for spring chickpeas, and values from 1.99×10^{-10} to 10.16×10^{-10} m^2 s^{-1}, in temperatures from 20 °C to 45 °C for winter chickpeas. These values also agree with those found by Prasad et al. (2010), who when assessing temperature dependency on the hydration kinetics of chickpeas, have reported diffusion coefficient values from 1.92×10^{-9} m^2 s^{-1} to 3.23×10^{-9} m^2 s^{-1} for hydration temperature from 40 °C to 60 °C, respectively.

As showed in Table 1, the values found for the hydration constant $k$and the quality of adjustment agree with the results of Abu-Ghannam (1998), who, when studying the texture modeling of the hydration process in red bean, found hydration constants k, from 1.5×10^{-2} min^{-1} to 5.96×10^{-2} min^{-1}, in hydration temperatures from 20 °C to 60 °C, respectively. Abu-Ghannam and McKenna (1997b) have reported values for $k$from 2.42×10^{-3} min^{-1} to 5.96×10^{-2} min^{-1} when studying the effects of blanching in red bean with temperatures also from 20 °C to 60 °C, respectively. When Gowen et al. (2007b) studied the effects of blanching in chickpea water uptake, they found values of $k$from 1.4×10^{-2} min^{-1} to 2.3×10^{-2} min^{-1}, for non-blanching and blanching treatments, respectively. When assessing the influence of blanching on the kinetics of water uptake in soybean, Gowen et al. (2007a) found values for k of 1.08×10^{-2} min^{-1} and 1.90×10^{-2} min^{-1} in soybean submitted and not submitted to the process of blanching, respectively.

Peleg's constants k_1 and k_2 and the quality of adjustment are in accordance with the values found by Turhan et al. (2002), who have reported on their work values of k_1 from 2.22 h d.b.$^{-1}$ to 0.432 h d.b.$^{-1}$ and k_2 values from 0.715 d.b.$^{-1}$ to 0.771 d.b.$^{-1}$ in temperatures ranging from 20 °C to 40 °C in chickpea *winter*. The

Table 1
Values of diffusion coefficients, constants of Abu-Ghannam and Peleg, and metrics used to assess the quality of adjustments, where $T_iP_j; 1 \leqslant i \leqslant 3$ and, $1 \leqslant j \leqslant 5$, in which T_1P_j, T_2P_j and T_3P_j are the temperatures 10 °C, 25 °C and 40 °C, and $T_iP_1, T_iP_2, T_iP_3, T_iP_4$ and T_iP_5 represent the absolute pressures 0.10 MPa, 0.15 MPa, 0.20 MPa, 0.25 MPa and 0.30 MPa, respectively.

Treatment	Eq. moisture content M_{eq} (d.b.)	Analytical model			Abu-Ghannam model			Peleg model				Numerical solution	
		D ($m^2\ s^{-1}$)	R^2	RMSE	k (min^{-1})	R^2	RMSE	k_1 (h d.b.$^{-1}$)	k_2 (d.b.$^{-1}$)	R^2	RMSE	R^2	RMSE
T_1P_1	1.39^{bcd}	7.38×10^{-11}	0.986	0.0316	0.0036	0.922	0.0285	2.29	0.73	0.971	0.0576	0.953	0.0731
T_1P_2	1.41^{cde}	8.29×10^{-11}	0.986	0.0308	0.0039	0.909	0.0342	1.95	0.74	0.967	0.0628	0.958	0.0709
T_1P_3	1.37^{bc}	9.40×10^{-11}	0.985	0.0339	0.0040	0.950	0.0210	2.05	0.72	0.981	0.0484	0.956	0.0729
T_1P_4	1.40^{bcd}	1.13×10^{-10}	0.976	0.0449	0.0048	0.971	0.0134	1.77	0.68	0.984	0.0473	0.950	0.0838
T_1P_5	1.29^{a}	1.14×10^{-10}	0.993	0.0233	0.0049	0.928	0.0249	1.60	0.81	0.985	0.0400	0.963	0.0621
T_2P_1	1.40^{bcd}	1.30×10^{-10}	0.971	0.0510	0.0051	0.987	0.0078	1.77	0.65	0.988	0.0427	0.946	0.0895
T_2P_2	1.42^{de}	1.58×10^{-10}	0.955	0.0672	0.0061	0.978	0.0130	1.72	0.58	0.986	0.0491	0.933	0.106
T_2P_3	1.45^{e}	2.15×10^{-10}	0.965	0.0597	0.0083	0.985	0.0096	1.14	0.60	0.988	0.0462	0.947	0.0985
T_2P_4	1.43^{de}	2.52×10^{-10}	0.964	0.0616	0.0098	0.991	0.0052	0.97	0.62	0.989	0.0448	0.949	0.0966
T_2P_5	1.42^{de}	2.50×10^{-10}	0.961	0.0657	0.0098	0.994	0.0037	1.02	0.60	0.992	0.0379	0.946	0.101
T_3P_1	1.32^{a}	2.48×10^{-10}	0.961	0.0658	0.0098	0.992	0.0042	1.11	0.65	0.992	0.0362	0.947	0.0932
T_3P_2	1.32^{a}	3.64×10^{-10}	0.982	0.0438	0.0144	0.993	0.0034	0.67	0.70	0.996	0.0261	0.968	0.0708
T_3P_3	1.36^{b}	3.72×10^{-10}	0.958	0.0727	0.0147	0.998	0.0011	0.74	0.62	0.993	0.0356	0.945	0.104
T_3P_4	1.29^{a}	4.78×10^{-10}	0.982	0.0466	0.0194	0.997	0.0011	0.53	0.70	0.996	0.0260	0.973	0.0678
T_3P_5	1.32^{a}	5.21×10^{-10}	0.981	0.0474	0.0203	0.995	0.0024	0.48	0.70	0.993	0.0336	0.969	0.0733

Same letters in columns indicate equilibrium moisture content equal to 0.05 level, of significance by the Tukey test.

increased rate of water uptake k_1 with increasing temperature is an expected behavior of sorption as observed by Lopez et al. (1995) who, when examining water uptake in hazelnut, with temperatures from 15 °C to 30 °C, have found a linear increase of k_1 with increasing temperature. Naviglio et al. (2013) studied the influence of the use of cyclical pressures in the hydration process and flavoring of cannellini beans and obtained the values of $k_1 = 0.1738$ and $k_2 = 0.894$.

According to Turhan et al. (2002), the constant k_2 is related to the maximum capacity of water uptake, i.e., the smaller the value of k_2, the greater the water absorption capacity. The amounts of k_2 presented in this paper are in agreement with those of other cultivars of chickpea in the literature. The mean value for varieties Kaniva, Garnet, and Macareena was 0.89 for temperatures ranging from 25 °C to 42 °C Hung et al. (1993). In this study, the mean adjusted to k_2 was 0.67 (Table 1).

The effects of temperature on feedstock water uptake capacity, i.e., on k_2, varies and depends on the type of feedstock used, and also whether the loss of soluble solids during soaking is taken into account in the calculation of moisture content samples Abu-Ghannam and McKenna (1997b) and Sayar et al. (2001).

Table 1 shows that the numerical solution of the diffusion equation has a good fit to experimental data. Obviously, there were differences among the values estimated by the analytical solution of Fick's second law and by the finite element formulation, since the analytical solution is one-dimensional and considers the spherical geometry. Results on the quality of numeric adjustment and the model of Peleg confirm the values of Waezi-Zadeh et al. (2011), who used the model of Peleg and the finite element method to model water uptake in date fruit. Results from the numerical simulation of the water uptake kinetics by using different temperatures and pressures are described by Naviglio et al. (2013) and Montanuci et al. (2014), who evaluated this process in cannellini beans and barley grains, respectively.

Fig. 2 shows the hydration curves obtained from all treatments, considering the experimental data and the results from the adjust of the analytical model, the Abu-Ghannam and McKenna (1997b) model, the Peleg (1988) model and the two-dimensional numerical solution of the diffusion equation using the finite element method.

Fig. 2 also illustrates the variation in moisture content during hydration and, as expected, it suggests that temperature and pressure influence the mass transfer process. Similar results were obtained by Montanuci et al. (2014) evaluating the barley water absorption and by Ahromrit et al. (2007) who studied the influence of temperature and pressure on starch gelatinization in glutinous rice. All hydration curves have similar behavior characterized by high uptake rate within the first two hours of hydration, followed by a reduction in the rate of water uptake in chickpeas; and this first phase of the process is responsible for about 50% of total grain water uptake. Then the product keeps on absorbing water, but at lower rates. Treatments presented an equilibrium moisture content from 1.29 to 1.45 d.b. and the hydration time reduced with increasing pressure or temperature, results that can be confirmed with the works of Abu-Ghannam and McKenna (1997a), Haladjian et al. (2002), Gowen et al. (2007b) and Prasad et al. (2010).

4.1. Effects of temperature and pressure on water diffusion during soaking of chickpeas

It can be seen in Table 1 an increase of the diffusion coefficient D, when increasing temperature and pressure, illustrating the variation of the natural logarithm of the diffusion coefficient as a function of inverse temperature of hydration expressed by Arrhenius equation for the five pressures studied. By adjusting the linear regression of expression (10) to the experimental data, the D_T and E_a constants were determined. These values are shown in Table 2 along with the corresponding coefficients of determination R^2.

In addition to associate the diffusion coefficient with temperature by using the Arrhenius equation, it is possible to define this coefficient as a function of pressure hydration employing a Eyring equation, by performing a linear regression fit of expression (11) to the experimental data in order to determine the D_P and ΔV constants, which are shown in Table 3 along with the values of R^2, illustrating the variation of the diffusion coefficients as a function of pressure hydration.

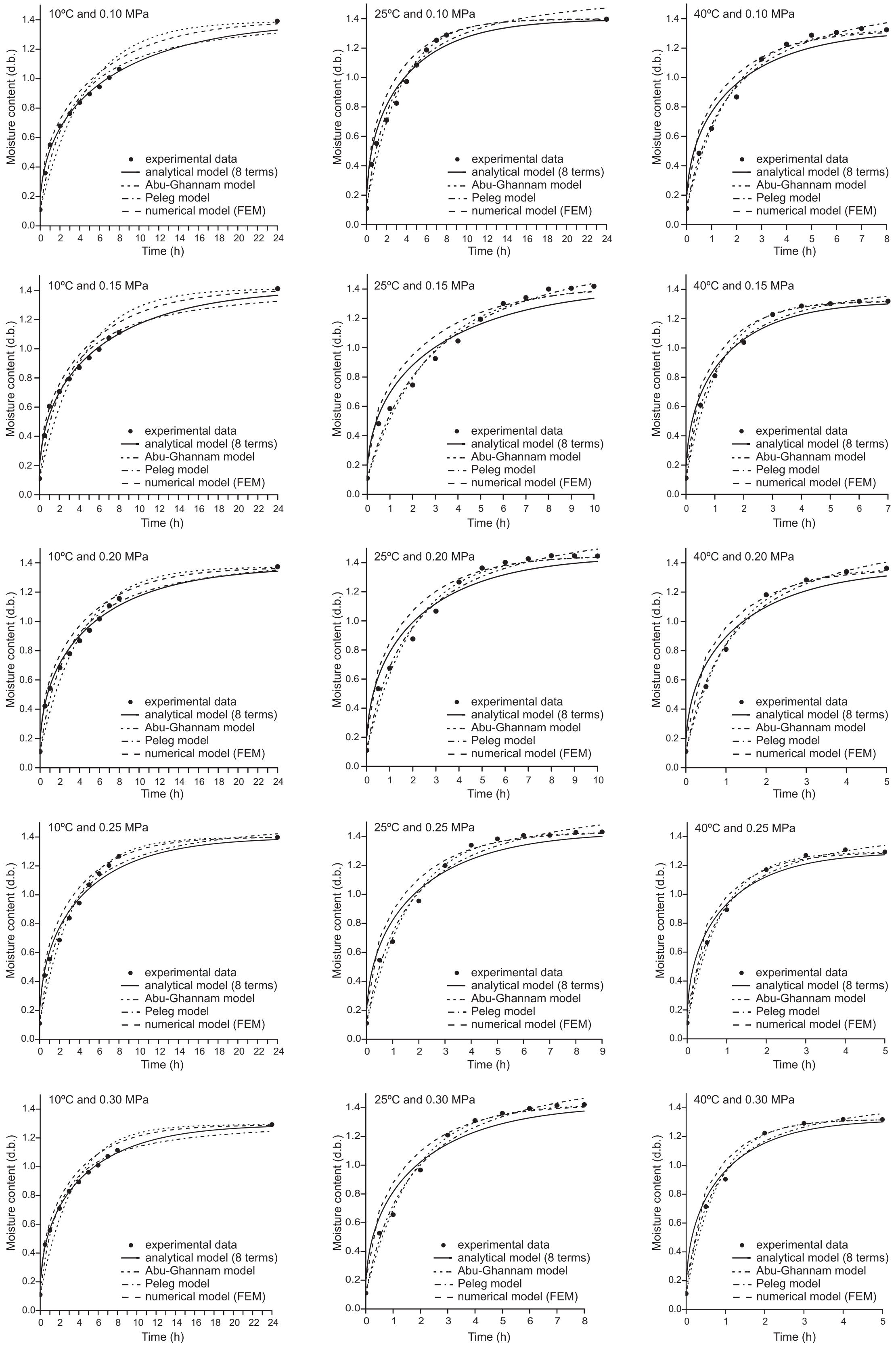


Fig. 2. Water uptake curves.

As seen in Table 2, there is a linear dependence between the diffusion coefficient and the hydration temperature for different pressures. It is evident the contribution of the pressure in the hydration kinetics since the isobaric curves maintain a similar slope expressed by a similar activation energy, E_a, but different linear coefficients, which are the D_T constants.

Table 2
Values found of $D_T \times 10^{-4}$ and E_a.

Absolute pressure (MPa)	D_T (s^{-1})	E_a (kJ mol^{-1})	R^2
0.10	0.213	29.638	0.995
0.15	3.801	36.184	0.989
0.20	1.749	33.895	0.992
0.25	3.879	35.365	0.998
0.30	9.056	34.337	0.999

Although the low pressures used in the experiments are consistent with those used in domestic cooking, the temperatures used were limited to the range of 10–40 °C mitigating the gelatinization process. From Table 2, it can be noticed that the activation energy, E_a, a presented values between 29.638 and 36.184 kJ mol^{-1}, whereas diffusion coefficients showed larger variations in treatments with equal pressures and different temperatures, as can be seen in Table 1. It is important to observe that the E_a values seem to present a clear relationship with the variation of pressure. On the other hand, Table 3 shows a decrease of the activation volume ΔV, when increasing temperature. Ahromrit et al. (2007) obtained different results for E_a and ΔV when using high pressure systems in the evaluation of starch gelatinization of glutinous rice.

The result of the combined effects of pressure and temperature on diffusion coefficient are shown in Fig. 3, which represents a fit surface for the natural logarithm values of the diffusion coefficient as a function of the set of absolute values of temperature and pressure of hydration. This result was obtained by relating the variation of the natural logarithm of the diffusion coefficient, D, shown in Table 1 with the Arrhenius–Eyring equation, expressed in (12), and determining the $E_a, \Delta V$ and D_0 values through multiple linear regression to the experimental data with the Statistica 10 software.

According to the surface shown in Fig. 3, the nonlinear regression analysis based on the Eq. (12) had a good fit to the experimental data from the 15 treatments examined, having as correlation coefficient $R^2 = 0.983$. The Arrhenius–Eyring type equation expressed by (12) is written specifically for any of the conducted treatments, considering a particular temperature and pressure of hydration on the following form:

$$\ln D = -8.429 - \left(\frac{36040.01}{8.314}\right)\frac{1}{T} - \left(\frac{-7724.65}{8.314}\right)P \tag{15}$$

As noted in Eq. (15), the activation energy for the liquid diffusion of chickpeas was 36.040 kJ mol^{-1}, the activation volume was -7.724×10^3 cm^3 mol^{-1} and the value of D_0 was 2.184×10^{-4}, which are values close to those found by Yildirim et al. (2011) who have found 28.69 kJ mol^{-1} for the activation energy of chickpeas, in temperatures below 61.47 °C. Ahromrit et al. (2007) evaluated the starch gelatinization of glutinous rice during hydration at different temperatures and pressures and found D_T values between 5.609 and 69.276 s^{-1} and E_a values between 30.456 and 34.240 kJ mol^{-1}, considering temperatures between 20 and 70 °C. The authors also showed values of D_P between 1.131×10^{-5} and 6.560×10^{-5} s^{-1} and ΔV varied from -7.064 to -11.816 cm^3 mol^{-1}, when considering pressures between 300 and 600 MPa. When studying the influence of temperature on the hydration process of legumes, Seyhan-Gürtas et al. (2001) have found activation energy values from 48.6 to 49.8 kJ mol^{-1} for chickpeas. In another work, activation energy ranged from 48 to 18 kJ mol^{-1} in temperatures below and above 55 °C, respectively Sayar et al. (2001). Prasad et al. (2010) have found values of activation energy from 22.49 kJ mol^{-1} to 22.70 kJ mol^{-1} for chickpeas subjected to hydration within 40 °C to 60 °C, which is higher than for other grains, and according to these authors, this is probably due to the compact structure of the cotyledon in chickpeas. Gowen et al. (2007b) have reported values of activation energy for chickpeas subjected to blanching pre-treatment of 41.79 ± 4.83 kJ mol^{-1}, for samples hydrated at temperatures below 37 °C and 8 kJ mol^{-1}, for samples hydrated at temperatures above 37 °C. The increased pre-exponential factor D_0 compared to the works of the authors cited above may be justified by increased pressure in the system, resulting in greater fraction of collision.

Table 3
Values found of $D_P \times 10^{-10}$ and ΔV.

Temperature (K)	D_P (s^{-1})	$\Delta V \times 10^3$ (cm^3 mol^{-1})	R^2
283	0.588	−5.534	0.951
298	0.954	−8.829	0.912
313	1.896	−9.185	0.919

The results show that the combined effect of temperature and low pressure during the hydration process increases the diffusion coefficient reducing the time of hydration of the product. This behavior is typical of the first stage of hydration and can be seen, for example, in curves of hydration treatment T_3P_1(40 °C and 0.10 MPa) and T_2P_5(25 °C and 0.30 MPa), although they have different temperatures and pressures, resulting in diffusion coefficients very close, 2.48×10^{-10} and 2.50×10^{-10} m^2 s^{-1}, respectively. This is an indication that the diffusion coefficient also depends on the pressure of hydration and not only the temperature of hydration, supporting the Arrhenius–Eyring formulation shown in (12). As highlighted by Naviglio et al. (2013) the pressurization and depressurization produce impulsive forces which allow the opening of new channels within the grain increasing the speed of water absorption. Even if the pressure is kept constant during hydration, it can be observed a significant increase in initial rate (up to 1 h) of water absorption in the grain.

The analytical model described by Fick's second law, the model of Abu-Ghannam and the model proposed by Peleg presented a good adjustment to the experimental data. The value of fraction of collision $D_0 = 2.1846 \times 10^{-4}$ was higher when compared to the same parameter adjusted through the traditional Arrhenius equation, which does not take pressure into account. This may be due to increased pressure in system with constant volume, which consequently favors molecule contact and higher frequency of collision.

4.2. Numerical solution

The numerical solution of the two-dimensional diffusion equation analogous to the Eq. (4), in domain with very similar geometric shape to the real grain cross section, was obtained from the pde toolbox environment, implemented in the Matlab 2011 software. It has also presented a good adjustment to the experimental results, which can be noted on the hydration curves of the product and on the coefficients of adjustment. Fig. 4 illustrates results of the numerical simulation of the hydration process in chickpeas for treatment T_1P_1 (10 °C and 0.10 MPa).

Comparing the results matrix, i.e., the data obtained from simulations for different geometries and the results shown in Fig. 5, it was found that the use of the discretized domain shown in Fig. 1, which most appropriately describe the current profile of the product, provides a profile for better mean moisture content compared with the homogeneous case, and closer to the experimental results, as shown in Table 1. These results are obtained by employing in the numerical solution (FEM), (13), the same diffusion coefficient than the one obtained by a nonlinear regression analysis and used in the analytical model, (4).

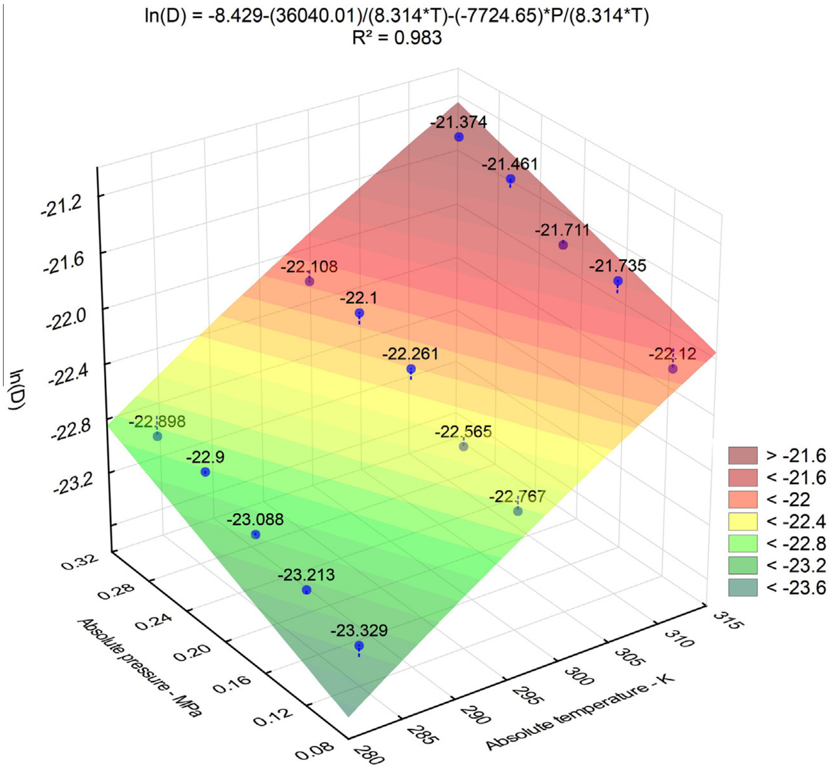


Fig. 3. ln(D), as a function of absolute temperature (T) and absolute pressure of hydration (P).

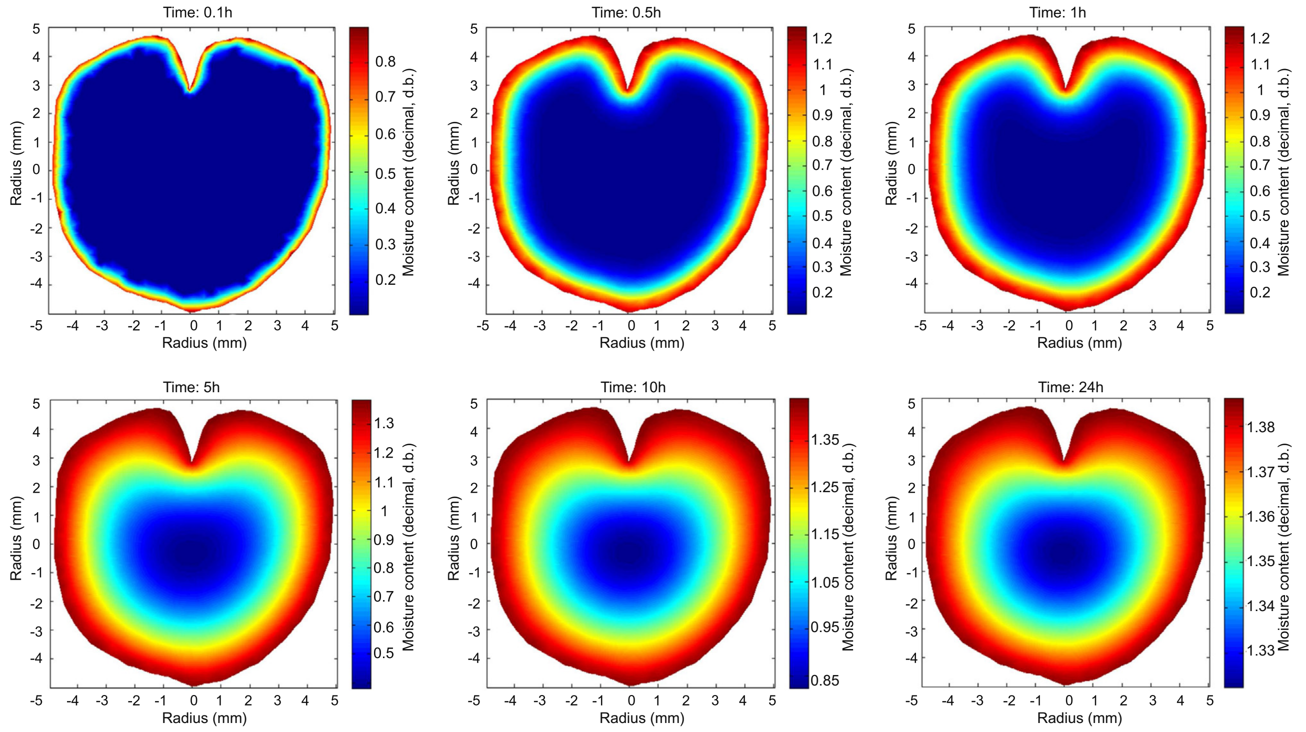
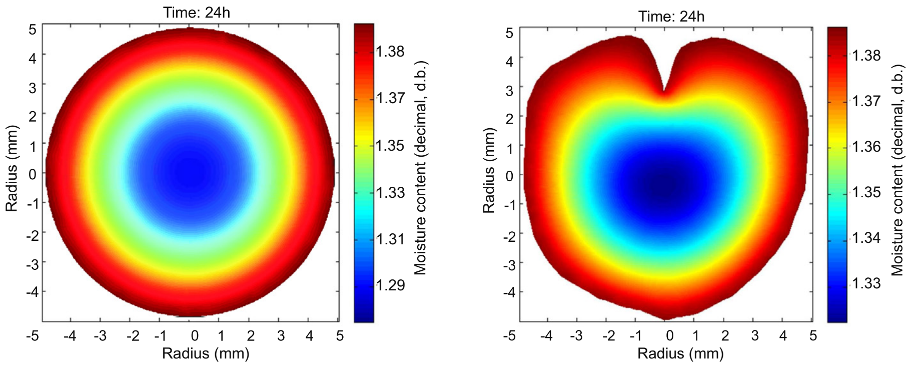


Fig. 4. Simulation of hydration in chickpea using the finite element method – 10 °C and 0.10 MPa.

These statements are corroborated by the relative error (ER). Denoting the average value of the moisture content of the numerical solution of spherical geometry by M_{sph}, and the average value of the moisture content of the numerical solution of non-spherical geometry by M_{nsph}, the accuracy of these solutions and the analytical model, M_{an}, when compared with the experimental data, M_{exp}. Table 4 shows these results for the T_3P_5 treatment, and the other treatments have similar comparative results.

As it can be seen in Table 4, the relative error when the hydration process tends to the equilibrium for the said treatment,



(a) Spherical geometry.

(b) Non spherical geometry.

Fig. 5. Comparison between different geometries for hydration in chickpea using the finite element method considering the same diffusion coefficient, $D = 7.38 \times 10^{-11}$ m/s^2 and the same time hydration, $t = 24$ h, for the treatment T_1P_1 (10 °C and 0.10 MPa). The spherical geometry contains 1724 elements, while the non-spherical geometry has 1668 elements.

Table 4
Relative error of numerical solutions with spherical and non-spherical geometries and analytical solution, to the experimental moisture values (d.b.), for the T_3P_5 treatment – (40 °C and 0.30 MPa).

Time (h)	M_{sph} (d.b.)	M_{nsph} (d.b.)	M_{an} (d.b.)	M_{exp} (d.b.)	ER_{sph} (%)	ER_{nsph} (%)	ER_{an} (%)
0	0.124	0.131	0.202	0.110	12.731	18.623	82.899
0.5	0.727	0.826	0.750	0.714	1.804	15.721	5.064
1	0.942	1.030	0.947	0.904	4.252	13.969	4.717
2	1.162	1.216	1.156	1.224	5.081	0.638	5.578
3	1.255	1.281	1.263	1.292	2.911	0.868	2.260
4	1.292	1.304	1.321	1.320	2.086	1.166	0.112
5	1.307	1.313	1.353	1.318	0.856	0.418	2.612

reached at $t = 5$ h, the combined effect of temperature at low pressure leads to results whose relative error was 2.612% smaller, indicating that the solutions provided for this chickpeas hydration study are acceptable. In addition, it can also be noted from Table 4 that the larger difference to the initial condition refers to the analytical solution (5) since at $t = 0$, it results the sum of the first 8 terms of the analytical solution, plus the contributions of the initial and equilibrium moisture contents, which provides a poor estimate to the initial condition. Moreover, it can be seen that the numerical solution of non-spherical geometry has a monotonic behavior in the initial measurements of hydration, converging to the experimental data for times closer to those of equilibrium.

4.3. Weibull analysis

Table 5 shows the scale and shape parameters adjusted to experimental data measured for different evaluated temperatures and absolute pressures of hydration.

As seen in Table 5, the mean values set for the shape parameter, β, was equal to 0.846 indicating that the mechanism of water absorption can be considered mainly diffusive (Cunha et al., 2001). Furthermore, with increasing temperature and pressure there is a trend of parameter β to value 1, indicating that the phenomenon can be represented by first-order kinetics. The scale parameters, α, presented decreasing values between 4.999 h and 0.813 h, indicating a reduction in the length of time required to achieve 63% of total moisture for the evaluated treatments, in accordance with the increase of temperature or pressure, and hence of rate of absorption. Kliger et al. (2011), found values of $\alpha = 2.38\ \text{h} \pm 0.37$ and $\beta = 0.77 \pm 0.11$, respectively, to evaluate the kinetics of water absorption in chickpea seeds. In Ghafoor et al. (2014) assessed the effects of ultrasound application in the navy beans hydration kinetics, and found values of $\alpha = 12719.87$ s (≈ 3.53 h) and $\beta = 1.13$ for control and $\alpha = 7964.79$ s (≈ 2.21 h) and $\beta = 1.26$, for hydration with sonication, respectively. Rafiq et al. (2015), by studying the influence of drying temperature and hydration on the kinetics of water absorption in parboiled rice, reported values of α and β between 48.45 min (≈ 0.8075 h) and 165.19 min (≈ 2.7532 h), and 0.6120 and 0.8930, respectively. Prasad et al. (2010), evaluated the influence of temperatures between 40 and 60 °C on the hydration kinetics of chickpea splits and the α values remained between 0.2730 h and 0.5060 h and β values between 0.9312 and 0.9638.

5. Conclusions

In this work, we have examined the behavior of chickpea water uptake curves subjected to different temperatures and pressures of hydration. In addition, it was possible to determine the grain liquid diffusion coefficient, as well as the activation energy E_a, the activation volume ΔV, and fraction of collisions, D_0, during hydration, employing the Arrhenius–Eyring type equation to explain the dependency of the diffusion coefficient on temperature and pressure of hydration.

Although the numerical solution has provided a considerable approximation to the experimental data, this study did not consider the influence of the volume variation (swelling) of the

Table 5
Weibull parameters fitted to experimental moisture content data.

Parameters	10 °C					25 °C					40 °C				
	0.10 (MPa)	0.15 (MPa)	0.20 (MPa)	0.25 (MPa)	0.30 (MPa)	0.10 (MPa)	0.15 (MPa)	0.20 (MPa)	0.25 (MPa)	0.30 (MPa)	0.10 (MPa)	0.15 (MPa)	0.20 (MPa)	0.25 (MPa)	0.30 (MPa)
α	4.999	4.485	3.999	3.365	3.256	3.181	2.657	1.971	1.686	1.697	1.716	1.131	1.140	0.877	0.813
β	0.638	0.612	0.698	0.771	0.629	0.865	0.893	0.898	0.953	0.973	0.961	0.869	1.075	0.927	0.921
R^2	0.989	0.989	0.990	0.990	0.996	0.992	0.982	0.985	0.992	0.994	0.992	0.996	0.999	0.998	0.995

product throughout the hydration process. This factor, associated with a variable diffusion coefficient over time, geometric conformations and boundary conditions more appropriate to the product, are considered to be relevant to the mathematical modeling of moisture diffusion in agricultural products and they are being investigated. Furthermore, a solution by the finite element method (FEM) has been considered in order to resolve a representative spatial discretization of the grain used in the assessment of the hydration process, although the system presented in Luikov (1966) has not been solved in this study. Therefore, in terms of space–time evolution, the numerical solution provides a significant approximation for the variation of the moisture content inside the product, whose distribution depends on temperature and pressure, which are the variables considered in the model.

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