Modelling mass transfer during water absorption of closed mouth pistachios

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Abstract: This study was undertaken to analyze the kinetics of water absorption and to derive an equation for the rate at which water is absorbed by closed mouth pistachios. We used Kaleh_ghoochi, the major variety of Iranian pistachios. The water-absorption rate equation of closed mouth pistachios between 5 ℃ and 25 ℃ was presumed based on the Peleg equation. The Peleg coefficients k_1 and k_2 were negligible changed with water temperature depending on the product and can be useful in estimating approximate immersing time and temperature for splitting mouth of pistachios.

Keywords: pistachios, water absorption, Peleg equation, modelling

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1 Introduction

Pistachio (Pistachio vera L.) is an important agricultural production in Iran. In 2013, Iranian farms produced 478,600 tons of pistachios (TNA, 2015) and only earned 149 million euros by exportation in first half of 2015 to European Community countries (FAOSTAT, 2015). Pistachio nuts are cultivated in grape-like cluster and an exterior hull encases each nut. When fully grown the hull turns rosy and the inside shell splits, signifying that the nut is ready to be harvested (Kouchakzadeh, 2013).

Pistachio shells crack open naturally once they ripen (smile pistachio), but sometimes the shell splits without breaking (Figure 1). These, also, are considered lower in quality or from trees that were not well maintained and or irrigated. Over one third of crop yields were not split open naturally after ripening. Frequently, closed pistachios are cracked open by mechanical methods. First, unsplit pistachios were hammered by machine to make small cracks. This process takes 10-14 days of working time for 25 tons of pistachios load. Then the pistachios were washed and steeped in water for about five hours in stainless steel silos. At this step, nuts have reached to the softest peel and could be cracked open by thermal shocking. Then, the nuts were sent off to dryers where pistachios in bulk expose hot air at the temperature of 90 ℃ to reach about 5% of moisture content. Such a process for 25 tons of pistachios with the approximately volume of 55 m^3 takes three to four days and consumes about 3500 MJ heat energy that is supplied by gas torches and 40 kilowatts hour electricity (Kouchakzadeh, 2013). With none hammering process, the nuts should be steeped in cold water for 24 h and when reached to the softest peel, could be cracked open by thermal shocking. So, the nuts were sent to dryers where pistachios in bulk expose hot air at the temperature of 90 ℃ to reach about 5% of moisture content.

Figure 1 Smile and closed mouth pistachios

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The most difficulty part of this method is the inability of fast cutting moisture content to about 5%, which can produce conditions in with Aflatoxin (fungal metabolites showing toxin) growth. Thermal shock conditions are produced by rapidly moving the pistachios between two temperature extremes, and usually require that the transition time between the extremes is short, thereby creating a shock condition. Pistachios must remain at an extreme temperature before reaching equilibrium which can vary in a few minutes, depending on the method of producing the temperature extremes, the capacity for heat transmission, and the mass of the pistachios. The most used methodologies for producing thermal shock environments are hot-air thermal shock systems using separate chambers and a mechanism to move the pistachios between the chambers. Although these chambers are readily available, they are slow to operate and provide a low heat exchange rate to the pistachios.

By lowering or eliminating features such as hammering process that are costly and delaying to produce, the pistachios openings process will be able at lower costs to improve quality with low risk of Aflatoxin growth. Figure 2 shows the schematic diagram of these processes (Kouchakzadeh, 2013).

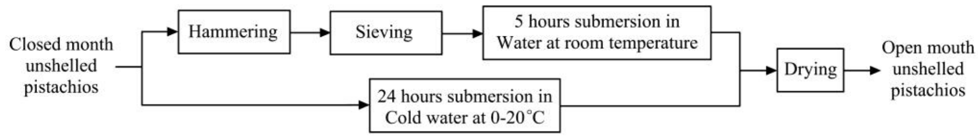

Figure 2 Water openings method of pistachios mouth

Comprehension water absorption in pistachio during immersing is useful because it restrains the following operations and quality of the final product. So, modeling water transfer during soaking has attracted consideration. Mathematical models may be used to characterize the drying and rehydration processes and shows the significance of the different factors governing moisture transfer. Moreover, the models can provide a method for the optimization of the different factors affecting the dehydration and rehydration conduct of the in-shell seeds and help in the processing and later the growth of quality value-added products.

Wet basis moisture content is described by the equation as:

$$M = \frac{W_w}{W_t} = \frac{W_w}{W_w + W_d} \tag{1}$$

Where, M is moisture content (kg water/kg matter); W_w, W_d and W_t are the weight of water (kg), weight of dry matter (kg) and the total weight of the material (kg), respectively. The hydration kinetics can be described using empirical and theoretical models. For describing the moisture diffusion of different seeds has been used the Fick's second law of that expresses the diffusion of a liquid in a solid can be written as (Brooker et al, 1992):

$$\frac{\partial M}{\partial t} = D_{eff}\left(\frac{\partial^2 M}{\partial r^2} + \frac{j\partial M}{r\partial r}\right) \tag{2}$$

where, D_{eff} is the diffusivity; M is the moisture content at any time; r is the radial coordinate; t is the time and j is the coefficient; when j is equal to 0 for an infinitive slab, 1 for a cylinder and 2 for a sphere. The solution to the equation above was given as (Kouchakzadeh, 2011):

$$\frac{M - M_e}{M_0 - M_e} = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{(-n^2\pi^2 tD_{eff}}{r^2}\right) \tag{3}$$

where, M_0 is initial moisture content (kg water/kg matter); M_e is dynamic equilibrium moisture content (kg water/kg matter) at the beginning of falling rates; r is the radius of dry material and D_{eff} is the diffusivity coefficient in pistachio nut. The moisture ratio may be simplified to M/M_0 rather than $(M-M_e)/(M_0-M_e)$ because of the value of dynamic equilibrium moisture content M_e is very small compared to M and M_0 (Kouchakzadeh and Shafeei, 2010).

Temperature is one of the parameters affecting the diffusivity of a foodstuff. The dependence of diffusivity on temperature is described by the Arrhenius type relationship:

$$D_{eff} = D_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where, D_0 is a constant (m^2 s^{-1}); E_a is activation energy (kJ mol^{-1}); R is gas constant (8.314 J/mol K), and T_0 is absolute temperature (K).

The water absorption of foods is decided by permitting a dry sample to absorb moisture. The equilibrium moisture is determined by periodically weighting the sample up to the time a constant weight is reached. The data of taking up and holding by absorption in the form of sample's moisture vs. time have been explained by mathematical models. A model to depict water sorption processes is empiric Peleg model which is defined by Peleg (1998):

$$M = M_0 + \frac{t}{(K_1 + K_2 t)} \tag{5}$$

where, K_1 is the Peleg rate constant (h, kg matter/kg water), and K_2 is the Peleg capacity constant (kg matter/kg water).

The rate of sorption R can be got by derivative of the Peleg equation:

$$R = \frac{dM}{dt} = \frac{K_1}{(K_1 + K_2 t)^2} \tag{6}$$

The Sorption processes in different foods have been described by Peleg model. Turhan et al. (2002) applied the model for studying water absorption of chickpea during soaking. Lazaro and Favier (2005) investigated the applicability the Peleg equation on water absorption in sorghum and millet during tempering. Corzo and Bracho (2006) used it for describing mass transfer during osmotic dehydration of sardine sheets. Salimi Hizaji et al. (2010) studied the effect of water temperature and storage time on rehydration kinetics of air dried potato cubes using the model. The Peleg model was also exploited to model mass transfer during osmotic dehydration of apple in sugar beet molasses (Misljenovic et al., 2011). Checmarev et al. (2013) analyzed the applicability of Peleg model to the cooking-infusion of mackerel slices. Pavelkic et al. (2015) studied suitability of Peleg model on mass transfer kinetics during osmotic dehydration of pear cubes in sucrose solution. In these reports mostly the fit of the model was looked at various temperatures during cooking or curing steps. We have not found any research on modelling or equation about soaking of unshelled pistachios at cold temperatures that confine in closed mouth immersing process. So the purposes of this study were to investigate the moisture absorption by immersion of the pistachio closed mouth nuts under many temperatures and to appraise proper models that behavior.

2 Materials and methods

The fresh pistachios from Kaleh_ghoochi the major variety for exporting were used in this research. The unshelled closed mouth Pistachio nuts with the length from 10 to 12 mm graded by experts were got from local market Kermanshah province; Iran, during harvesting season in September 2014. The samples were collected after dehulling process; for each test, 100 pistachios were selected, stored in plastic bags, and placed in a refrigerator for future use. The initial moisture contents of pistachios samples were determined by oven drying at the temperature of 130℃ for 6 h according to a standard ASABE method (2005). First 100 closed mouth nuts weighted by a laboratory weighing platform (Model AB204, Mettler-Toledo AG, Switzerland) and then immersed in water and kept in cooled incubator (Model IPP 400, Memmert, Germany) for 24 h at temperatures 5℃, 10℃, 15℃, 20℃ and 25℃. After every 1h, samples were removed from the incubator, passing through rinse and dried with a towel to measure weight rising. After weighing the pistachios were returned to the incubator and left untouched for next 1h. All experiments were done in triplicates. The recorded weights then computed as nonlinear regression analysis with statistical computer program. The acceptability of Peleg models were determined by the coefficient of determination R^2, and the reduced value of mean square of deviation χ^2. The reduced chi-square can be calculated by Kouchakzadeh and Shafeei (2010):

$$\chi^2 = \frac{\sum_{i-1}^{n} (M_{\exp,i} - M_{pre,i})}{N - n} \tag{7}$$

where, $M_{\exp,i}$ is the experimental moisture content; $M_{pre,i}$ is predicted moisture content; N is number of observation, and n is number of constants.

3 Results and discussion

The moisture content of products as a function of immersing time is presented in Figure 3. It showed a characteristic absorption behavior at all temperatures. As is shown in Figure 3, the closed mouth pistachio's moisture contents after 24 h rise from about 0.4270 to

0.4539, 0.4566, 0.4591, 0.4639, and 0.4720 kg water/kg matter at water temperatures of 5℃, 10℃, 15℃, 20℃ and 25℃, respectively. The rate of sorption in various temperatures during immersing is shown in Figure 4. It was observed that sorption rates have three stages, first the moisture content rapidly rose with high slope vs. time and then decreased quickly with rise in soaking time and at last have very similar low-slope. In the first four hours, the maximum absorption rate lifted to 0.46 kg water/kg matter at 25℃, but afterwards in the next 21 hours reduced to 0.03 kg water/kg matter. During the first period, the rate of moisture content absorption from the surface is dependent on condition of places where soaking is occurred, but in the next stages the moisture migration from the surface to enter layers of products, and this stage is dependent on the rate of diffusion of moisture from in the external skin surface of nut to the kernel and moisture transfer interior of the kernel. The external factors and internal mechanism controlling the soaking process in four rate regimes are important in determining the saturation rate of products. The rate of water sucking up depends on temperature and the difference between water content at saturation with that at a given time, which acts as the driving force. Transition between the primary and secondary and final stages occurred after soaking. As expected for a thermally activated process, as the soaking water temperature was increased, the initial slope of the water intake curve increased, and the time taken to achieve equilibrium moisture content consequently decreased.

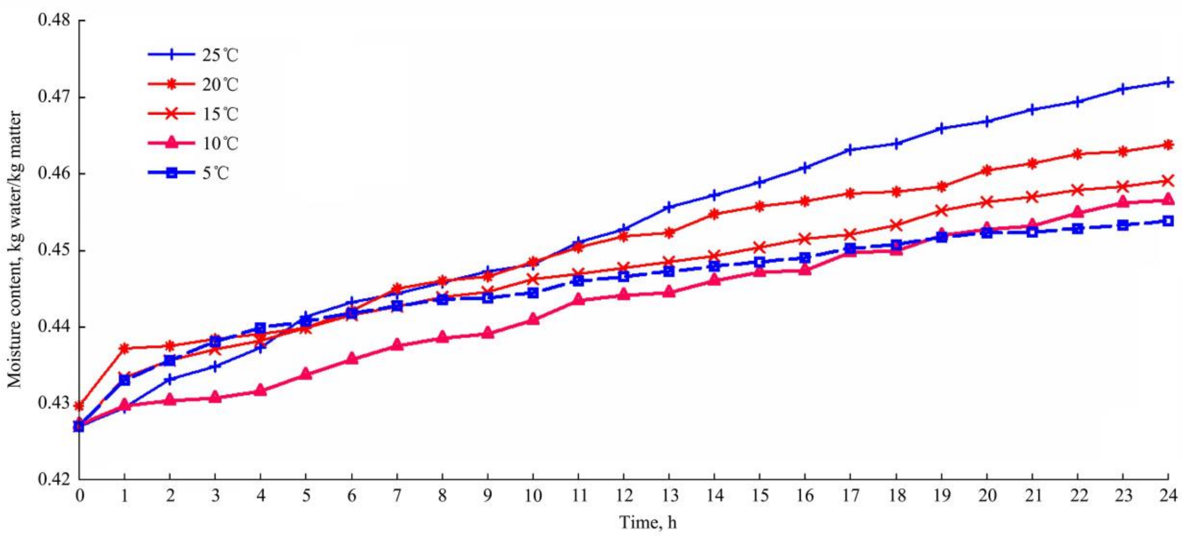

Figure 3 Moisture contents of immersed pistachios vs. time

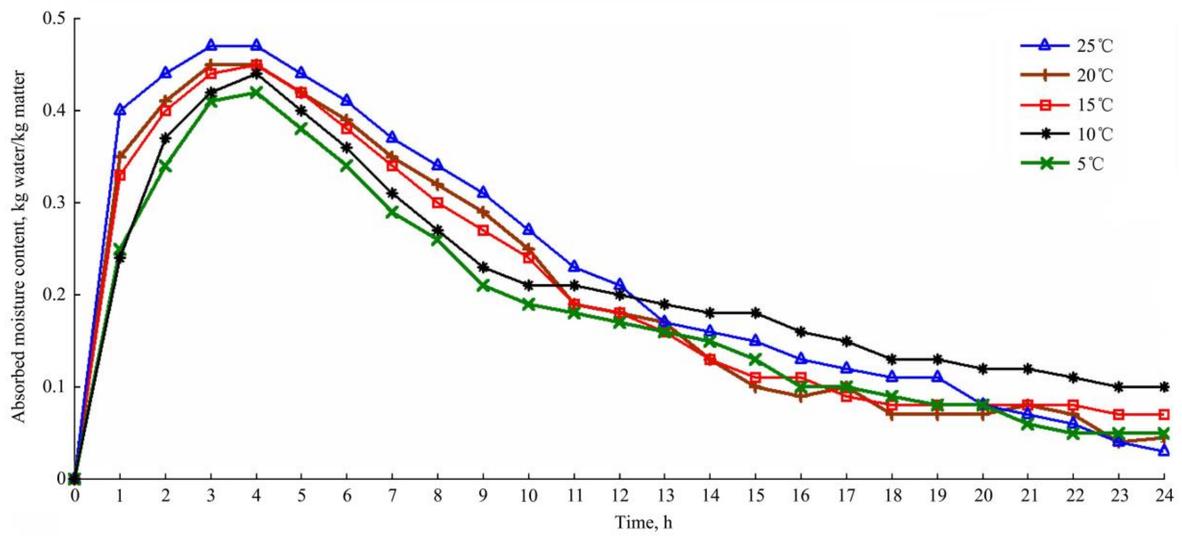

Figure 4 Moisture absorbed at various temperatures during immersing

3.1 Mathematical modelling

The fit of the Peleg equation (Equation (5)) by non-liner regression analysis was tested using data in any temperatures. Table 1 shows the Peleg rate and capacity constant, the values of coefficients of determination and reduced the value of mean square of deviation. k_1 is a constant that shows mass transfer rate, and the lower the k_1 is, the higher the initial water absorption rate becomes. Closed mouth pistachios did not show high difference in k_1 at all water temperatures. The average of k_1 was calculated as 0.17203 h kg matter/kg water with the standard deviation of 7×10^{-6} h kg matter/kg water. Increasing water absorption rate or reducing k_1, with growing temperature was expected. No literatures about pistachios immersing were founded. Zomorodian and Tavakoli (2010) studied the adsorption of pistachios nuts at constant temperature of 50℃, in humid air with relative humidity of 36% to 75% and did not used Peleg equation. Lopez et al. (1995) reported the k_1 linearly increased with raising temperature during water absorption of hazelnut kernels between 15℃ and 30℃. k_2 is a constant suggested to maximum water absorption capacity, the lower the k_2 resulted the higher water absorption capacity. The average of k_2 was calculated as 0.000581008 kg matter/kg water with the standard deviation of 3.85×10^{-6} kg matter/kg water. A low standard deviation shows that the Peleg rate and capacity constant are closely around the mean and water temperatures variation does not affect significantly. Effect of temperature on water absorption of foodstuffs is blended and depends on the type of foods and if soluble parts loss during immersion is important in the calculation of moisture content of samples. Some researchers reported no effect of temperature on k_2 in water absorption studies using the Peleg model (Sopade et al., 1992), (Sopade et al., 1994), (Maharaj and Sankat, 2000), (Turhan et al., 2002). But k_2 values were not always constant with temperature such as unhulled peanut between 2℃ and 40℃ (Sopade and Obekpa, 1990), grape cane (Karacabey et al., 2013), barley between 10℃ and 35℃ (Montanuci et al., 2013) and for corn kernel (Botelho et al., 2013). The model can be employed to predict successfully, or at least estimate, long rage moisture gains from empirical data acquired in tests of proportionately short duration. The predictions, it is necessary to be added, depending on the test duration itself, and the values arrived at regression of data obtained during experiments. Naturally, the predictions would improve if more data were included but with an error less than 0.1% (Bello et al., 2004). It needs to be remembered, however, as expressed in Peleg equation is only empirical model that was not derived from any set of physical laws or diffusion theories. Despite its showed success, therefore, its general applicability cannot be taken for granted. As for the equilibrium moisture contents, the model predictions, as previously stated, are significantly higher than those based on the assumption that true equilibrium is reached after 24 h.

Table 1 Modeling of Peleg equation according to immersing time for pistachios

Water temperature, ℃	5	10	15	20	25	Average	STDEV
k_1, h kg matter/kg water	0.0017203	0.0017203	0.0017204	0.0017203	0.0017202	0.0017203	0.00000007
k_2, kg matter/kg water	0.0581065	0.0581072	0.0581113	0.0581085	0.0581008	0.0581069	0.00000385
R^2	0.93936	0.96950	0.86644	0.93888	0.97642	0.93812	0.043565
χ^2	0.26062	0.1818	0.26493	0.22527	0.22501	0.23153	0.033603

4 Conclusions

The Peleg model will be able to characterize water absorption of closed mouth pistachios between 5℃ and 25℃. The Peleg coefficients k_1 and k_2 were negligible changed with temperature depending on the product and can be useful in estimating approximate immersing time and temperature for splitting mouth of pistachios. For the results, by substituting the average values of k_1 and k_2 in Equations (5) and (6), the Peleg model and rate of sorption in soaking process of closed mouth Kaleh_ghoochi pistachios is presented as:

$$M = M_0 + \frac{t}{(0.0017203 + 0.0581069t)} \quad (8)$$

$$R = \frac{0.0017203}{(0.0017203 + 0.0581069t)^2} \quad (9)$$

Equations (8) and (9) are valid for temperatures between 5℃ to 25℃, moistures in dry basis and time in hour.

According to the above mentioned results, water immersing for 4 h at 25℃ could lift up the moisture content of closed mouth pistachios to maximum 0.46 kg water/kg matter plus initial moisture. It seems that this raise is not the main cause of splitting pistachios nuts and a major factor would be the cooling process before thermal shocking.

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