

Water Diffusion Coefficients of Selected Legumes Grown in Turkey As Affected by Temperature and Variety

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Received: 14.01.2000

Abstract: The kinetics of water absorption by chickpeas (Koçbaşı, Kuşbaşı), lentils (green Pul) and beans (Battal, Dermason, Horoz, Şeker) grown in Turkey were studied by a gravimetric method during soaking at 15, 25 and 40°C to determine moisture diffusivity of these selected legumes. The water diffusion coefficients of the legumes were in the range $9.71 \times 10^{-11} - 5.98 \times 10^{-10} \text{ m}^2/\text{s}$ for the chickpeas, $3.53 \times 10^{-10} - 1.33 \times 10^{-9} \text{ m}^2/\text{s}$ for the lentils and $4.35 \times 10^{-11} - 3.79 \times 10^{-9} \text{ m}^2/\text{s}$ for the beans. An Arrhenius-type equation described the strong temperature effect on the diffusion coefficient with activation energies of 48.6-49.8 kJ/g-mol for chickpeas, 39.7 kJ/g-mol for lentils, and 33.6-50.8 kJ/g-mol for beans. It was shown that a satisfactory prediction of water absorption during soaking of the selected legumes was possible by using the analytical solutions to Fick's law of diffusion.

Key Words: diffusion coefficient, chickpeas, lentils, beans, soaking, modeling

Türkiye'de Yetiştirilen Bazı Baklagillerin Su Difüzyon Katsayılarına Sıcaklık ve Çeşit Etkisi

Özet: Bu çalışmada ülkemizde yetiştirilen nohut (Koçbaşı, Kuşbaşı), mercimek (yeşil Pul) ve fasulye'nin (Battal, Dermason, Horoz, Şeker) 15, 25, ve 40°C'da ıslatma işlemi sırasında su absorplama kinetiği gravimetrik olarak incelenmiştir. Baklagillerin su difüzyon katsayıları nohut için $9.71 \times 10^{-11} - 5.98 \times 10^{-10} \text{ m}^2/\text{s}$, mercimek için $3.53 \times 10^{-10} - 1.33 \times 10^{-9} \text{ m}^2/\text{s}$ ve fasulye için $4.35 \times 10^{-11} - 3.79 \times 10^{-9} \text{ m}^2/\text{s}$ aralığında değişmiştir. Sıcaklığın difüzyon katsayısına güçlü etkisi Arrhenius denklemi ile ifade edilmiş ve aktivasyon enerjileri nohut için 48.6-49.8 kJ/g-mol, mercimek için 39.7 kJ/g-mol ve fasulye için 33.6-50.8 kJ/g-mol olarak bulunmuştur. Bu çalışmada incelenen baklagillerin ıslatma işleminde absorpladıkları su miktarlarını, Fick difüzyon denklemi ile, tatminkar bir doğrulukla, hesaplanın mümkün olduğu gösterilmiştir.

Anahtar Sözcükler: Difüzyon katsayısı, nohut, mercimek, fasulye, ıslatma, modelleme

Introduction

Turkey produces significant quantities of legumes mainly comprising chickpeas, lentils and dry beans. The production figures were, in metric tons, about 730 000 for chickpeas, 615 000 for lentils and 225 000 for dry beans which, respectively, accounted for 8.34%, 21.96% and 1.22% of the global production of these legumes in 1996 (FAO, 1996).

Whether used at home to prepare a variety of Turkish dishes or in commercial practice (e.g., canning), dry legumes need to be rehydrated by soaking in water or salt solutions before further processing. Soaking is considered necessary to achieve desired palatability and digestibility and to reduce cooking time, but its long duration has been, and continues to be, a major drawback (Deshpande et al., 1989). Researchers have already demonstrated that increasing the temperature of the

soaking medium is an effective way to accelerate water uptake by various seeds and hence, to shorten the soaking time (Quast and de Silva, 1977; Kon, 1979; Sopade and Obekpa, 1990; Thakor et al., 1995 and Abughannam and McKenna, 1997). In sorption process and equipment design it is highly desirable and of practical importance to predict the moisture gain by legumes as a function of time and temperature. This, however, depends on the availability of moisture diffusivity data for the variety being considered.

The water absorption kinetics of dry legumes during soaking has been described either by a two-parameter empirical Peleg model (Peleg, 1988) or by analytical expressions derived from Fick's law of diffusion (Hsu, 1983 and Tang et al., 1994). Although the empirical model is simple to apply and has been shown to successfully describe the water absorption behavior of

various legumes (Sopade and Obekpa, 1990 and Hung et al., 1993), it is not, however, derived from any set of physical laws or diffusion theories (Peleg, 1988).

Data on chemical composition and physical characteristics of legumes grown in Turkey are available (Gürses, 1981 and Keskin, 1975). Moreover, Akgün et al. (1987) investigated the effect of soaking on mineral losses from the legumes, Karaali and Atakül (1994) reported the changes in composition during germination of the various dry legumes, and Ercaan et al. (1995) investigated cooking quality and composition of chickpea genotypes grown at two locations in Turkey. However, data on moisture diffusion properties of legumes grown in Turkey are mostly lacking. It was thus the purpose of this study to determine water diffusion coefficients at different soaking temperatures for the selected varieties of chickpeas, lentils, and dry beans grown in Turkey. Kon (1979) showed that water imbibition at temperatures greater than 50°C has an adverse effect on the cooking rate of beans and the samples soaked at 40°C have the shortest cooking time and the minimum soluble solid losses. Hence, in our study the soaking temperatures were chosen as 15°, 25° and 40°C to keep the losses to a minimum and still enable determination of the temperature effect. The water absorption process was described by using Fick's law of diffusion.

Materials and Methods

Materials: Chickpeas (*Cicer arietinum*), lentils (*Lens culinaris*) and white beans (*Phaseolus vulgaris*) grown in Turkey and from the 1992 harvest were supplied by the Turkish Grain Board. Two varieties of chickpeas (Koçbaşı and Kuşbaşı), one of lentils (green Pul) and four of white beans (Battal, Dermason, Horoz, Şeker) were used in soaking tests. All legumes were received in field dried form and stored at room temperature until used in experiments.

Moisture Content: Initial moisture contents of legumes were determined in triplicate by heating 3 g of sample in an oven at 130°C for 1 h (AOAC, 1980).

Seed Dimensions: A micrometer was used to measure dimensions of 15 seeds in three perpendicular directions (Sefa-Dedeh and Stanley, 1979). Then each cultivar was assigned a shape (sphere or slab) according to the appearance of seeds and the ratio of measured dimensions. The equivalent dimensions for the assigned shapes were calculated as follows:

A) Sphere: The volume of 50 to 100 seeds was measured in triplicate by water displacement in a graduated cylinder. Average volume was equated to the volume of a spherical object (i.e., $4\pi R^3/3$) and the radius R was obtained.

B) Slab: The volume of 100 to 300 seeds was measured in triplicate by water displacement in a graduated cylinder. Average volume was equated to the volume of a slab (i.e., $AxBxC$). Two more equations were obtained from the measured ratios of width to length and thickness to length. Hence, three equations were solved for three unknowns (A, B, C).

Soaking Experiments: 30 ± 0.5 g of dry seeds of each cultivar was weighed into a 250-mL jar and 150 mL of distilled water was added. Measurements of weight gain were made after 0.5, 1, 2, 3, 4, 5, 6, 7 and 18 h of soaking. At each specified time, soaking water was drained and seeds were blotted dry with tissue paper before measuring the increase in weight using an electronic balance (BB2440, Mettler-Toledo AG, Switzerland). Soaking experiments were conducted at 15, 25 and 40°C using an incubator (M5040 BCD, ElectroMag, Istanbul). Weight-gain data were corrected for loss of soluble solids, which was measured by a digital conductivity meter (LF/95, WTW, Germany). The soluble solid losses in our soaking experiments were small (below 1% of dry matter) in agreement with the results of Kon (1979).

Water Diffusion Coefficients: Analytical solutions of one-dimensional Fick's law of diffusion with constant diffusion coefficient for sphere and infinite plate are given respectively as (Crank, 1975):

$$MR_{sph} = \frac{M_t - M_o}{M_\infty - M_o} = 1 - \sum_{n=1}^{\infty} \frac{6}{\pi^2 n^2} \exp \left[- \frac{D_{eff} n^2 \pi^2 t}{a^2} \right]$$

$$MR_{slb} = \frac{M_t - M_o}{M_\infty - M_o} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[- \frac{D_{eff} (2n+1)^2 \pi^2 t}{4a^2} \right]$$

where MR is the moisture ratio, M_t is the average moisture at time t, M_o is the initial moisture, M_∞ is the moisture after 18 h of soaking, n is the number of terms

in summation (equal to 1000 in this study), D_{eff} is the effective water diffusion coefficient, and a is the characteristic length of the seed (equal to radius for sphere and half-width, half-thickness and half-length for slab). All moisture terms were computed on wet-basis.

We then formulated the problem as a root finding equation:

$$f(D_{\text{eff}}) = MR_{\text{expt.}} - MR_{\text{calc.}}$$

and searched for the D_{eff} value which made the function $f(D_{\text{eff}}) = 0$ with a tolerance of 10^{-6} . MR_{expt} represents moisture ratio from experimental data and MR_{calc} represents moisture ratio from model predictions. We used commercial software Mathcad (MathSoft, Inc., Cambridge, MA) to find the optimum D_{eff} value. Three-dimensional solution for slab geometry was obtained by combining the three solutions of the one-dimensional problem (see eqn. for slab above) for half-width, half-thickness and half-length (Geankoplis, 1972).

Temperature dependency of D_{eff} was described by an Arrhenius type equation:

$$D_{\text{eff}} = D_0 e^{-E/RT}$$

where D_0 (m^2/s) is a constant, E (kJ/mol) the activation energy, R (8.314 J/mol K) the gas constant and T (K) the absolute temperature. Activation energy values were obtained from the linear regression ($\log D_{\text{eff}}$ vs. $1/T$) analysis.

Results and Discussion

Initial moisture contents, dimensions, and 1000-seed weight of the legumes studied in this work are given in Table 1. The data presented in this table are in general agreement with those reported by Gürses (1981). Based on the equivalent dimensions given in Table 1 the lowest surface area per unit mass of seed (or, specific surface area, SSA) ranged from 0.53 mm^2/mg (Koçbaşı) to 1.53 mm^2/mg (Pul) (see Table 2). In general, for different cultivars of a legume, one can expect an inverse relation between the rate of absorption and seed size, since a larger seed provides a smaller surface area per unit mass for moisture transfer (Hsu et al., 1983).

The water absorption curves of dry legumes at three soaking temperatures are shown in Figures 1 and 2. The

Table 1. Moisture content and physical characteristics of selected dry legumes grown in Turkey.

Legume	Moisture (% wb)	Measured 1 dimensions (mm)			Assigned geometry	Equivalent dimensions (mm)	1000-seed weight (g)
Chickpeas							
Kuşbaşı	10.5	7.85 (0.31)	8.09 (0.31)	10.0 (0.45)	sphere	R = 4.11	365
Koçbaşı	10.8	8.16 (0.50)	8.33 (0.29)	10.18 (0.38)	sphere	R = 4.14	407
Beans							
Battal	12.2	5.81 (0.42)	9.93 (0.53)	17.10 (0.73)	slab	A = 4.30 B = 7.35 C = 12.66	466
Dermason	13.1	5.90 (0.33)	8.88 (0.27)	14.63 (0.75)	slab	A = 4.38 B = 6.59 C = 10.85	428
Horoz	12.7	6.25 (0.44)	8.04 (0.33)	16.49 (0.66)	slab	A = 5.03 B = 6.48 C = 13.28	425
Şeker	12.6	7.15 (0.41)	8.34 (0.40)	10.34 (0.34)	sphere	R = 4.24	414
Lentil							
Pul	10.1	2.49 (0.11)	6.78 (0.34)	6.96 (0.30)	slab	A = 1.84 B = 5.00 C = 5.13	58

1 Values in parentheses are standard deviations (n=15)

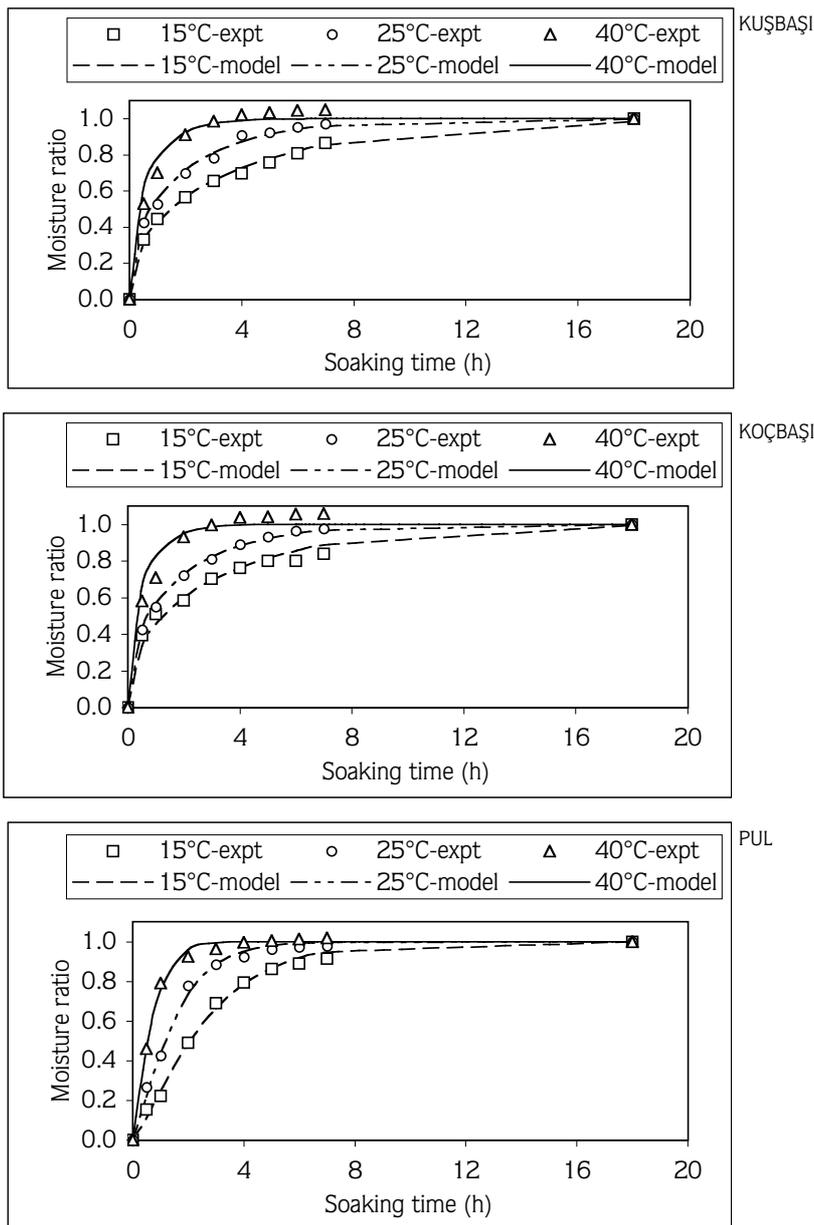


Figure 1. Water absorption by dry chickpeas (Kaçbaşı and Kuşbaşı) and lentils (Pul) during soaking at different temperatures.

rate of water absorption by the legumes increased with the increase in temperature of the soaking water, which has also been observed for other legumes (Quast and de Silva, 1977; Kon, 1979; Sopade and Obekpa, 1990; Abughannam and McKenna, 1997; Tang et al., 1994; Hung et al., 1993 and Hsu et al., 1983). When soaked at 40°C all legumes reached their maximum water absorption level (i.e., MR at 18 h) within 7 h of soaking. Therefore, as expected, the temperature of the soaking medium was a major factor in reducing the soaking time in the

processing of dry Turkish legumes. A shorter soaking step not only means less processing time but also signifies retention of more soluble solids in the seeds. As Kon (1979) showed, losses of total solids, N-compounds, total sugars, oligosaccharides, Ca, Mg, and vitamins (thiamine, riboflavin, niacin) were very small at soaking temperatures up to 50°C, but increased three to four times at soaking temperatures of 60°C or above.

From Fig. 1 it can be seen that the water absorption curve from the diffusion model closely followed the

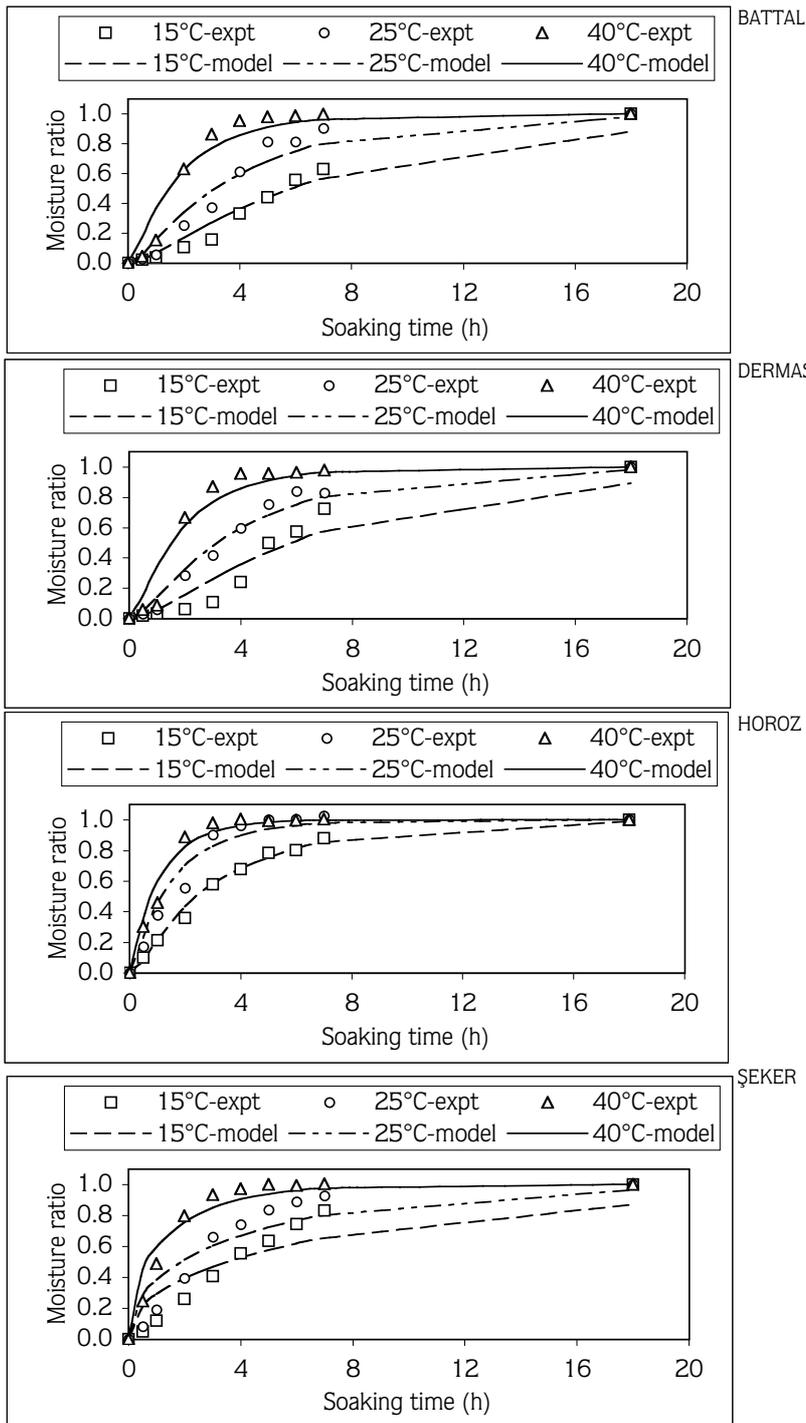


Figure 2. Water absorption by dry beans (Battal, Dermason, Horoz, Şeker) during soaking at different temperatures.

experimental data for chickpeas and lentils at all temperatures. However, the diffusion model described rather poorly the water absorption by dry beans (except for Horoz variety) especially at 15° and 25°C (Fig. 2). The experimental data of Battal and Dermason varieties

at 15°C, and to a lesser degree at 25°C, showed a lag period before conforming to the typical diffusion pattern. The lag period practically disappeared at 40°C indicating temperature sensitivity of the mechanism responsible for the initial slow absorption. This kind of slow absorption

Legume	D _{eff} (m ² /s) ¹			Area/Mass (mm ² /mg)
	15°C	25°C	40°C	
Chickpeas				
Kuşbaşı	9.71x10 ⁻¹¹ (0.00026)	1.85x10 ⁻¹⁰ (0.00035)	4.90x10 ⁻¹⁰ (0.0022)	0.58
Koçbaşı	1.15x10 ⁻¹⁰ (0.0012)	1.98x10 ⁻¹⁰ (0.00009)	5.98x10 ⁻¹⁰ (0.0029)	0.53
Beans				
Battal	4.87x10 ⁻¹⁰ (0.0039)	9.20x10 ⁻¹⁰ (0.0066)	1.98x10 ⁻⁹ (0.0087)	0.77
Dermason	3.79x10 ⁻¹⁰ (0.0086)	6.95x10 ⁻¹⁰ (0.0026)	1.46x10 ⁻⁹ (0.01)	0.69
Horoz	1.20x10 ⁻⁹ (0.00082)	2.56x10 ⁻⁹ (0.0049)	3.79x10 ⁻⁹ (0.0032)	0.87
Şeker	4.35x10 ⁻¹¹ (0.0147)	8.18x10 ⁻¹¹ (0.0148)	2.35x10 ⁻¹⁰ (0.0071)	0.55
Lentil				
Pul	3.53x10 ⁻¹⁰ (0.0005)	6.25x10 ⁻¹⁰ (0.00061)	1.33x10 ⁻⁹ (0.00036)	1.53

Table 2. Effective water diffusion coefficients of selected dry legumes grown in Turkey.

¹Values in parentheses are calculated from $\frac{1}{n} \sum_{i=1}^n (MR_{\text{expt.}} - MR_{\text{calc.}})^2$ where n was equal to 10 in this study.

Table 3. Activation energy of water diffusion during soaking of selected dry legumes grown in Turkey.

Legume	E (kJ/g mol)	Regression coefficient
Chickpeas		
Kuşbaşı	48.6	0.9994
Koçbaşı	49.8	0.9897
Beans		
Battal	41.9	0.9985
Dermason	40.4	0.9989
Horoz	33.6	0.9264
Şeker	50.8	0.9973
Lentil		
Pul	39.7	0.9998

at the beginning of soaking is also observed in some cultivars of cowpeas and associated, via SEM micrographs, with the thickness of the seed coat and the size of hilum and micropyle (Sefa-Dedeh and Stanley, 1979). Researchers, using autoradiography and NMR techniques, have also demonstrated that these anatomical parts play an important role in controlling the water entry into dry seeds (Jackson and Varriano-Marston, 1980; Heil et al., 1992 and Marconi et al., 1993).

The effective water diffusion coefficients of the legumes obtained by the root finding procedure are presented in Table 2, along with the residual sum of squares. Examining Table 2 for dry beans indicated a clear positive relation between the diffusivity, D_{eff}, and the specific surface area (SSA). A similar relation has also been reported for soybeans (Hsu et al., 1983). On the other hand, Hung et al. (1993) calculated higher water absorption rates for large-seed (i.e., smaller SSA) cultivars of chickpeas. It is also worth mentioning that beans of the Dermason variety and lentils (Pul) have similar diffusion coefficients despite the large difference in their SSA (Table 2). Therefore, the relation between D_{eff} and SSA appears to be valid only for some legumes rather than being a general rule for all legumes. Moreover, SSA seems to be one of several factors controlling the rate of water absorption in legumes, and sometimes it is not the dominant one (e.g., in chickpeas).

Since Hung et al. (1993) employed an empirical model to describe water absorption by chickpeas we cannot provide a direct comparison of our results with their data. However, diffusivity values reported in this study were

quite similar to the published literature results for different grains such as soybean ($2.15 \times 10^{-9} \text{ m}^2/\text{s}$ at room temperature) (Deshpande et al., 1994) and white rice ($5.2 \times 10^{-11} \text{ m}^2/\text{s}$ at 30°C) (Engels et al., 1986).

The variation of moisture diffusivity with the soaking temperature was consistent with the observations of Quast and deSilva (1977) and Hung et al. (1993) for the beans, peas and soybeans, and the cultivars of chickpeas, respectively. Arrhenius equation was sufficient to describe the temperature effect on the moisture diffusivity, as the regression coefficient of fitting was 0.93 or higher (Table 3). The activation energy values for water diffusion in the legumes were also presented in Table 3. Examining Table 2 indicated that the values of D_{eff} were highest for the Horoz bean and lowest for the Şeker bean. Data in Table 3 indicated that the temperature sensitivity of D_{eff} was highest for Şeker with E being 50.8 kJ/g-mol and lowest for Horoz with E being 33.6 kJ/g-mol . The activation energy values obtained in this study were comparable to 44.3

kJ/g-mol for soybean and 51.4 kJ/g-mol for pigeonpea, as reported by Singh and Kulshresta (1987).

Conclusions

The duration of soaking for dry Turkish legumes was reduced from 18 h to 7 h by increasing the temperature of the soaking water to 40°C . The simple Fick's diffusion equations successfully simulated the water absorption kinetics of the chickpeas and lentils at all temperatures. However, the model was not able to simulate the initial slow absorption, which was observed with the beans soaked at 15°C . The effective water diffusivity values of the selected Turkish legumes varied from 4.35×10^{-11} to $3.79 \times 10^{-9} \text{ m}^2/\text{s}$, giving nearly a 90-fold variation. The temperature dependency of D_{eff} was adequately described by an Arrhenius equation with the activation energies ranging from 34 to 51 kJ/g-mol . Data presented in this study on D_{eff} and the temperature dependence of D_{eff} for the selected legumes can help in better design of sorption process and equipment.

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