Kinetic model and effective diffusivity of frozen-dried European blueberry (Vaccinium myrtillus)

Dondurularak kurutulan yaban mersinin (Vaccinium myrtillus) kinetik modeli ve efektif difüzivitesi

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Bu makaleye şu şekilde atıfta bulunabilirsiniz (To cite to this article): Ayrıksa M., Acar B., Dağdeviren A., Roshanaei K., Coşkun T., Ongun G.K., ve Özkaymak M., “Kinetic model and effective diffusivity of frozen-dried European blueberry (Vaccinium myrtillus)”, Politeknik Dergisi, º(*)*: *, (*).

Erişim linki (To link to this article): http://dergipark.org.tr/politeknik/archive

DOI: 10.2339/politeknik.917063
Kinetic Model And Effective Diffusivity Of Frozen-Dried European Blueberry (Vaccinium Myrtillus)

Highlights
- Investigation of Freeze-Drying characteristic of European Blueberry.
- The proper kinetic drying model was specified by using MATLAB software.
- The effective diffusivity ($D_{eff}$) values were computed by drawing drying value.

Graphical Abstract
The effective diffusivity ($D_{eff}$) values were computed by drawing experimental drying data in terms of ln (MR) was plotted versus time. The effective diffusivity coefficient must be ranged from $10^{-12}$ to $10^{-8}$ m$^2$/s for food products in literature and it is determined that the calculated effective diffusivity coefficients for European Blueberry products have good agreement with the literature.

Aim
Aim of the present work was to identify the proper kinetic drying model by calculating MR and DR values for 8 different drying model with measuring mass losses in every two hours.

Design & Methodology
The European Blueberry fruit was sliced into thicknesses as 5 mm, and those sliced specimens were put in the freeze-drying device. Considering the experimental results, 8 different kinetic drying models were performed using MATLAB software.

Originality
Freeze-drying process of European Blueberry and investigation drying characteristic of process.

Findings
Results have shown that the effective diffusivity coefficients were within the limits that were presented in the literature as $10^{-12}$ to $10^{-8}$ m$^2$/s for food products. Among the 8 different kinetic drying models, the Page model was chosen as a proper kinetic drying model for European Blueberry products.

Conclusion
The proper kinetic drying model was specified by calculating MR and DR values for 8 different drying model with measuring mass losses in every two hours. The proper kinetic drying model was the Page model because the $R^2$ value was about 0.014686, $X^2$ value was about $2.875 \times 10^4$, RMSE value was about 0.9978 respectively.

Declaration of Ethical Standards
The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.
Kinetic Model And Effective Diffusivity Of Frozen-Dried European Blueberry (Vaccinium Myrtillus)

Araştırma Makalesi / Research Article

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(Geliş/Received : 15.04.2021; Kabul/Accepted : 29.04.2021; Erken Görünüm/Early View : 01.06.2021)

ABSTRACT

In current study, the freeze-drying (FD) method has been investigated. This method is the healthiest drying method that used in recent years by extending the shell life of the products and preserving the beneficial flavors in its content. Antioxidant, antimicrobial, antidiabetic, anti-inflammatory, antiseptic, etc., are the most emphasized role among the berries. Thus, blueberry is one of the great aspects to be a case for drying. Blueberry (Vaccinium Myrtillus), which is an opulent source of many phenolic compounds with known properties, has been investigated. In the study, blueberries by the weight of 100 gms and with a thickness of 5 mm were placed in the drying device, and the data were processed by observing the weight loss every two hours after being subjected to the drying process for 14 hours. 8 different kinetic drying models were applied to the acquired data using the Matlab program. As a result of the application, the estimated standard errors (RMSE), chi-square ($X^2$), regression coefficients ($R^2$) were calculated, error analysis was performed, $R^2$, $X^2$, and RMSE values were found, as 1.4686 × 10$^{-2}$, 2.875×10$^{-4}$ and 9.978 ×10$^{-4}$. According to these results, it was determined that the most suitable model is the Page model. Also, the effective diffusivity coefficients for blueberries were calculated as 2.57665 × 10$^{-12}$ m$^2$/s.

Keywords: Drying kinetics, drying of European blueberry, kinetic drying model, page model.

Dondurarak Kurutulan Yaban Mersinin (Vaccinium Myrtillus) Kinetik Modeli Ve Efektif Difüzivitesi

ÖZ

Bu çalışmada dondurarak kurutma (FD) yöntemi kullanılmıştır. Bu yöntem, ürünün raf ömrünü uzatması ve içeriğindeki faydalı aromaların korunması ile son yıldarda kullanılabilecek ve sağlıklı olarak gösterilen kurutma yöntemidir. Kurutma için meyve ürünlerinde önemli bir yere sahip olan antioksidan, antimikrobiyel, antiseptik vb. özelliklere sahip meyve olayan yaban mersini (Vaccinium Myrtillus) kullanılmıştır. Çalışmada 100 gr ve 5 mm et kalınlığına sahip yaban mersinleri kurutma cihazının içerisine yerleştirilmiş, 14 saat kurutma işlemine ve her iki saatte bir ağırlık kayıplar gözlemlenerek veriler üretilemiştir. Elde edilen verilerle Matlab programı kullanılarak 8 farklı kinetik kurutma modeli uygulanmıştır. Uygulama sonucunda tahmini standart hatalar olan (RMSE), chi-kare ($X^2$), regression coefficients ($R^2$) hesaplanmıştır, hata analizleri yürütülmüş ve $R^2$, $X^2$, RMSE değerleri sırasıyla 0.014686, 2.875×10$^{-4}$ ve 9.978 olarak bulunmuştur. Bu sonuçlara göre en uygun modelin Page modeli olduğu belirlenmiştir. Ayrıca yaban mersinin en efektif difüzivite katsayısının 2.57665 × 10$^{-12}$ m$^2$/s olarak hesaplanmıştır.

Anahtar Kelimeler: Kurutma kinetiği, yaban mersinin kurutulması, kinetik kurutma modeli, page model.

1. INTRODUCTION

Since the production of some foodstuffs changes seasonally, it is not possible to get them at any time due to our demands. This causes the necessity of preserving the products obtained in the season without damaging the properties. Nowadays, many methods are used to preserve foods without spoiling the properties. The most common way to conserve food is the drying method. Fruits and vegetables, which their most components are water, vitamins, carbohydrates, proteins, and lipids, are functional foods that are sources of many micronutrients and bioactive compounds. These foods and vegetables are mainly classified by their antioxidant capacity [1]. Special drying techniques are used to prevent deterioration and deformations in the product due to oxidation, thermal decomposition, or enzymatic browning and to stretch the shelf life of the product. Due to the customers' taste the quality features and texture, color, and aroma of the products should be sustained as pure and be preserved. These structural properties depend on the water content in the product may be lost or changed during drying. Many studies have been done to develop the grade of fruits after drying. Freeze-drying technology under vacuum is one of the drying methods which has been investigated so much by scientists [1]. The freeze-drying automation and applied science is widely used in different types of coffee like instant coffee and their production, as it is famous due to one
of the greatest technologies in preserving the aroma of coffee. Besides, freeze-drying technology is used in many areas such as fruit, fruit juices, vegetable, serum, drying the meat and milk [2,3]. In the freeze-drying process, the product is first should be frozen. Then quickly it would be taken to the drying cell and vacuumed with the vacuum pump that connected to this cell. At the same time, sublimation (transition from the solid phase to vapor phase) is provided by transferring heat to the product [4]. Freeze-drying technology has advantages such as extending the shelf life of the product by reducing its weight, saving the storage space with any required different more preservation processes. It provides the opportunity to get better quality products compared to other methods. However, being expensive is the disadvantage of the freeze-drying technology [5]. There are many studies regards the freeze-drying of fruits. Alejandro Reyes et al. investigated the effects of particle sizes, infrared radiation application, and freeze-drying methods (vacuum or atmospheric) on some nutritional values in blueberries. In so many research, the researcher found that in the vacuum freeze-drying method, the nutritional value called polyphenols is higher compared to the atmospheric freeze-drying method. Also, they observed that the amount of antioxidant potential of freeze-dried blueberries did not differ significantly from fresh fruit. As a result, they suggested the use of small particle sizes, infrared radiation application, and vacuum freeze-drying method to minimize the degradation of the nutritional values of freeze-dried blueberries [6]. Boris Nemzter et al. investigated the capacity of drying by the hot air as the name of (AD), and freeze-drying (FD), and diffraction window (RWD) methods of anthocyanins, phenolics, flavonoids, vitamins C and B, and antioxidants in blueberries, tart cherries (more cherries), strawberries and cranberries. They investigated the effects on retention as well as organic acids and proanthocyanins in cranberries, chlorogenic acid, and catechins in blueberries. They also examined changes in glass transition, color, specific heat, and surface morphology of dried fruits. They found that the quality behavior of dried fruits vary according to the product and drying method. However, they observed that the products dried with the RWD method displayed higher vitamin B retention than the products dried with the FD method. In their study, they observed that the products dried by the AD method exhibited significantly lower retention in most of the measured quality indices [7]. Hien Thi Ngo et al. executed a study on the effect of prior freezing circumstances on the quality of blueberries in a freeze-drying. In the study, it was observed that the size of ice crystals formed in frozen fruit was dependent on the freezing rate and these sizes caused some aroma loss in the product. They set the freezer temperature to -20 °C, -40 °C, -60 °C or -80 °C to apply the blueberry freezing process at different speeds. In the drying process, they did the sublimation phenomenon and process by using a transparent vacuum dryer that was heated by a far located infrared heater and connected to the vacuum pump via a vapor cooling trap. They obtained the measurement of the blueberry benzaldehyde substance in the captured steam by analysis with GC-MS. They observe that the volatility of typical volatile compounds such as acetic acid, 2-hexanol, and 3-hexanol in products frozen at different speeds before freeze-drying decreased while the freezing rate increased. It has been observed that by fast drying of blueberries in deep freeze, volatile aroma compounds such as benzaldehyde can be preserved [8]. Kai Fan et al. examined the development of the use of microwave heat sources in the last 10 years to shorten and decreasing the drying process in freeze-drying. They have found that, due to its high cost, the drying practices have been limited to small-scale processes in drying high-value foods such as fruit and vegetables. They realized that more research and development is needed to go beyond the existing boundaries for a wider product range and industry-scale applications [9]. Liovic, Nikolina et al. researched the effects of freeze-drying, pasteurization, and antioxidant activity of blueberry phenolics. They evaluated the antioxidant capacity of blueberry. They determined that phenolics demonstrated high stability after the simulated gastric digestion stage, especially in the freeze-drying system. As a result, they confirmed that the use of freeze-drying and high-intensity ultrasound can provide better digestion and higher antioxidant activity of blueberry phenolics after digestion [10]. Yeşim Daşdemir, in her study dried blueberries with two different methods (traditional method and freeze-drying method) and mixed black tea with different concentrations of the fruit (20%, 30%, 40%, and 50%) achieved and obtained a new and natural fruit-containing product. She examined the capacity level of produced number of antioxidants in black teasing her research. According to the determination of her study, plain fruit teas that dried by lyophilization (FD) method showed higher antioxidant activity than the plain fruit which teas dried by traditional method. According to the method, the highest antioxidant activity in hot infusions of teas is in the black tea sample with fruit (LM50 78.85%) prepared from blueberry dried by lyophilization method, and the highest antioxidant activity in cold tea infusions, again in the fruit tea sample prepared from fruit dried by lyophilization method (LM40 74.41%). According to the sensory evaluation results, they saw that the consumer liked much the sample of LM50 (50% lyophilized fruit that has a mixture of 50% black tea mixture) that had been examined as a sample. Maite Harguindeguy and Davide Fissore investigated the effects of freeze-drying processes on some nutritional properties in foodstuffs. The researcher observed the effects of ultrasound (US), microwave (MWD), and infrared (IR) processes that are used to speed up the process in vacuum freeze-drying (VFD) and atmospheric freeze-drying (AFD) methods on ascorbic acid, compounds contain of phenolic, and capacity of total antioxidant. They found freeze-drying had a similar and mild effect to infrared (IR) and ultrasound (US) in terms of total antioxidant capacity [11]. Krmaci et al. Freeze-dried strawberries cut in 5 mm and 7 mm thickness and calculated the moisture rates by taking the weight loss during (MR). As a result, they determined the most suitable kinetic drying model according to the estimated standard error (RMSE) and correlation values loss during drying (MR) [12].
As a result, they determined In this study, they preferred blueberry fruit as a case research for freeze-drying. Blueberry (Vaccinium Myrtillus) is a plant species that grows in temperate climates and belongs to the berry group. Rabbiteye (Vaccinium ashei) species of this fruit that are cultivated [13,14]. Names defined blueberry in our country such as Blueberry, Morsivite, bush strawberry, Likapa, Ligarba, Bearberry, and Trabzon tea. In our country, the Black Sea Region, Marmara Region and Eastern Anatolia people show adorable effort to have made Blueberry widespread. It is exhausted as fresh fruit, fruit juice industry (mixed with other fruit juices), pharmaceutical industry (dried or powdered fruits, flowers, roots, and leaves), milk and dairy technology, dried fruit technology, the fruit tasted pieces of bread, muffins, cake, pudding and cakes, spice industry, fruit salads, jam, marmalade, canned food industry, and diet menus the freeze-drying technology has been widely used. The high concentrations of antioxidants and anthocyanins besides, the high content of other phenolic substances make blueberries superior among vegetables and fruits [15]. It has been proven that blueberries have many benefits in terms of health, as well as some values in the blood too like LDL cholesterol, total cholesterol, uric acid, insulin, insulin resistance, BKI. Studies conducted in recent years show blueberry fruit is beneficial in the prevention of age-related chronic diseases. Blueberries can reduce the microorganisms involved to prevent symptomatic urinary tract infections in women.

2. MATERIAL AND METHOD

In the experimental study, blueberries set with a thickness of 5 mm and weight as 100 g each were placed in 7 containers. The blueberry samples placed in the containers were put in the deep freezer the day before the experiment and had waited for a day. The experiments were started the next day.

![Figure 1. Blueberry fruit](image1)

The drying device that is used in the study as a freeze-drying device, by the Labogene brand, and as a Scanvac Coolsafe type device and version has been used. By reducing the evaporator temperature down to -55 °C, it is possible to freeze the products in the device. To provide the 1×10⁻² kPa pressure that we need in the study, a vacuum pump with a vacuum power of 4×10⁻⁴ mbar was used furthermore; this pump was connected to the drying device. The Figure 2 shown schematic view of the freeze drying device that used in the experiments. The operation of the device in Figure 2 is based on the principle of increasing the temperature of a frozen product in a low pressure in the specified circumstances and realizing the sublimation.

![Figure 2. The freeze-drying device](image2)

While the compressor shown in the figure 2 adjusts the temperature inside the cabin, the vacuum pump decreases the ambient pressure. Thus, the necessary environment and conditions for sublimation is provided. In this study, the product was placed in the drying room and then the device was operated by specified temperature and pressure that had been set from the control panel of the device. Freeze drying time of samples was set as 14 hours. The time and temperature chart are arranged as shown in Figure 3. According to the planned and organized system, blueberries taken out of the freezer at -15 °C and after, placed in the device and stored for 60 minutes. It is adjusted at -40 °C and 1×10⁻² kPa pressure, and then, keeping the pressure constant for 180 minutes (almost 3 hours) at -30 °C, 180 minutes (almost 3 hours) at -20 °C, 120 minutes (almost 2 hours) at -10 °C, 120 minutes (almost 2 hours) at 0 °C, , 120 minutes. At 5 °C, and finally at 10 °C for 60 minutes (An hour). After the mentioned tasks, freeze-drying process is performed at the end of a total of 14 hours.

![Figure 3. The temperature values as a function of drying time](image3)

In this study, 7 different samples were prepared to measure their weight loss every two hours. To do the stated measurement, the first sample had placed in the device and the device started. After 2 hours, the sample was removed and as the sensitivity scale of the device by 1×10⁻³ g, the weight loss of the sample was measured by the appliance. Then the second sample had put into the device and the equipment operated dependent on the same drying settings and adjustments. After that, the sample had taken from the device at the end of the fourth hour, and the weight lost at the end of the 4th hour was calculated. This declared process applied as 6, 8, 10, 12,
and finally 14 hours for each sample. Then the samples were placed in the oven and approximately 60 minutes kept waited. The sample is taken from the oven and placed in a desiccator that contained curved glass with plenty of silica gel therefore had taken about 15 minutes to wait. After the 15th minutes finally, the sample taken from the desiccator weighed on a precision balance and scale beside the result recorded. The purpose of this process is to remove as much moisture as possible in the product because of freeze-drying technology, to calculate the moisture content of the product more accurately. Consequently, of the determination of the moisture content with applying the heat in the oven and desiccator, it was precise that 1×102 g product contained 6.5979×10 g of moisture, and 3.4021×10 g was the dry part of the sample. In the calculations, which were done after the scaling procedure, the desired equilibrium moisture was the dry part of the product with 3.4021×10 g. Figure 4 shows the weight loss curve of blueberry samples taken every two hours because of the freeze-drying technique.

![Figure 4. Weight loss of blueberry sample over time.](image)

Theoretical models can be applied for any item and condition. However, the solution for the theoretical models includes many parameters and complex structures, which reduces the usefulness of such models. Although semi-theoretical models are less complex than other models, the semi-theoretical model's parameters contain fewer parameters than other ones. They are only related to the parameters which in some cases, limits their convenience and utility. There are no complex mathematical equations in determining the drying rate based on experimental data. However, the equations obtained are valid for the sample and experimental conditions. The equation, which is the most widely used in semi-theoretical models, is known as the "logarithmic drying" equation [15]:

\[
MR = \frac{M_f - M_d}{M_i - M_d} 
\]

\[
DR = \frac{M_{i+dt} - M_i}{dt} 
\]

The change of moisture rate (MR) over time (t), which is a dimensionless term, can be determined by the equation given in Equations 1 and 2.

In the equation (M₀) the initial moisture content (g water/ g dry matter), (Mᵢ) the moisture content at the time t (g water/ g dry matter), (Mₑ) is the equilibrium moisture content (g water/ g dry matter). The part on the left side of the equation gives the moisture ratio (MR) values which in non-dimensional and shows the difference and alteration of the blueberry as a function of t moment of drying and could be computed so easily by the declared equation [17].

In the current work, measurement uncertainty of weight was ± 0.5 g, which contains a measurement error of the ± 0.001 g by precision balance.

The uncertainty in the measurement of the freeze-drying device pressure’s was 1%. The uncertainties of efficiency, which were calculated by directly measured values, such as temperature, the pressure, and heating power input, generally are denoted as ∂x, described as follows [18], [19]:

\[
w_R = \left[ \left( \frac{\partial R}{\partial X_1} \right)^2 + \left( \frac{\partial R}{\partial X_2} \right)^2 + \ldots + \left( \frac{\partial R}{\partial X_n} \right)^2 \right]^{1/2} 
\]

where R is given function of the independent variables X₁, X₂, X₃,…, Xₙ and w_R is the uncertainty of the results. Through calculations, the uncertainty values of efficiency were less than 2%.

4. RESULT AND DISCUSSION

Figure 5 shows the experimental moisture rate graph of the blueberry sample obtained because of freeze-drying for 14 hours.

![Figure 5. Humidity rate of blueberry sample due to time](image)

After determining the moisture content of the products and recording the weight loss due to time, a graph-based on mathematical models was created and the most suitable one was determined and emphasized from 8 different drying kinetic models. MATLAB program as main software was used to perform and run these operations. Table 1 indicates a total of 8 different drying kinetic models showing the estimated moisture content (MR) which be used in the MATLAB software program [20].
Table 1. Empirical and semiempirical equations for drying kinetics

| Model no | Model name         | Model parameters       | Model parameters       | R²      | X²          | RMSE      |
|---------|--------------------|------------------------|------------------------|---------|-------------|-----------|
| 1       | Newton             | k: 0.7863              |                        |         |             |           |
| 2       | Page               | k: 1.339 n: 0.3772     |                        | 0.9978  | 2.875×10⁻⁴  | 0.014686  |
| 3       | Modified Page I    | k: 2.723 n: 0.3469     |                        | 0.9976  | 3.118×10⁻⁴  | 0.015294  |
| 4       | Henderson ve Papis | a: 0.995 k: 0.7834     |                        | 0.9748  | 3.253×10⁻³  | 0.027158  |
| 5       | Logarithmic        | a: 0.95 c: 0.04889 k: 0.9892 |                   | 0.9901  | 1.553×10⁻³  | 0.03096  |
| 6       | Two-term ekspenential | a: 0.3662 k: 1.568 |                        | 0.9801  | 2.578×10⁻³  | 0.0043974 |
| 7       | Wang ve Singh      | a: -0.02329 b: 0.01226 |                       | 0.6593  | 4.406×10⁻²  | 0.181178  |
| 8       | Diffusion Approach | a: -0.2702 b: 1.006 k: 0.7787 |                | 0.9748  | 3.908×10⁻³  | 0.049422  |

The root-mean-square errors (RMSE), reduced Chi-square (X²) of estimated values, and the coefficient adequacy of the decision (R²) of kinetic models to prove the harmony and agreement between the moisture ratio of experimentally models and the predicted and estimated moisture and humidity values as statistical approach, can be found with the help of equations[21, 22].

\[
RMSE = \left[ \frac{1}{N} \sum_{i=1}^{n} (MR_{pre,i} - MR_{exp,i})^2 \right]^{1/2} \tag{4}
\]

\[
X^2 = \frac{\sum_{i=1}^{n} (MR_{exp} - MR_{pre})^2}{N-z} \tag{5}
\]

\[
R^2 = 1 - \frac{\sum (MR_{exp} - MR_{pre})^2}{\sum (MR_{pre})^2} \tag{6}
\]

The estimated root means square error (RMSE) in Equation 3 indicates the deviation between the estimated kinetic values and the experimental model. It is also stated in Equation 4 that the harmony increases with the reduced Chi-square (X²) value. In addition to these, the modeling coefficient of determination (R²) value in Equation 5 of the model explains the experimental data is an indicator of the usability of the model.

Figure 6. Dried blueberries

Figure 6 reveals freeze-dried blueberries samples. According to the statistical evaluation results, the coefficients found in the most suitable model are determined by the multiple regression method. In the light of the data obtained, 8 models were applied, and the most suitable drying model was determined from these 8 different models. These determination criteria depend on the R², X², and RMSE values obtained from the models that shown in Table 2.
In the study, a total of 7 blueberry samples, each with a thickness of 5mm, set as 100 grams, were subjected to freeze-drying for 14 hours. MR (moisture content) was calculated with the weight loss data taken every two hours in different samples and the most suitable model was determined on 8 different drying models using the MATLAB program. In the calculation, it was seen that the most suitable model was the PAGE model with the R² value of 0.978 × 10⁻¹, the X² value of 2.57665 × 10⁻¹₂–10⁻¹₄ m²/s, and the RMSE (root mean square root) value of 9.978 × 10⁻¹, which is the closest value to 1, and the most suitable model with an R² value such as 9.978 × 10⁻¹, which is the closest value to 1, and the closest to zero by 2.875 × 10⁻¹⁴ as X². Further another factor supporting the suitability of the PAGE model is that the root means square error (RMSE) value as the closest to 0, such as 1.46868 × 10⁻² as a supporting factor for the PAGE model. The comparison of the moisture rates acquired from the calculated page model with the RMSE values and results of 8 kinetic models using the MATLAB program. In the calculation, it was seen that the most suitable model was the PAGE model with the R² value of 9.978 × 10⁻¹, the X² value of 2.875 × 10⁻¹⁴, and the RMSE (root mean square root) value of 1.46868 × 10⁻². It was confirmed that hawthorn’s effective diffusivity has good agreement with the general effective diffusivity range for drying food materials [24].

4. CONCLUSION

In Fig. 8, we found slope (K) from the graph. For 5mm thick blueberry slices, the effective diffusion value (Deff) was determined using Eq. 6, and its value was 2.57665 × 10⁻¹₂–10⁻¹₄ m²/s. From this research, the effective diffusion value was found within the reference range 10⁻¹₂–10⁻¹₄ m²/s for drying food materials. According to the literature, no research has been performed so far to establish hawthorn’s kinetic model, and no attempt has been made to quantify its effective diffusivity or moisture content in the freeze-drying process [23]. We conclude that hawthorn’s effective diffusivity has good agreement with the general effective diffusivity range for drying food materials [24].

Nomenclature

| Symbol | Description |
|--------|-------------|
| a, b, c, n | The constants of the models |
| z | Number of parameters in the model |
| k, kₙ, kₐ | Drying rate constants (min⁻¹) |
| t | Time (min) |
| M₀ | The initial moisture content (g water/g dry matter) |
| Mₜ | The moisture content at a time t (g water/g dry matter) |
Mₐ The final equilibrium moisture content (g water/g dry matter)
MR The moisture ratio (dimensionless)
N Number of observations
MC Moisture content (g water/g dry matter)
DR Drying rate (g water/g dry matter)
Dₑeff The effective diffusivity (m²/s)
L Half-thickness of samples (m)
R² Coefficient of determination
χ² Reduced chi-square
RMSE Root mean square error

DECLARATION OF ETHICAL STANDARDS
The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS’ CONTRIBUTIONS
Mutlucan AYRIKSA: Wrote the manuscript.
Bahadır ACAR: Performed the experiments and analyze the results.
Abdullah DAGDEVİREN: Performed the experiments and analyze the results.
Khandan ROSHANAEİ: Wrote the manuscript.
Tuba ÇOŞKUN: Wrote the manuscript.
Gökknur K. ONGUN: Wrote the manuscript.
Mehmet ÖZKAYMAK: Wrote the manuscript.

CONFLICT OF INTEREST
There is no conflict of interest in this study.

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