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Determination freeze-drying characteristics of ottoman strawberries

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Highlights

- Investigation of Freeze-Drying characteristic of Ottoman Strawberries.
- The appropriate kinetic drying model was determined using the MATLAB program.
- The effective diffusivity (D_{eff}) values were computed by drawing drying value.

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Abstract

This study was performed to define the kinetic drying model and to define the effective diffusivity coefficient of the fruit, which is called ottoman strawberries in the literature. In the study, strawberries by the weight of 100 g 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 $9,998 \times 10^{-1}$, $6,993 \times 10^{-5}$ and 0.7242×10^{-2} . According to these results, the model of strawberry was determined that the most suitable model is the Page model. Also, the effective diffusivity coefficients for ottoman strawberries were calculated as $2.73286 \times 10^{-10} \text{ m}^2/\text{s}$. It was confirmed that the calculated effective diffusivity value was within the reference range mentioned in the literature ($10^{-12} \text{ m}^2/\text{s} - 10^{-8} \text{ m}^2/\text{s}$) for food products.

1. INTRODUCTION

Morphological character determination, flowering and harvest periods control and determination of Ottoman strawberry were made by the Ministry of Agriculture and Forestry Seed Registration and Certification Center Directorate 3 times in 2017 and 2 times in 2018. At the 'Fruit Registration Committee' meeting attended by the representatives of 6 relevant official institutions on October 26, 2018, Ottoman strawberry took its place in the plant literature as a strawberry variety with the 1393rd number among the registered fruits [1]. Stating that the benefits of strawberry, the indispensable fruit of the summer months, are countless, experts pointed out that strawberry, which is one of the most popular fruits with its color, smell, and taste, contains plenty of phosphorus and iron. Stating that strawberry is rich in B, C and K vitamins, experts say, "Strawberry gives strength to the body, they argue that it has an effect on vascular occlusion and cholesterol. It strengthens the immune system because it is a very good antioxidant. It has a protective feature against cancer and ensures the regular functioning of the digestive system. Intestinal "Helps shed worms, cleans the blood, removes harmful substances from the body. Strengthens the gums, removes bad breath. Hollywood stars whiten their teeth by massaging them with strawberries. It has a calming effect, reduces stress, lowers blood pressure, lowers fever. It is good for rheumatism and liver ailments." "It moisturizes the skin and gives it a fresh look, adds beauty to the skin. It throws out the toxic substances accumulated in the body, prevents diseases such as atherosclerosis and kidney stones, and allows them to pass over time. It has diuretic properties," he said. Strawberry is a food that strengthens immunity. Strawberry has lethal effects for some viruses that have infiltrated our body: These include polio (polyomyelitis), viruses that cause some mouth and skin sores. In addition, traditionally, in folk medicine, strawberry is considered to be good for acne (pimples). It strengthens the nerves, expels intestinal worms,

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and reduces fever [2]. The first information about strawberry M.S. It is quoted by the botanist Tillius, who lived between 23 and 79 BC. Strawberry develops in France and begins to increase its cultural value in the following years. The Ottoman strawberry, which is unique to Karadeniz Ereğli, is also called the food and drink of the kings. It was first cultivated in the Black Sea Ereğli in the 1920s. Strawberry brought to Karadeniz Ereğli from the Istanbul region in these years entered the process of interaction with the other local culture, and a gentle and aromatic strawberry called Ottoman strawberry emerged. "Ottoman Strawberry is derived from Arnavutköy strawberry of European origin. In the early 1900s, its flower came to Halil Pasha and gained its original structure in the chestnut soil of our region; With its pink color, medium-sized oval appearance, rich aroma, and delicious scent, it has become the world's unique and only strawberry. It was planted by Mustafa, the coachman of the Pasha, for the first time. Our Ottoman Strawberry, which started to be produced with Kahyaoğlu Kadir and his Greek partner on the outskirts of Kestaneci Village (Kestaneci District), has been the first source of income for the local people for a long time, and it has been a gift that we can proudly present in our foreign visits [3]. In addition to fresh consumption, paradise dates are consumed by cutting them into salads, drying and freezing when they soften. The total amount of phenolic substance, which is the most important feature of the paradise date and gives a bitter taste, has decreased in marmalade compared to the raw material. As the fruit ratio was increased, the amount of total phenolic substance, carotene and lycopene increased accordingly [4]. By the 1985's, Ottoman Strawberry had almost disappeared. After 1994, free strawberry seeds are given to Ottoman Strawberry producers supported by the municipality and seedlings are grown in greenhouses established by the municipality. Today, more than 500 families in Karadeniz Ereğli still earn their living from the production of Ottoman Strawberry. fully ripe. In autumn, just before the leaf falls, the leaves turn into 3 different colors, these colors are green, orange-red and red. In addition, these colors are used as ornamental plants as they contribute to romance as well as their relaxing feature that does not tire the eye. The color of the fruits turns from yellow to red or orange, its shape is round, and its taste is divided into 2 as it is bitter and not bitter. Appearance is one of the most significant quality agents used in deciding the market value of the paradise dates as in other fruit types. The Ottoman Strawberry, which started to bear its first fruit in the end of May and the beginning of June, does not bear fruit anymore towards the end of June. Ottoman Strawberry, which demands great attention due to its delicate structure, is picked unharmed in the early hours of the morning by producers and is immediately put up for sale within 1-2 hours. Since the life of the collected strawberries in the open air is only 15-20 hours, it should be consumed immediately. Lihui Zhang et al. [5] investigated the effects of ultra-high pressure as a pretreatment, ultrasound, and their combination on the properties of vacuum freeze-dried strawberry samples. Drying time and total energy consumption decreased during vacuum freeze drying. The transverse relaxation times and peak area corresponding to free water were markedly reduced in the pretreated samples, indicating lower mobility in the pretreated samples. Vacuum freeze-drying of strawberry samples has been a promising technique. Lue-lue Huang et al. [6], While the color, aroma, and taste of freeze-dried strawberry chunks are very good, tissue collapse after rehydration limits the application of freeze-dried strawberry chunks in liquid carriers. The color of the strawberry pieces can be maintained to some extent by adding Na and β -Cyclodextrin to the coating. In this study, the effects of coating of freeze-dried parts and drying method after coating were investigated. The coated freeze-dried strawberry pieces were dried on a rimmed bed. The color of the strawberry pieces can be maintained to some extent by adding Na and β -Cyclodextrin to the coating solution. It was also found that the rehydration properties of the coated strawberry pieces were affected by the coating time as well as the drying conditions used. Baoguo Xu et al. [7] The effects of ultrasound assisted osmotic pretreatment at different frequency modes on the moisture and quality properties of strawberry slices before vacuum freeze drying were investigated. The results showed that the drying time of the ultrasound-irradiated strawberry slices was reduced by 15.25% – 50.00% compared to the control samples. It can be concluded that it is an effective pretreatment method for vacuum freeze-dried strawberry products. It greatly reduced the drying time by changing the moisture state and microstructure of the strawberry slices. The rehydration capacity, firmness and taste of the ultrasound-irradiated freeze-dried strawberry slices were improved. İbrahim Doymaz et al. [8], Convective drying kinetics of strawberries were investigated in the laboratory. Strawberries that were pretreated with alkaline ethyl alcohol solution and untreated were dried at selected temperatures of 50, 55 and 65 °C with a constant air velocity of 1.2 m/s. The drying rate curves showed that drying only took place during the period when the rate decreased. He found that the logarithmic model was a better model for describing the properties of strawberries at both

50 °C and 55 °C temperatures. The transport of water during drying is defined by the Fick equation, and the effective diffusion ranges from $4.95 \times 10^{-10} \text{ m}^2/\text{s}$ to $1.42 \times 10^{-9} \text{ m}^2/\text{s}$. Alica Lammerskitten et al. [9] In this study, the effect of pulsed electric field pretreatment on the microstructure of freeze-dried strawberry cubes was investigated. The samples were freeze-dried at 45 °C and 1 mbar pressure. In addition to the mechanical and acoustic properties, the color of the processed material was also analyzed. Strawberries that were pretreated with pulsed electric field were found to be crispier, less moisture content, more vivid in color and better in appearance than those that did not. In our study, was performed to define the kinetic drying model and to define the effective diffusivity coefficient of the fruit, which is called ottoman strawberries in the literature. In the study, strawberries by the weight of 100 g 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.

2. MATERIAL METHOD

The Ottoman Strawberry sample samples included in our study are shown in Figure 1. The weight of strawberry fruit is 100 gr, its thickness is cut 5 mm and placed in the test container and 7 pieces of this sample are prepared. After completing these preparations, it will be stabilized in the freezer and will be subjected to drying.



Figure 1. Ottoman Strawberry fruit

The device used in our experimental studies is the ScanVac Coolsafe type device of the Labogene brand. Several options are available to configure freeze drying to suit your specific needs. In order to have a long life machine capacity, the condenser of the device is coated with Teflon, and it has easy cleaning opportunity to protect it from corrosion problems while working with aggressive acids. This device is suitable for freezing products that need very low evaporator temperatures (-55 °C).

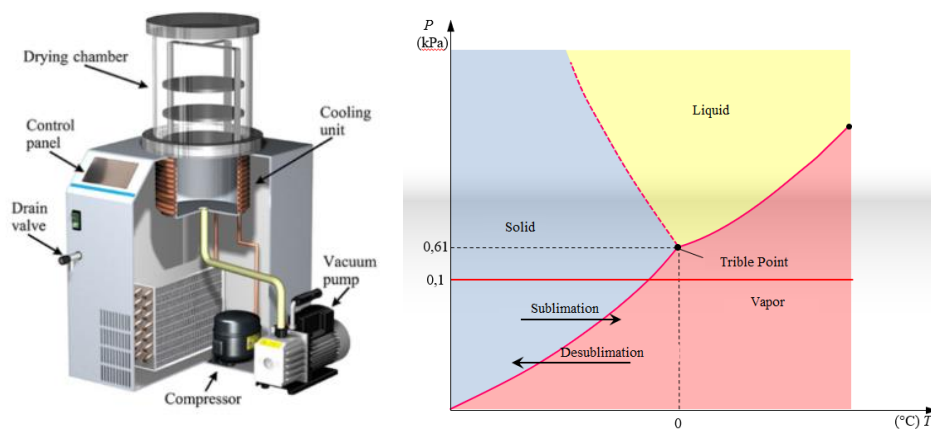


Figure 2. Schematic representation and logic of the freeze-drying device

The study was carried out by reducing the required pressure to 0.01 kPa with the device connected to the vacuum pump with a vacuum power of 1×10^{-4} mbar. According to the conditions of our experiment, we

reduced the pressure of 4×10^{-4} mbar of the vacuum pump with the vacuum power of the device to 0.01 kPa [10]. The freeze drying device used for the work is shown in Figure 2. The logic of freeze drying is based on sublimation. When the product is frozen, it freezes in the moisture inside. If the test head is kept below the critical pressure value and the temperature increase is created, the moisture passes directly to the gas phase and is separated from the product moisture. The operating principle of the ScanVac Coolsafe device is focus on the freeze-drying operation of the frozen product at low pressure, by increasing the temperature of the frozen crop and the desired drying, resulting in the sublimation process (when solid substances are heated, they directly go into gas without transition to an intermediate liquid state). In our study, the vacuum pump function brings the pressure of the drying chamber to the desired pressure in order to obtain the desired physical properties (temperature, pressure), while the compressor of the device adjusts the temperature suitable for the in-cabin drying processes. In order to keep the temperature and pressure in accordance with the conditions of our study, after the sample was placed in the drying room, the temperature and pressure control panel was adjusted, and the device was operated, and our experiment was carried out. Before starting our experiment, the required temperature, pressure and working times (freeze drying time for date samples 14 hours) were made on the control panel. The time and temperature chart were prepared in Figure 3.

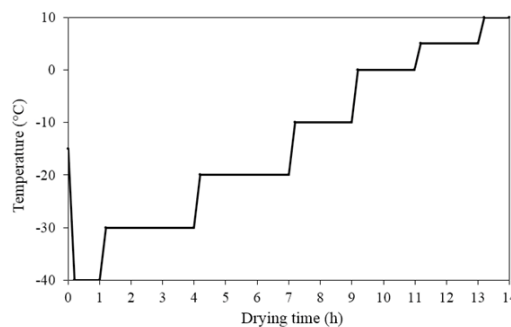


Figure 3. Time-temperature chart applied in experiments

According to the planned working system, the slices of the heavenly dates taken out of the deep freezer at -15°C are placed in the device and stored for the first 60 minutes. Our experiment is started at -40°C and 0.01 kPa pressure, and then, keeping the pressure constant, 180 minutes at -30°C , 180 minutes at -20°C , 120 minutes at -10°C , and at 0°C . 120 min., 120 min. At 5°C . and finally at 10°C for 60 min. The process is carried out and when I complete these steps, the freeze-drying process is completed at the end of a total of 14 hours. In order to determine the weight loss of the sample during the experiment, 7 different samples were changed every two hours in the study [11]. After taking the first sample to the device and running it to determine the weight loss, the weight loss of the date sample is determined by using the precision balance (balance with sensitivity of 0.001 gr) to confirm the weight loss at the end of two hours. After determining the weight loss of the first sample, the second sample is processed to the same drying settings and the device is operated and this time the process is continued for four hours instead of two hours, and the weight loss is measured after four hours. By performing the previous process for other date samples, the sample is taken to the device at the end of the 6th, 8th, 10th, 12th and last 14 hours and the loss of mass is determined. Mass loss of Ottoman Strawberry sample over time shown in Figure 4.

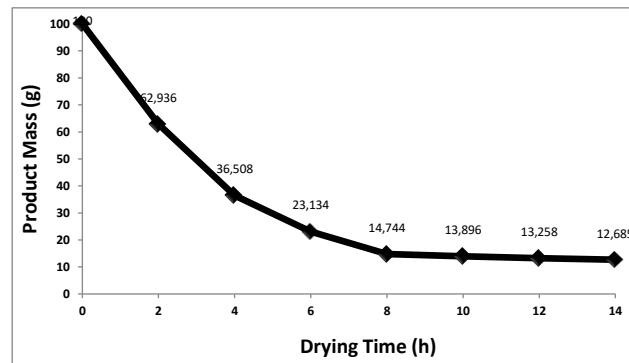


Figure 4. Mass loss of Ottoman Strawberry sample over time

Then it is placed in the oven and approximately 60 minutes. kept waiting. Some food products contain a certain amount of moisture, such as persimmon. In order to mensurate the amount of moisture in the sample of the heavenly date used in our experimental study at the end of drying, the sample is operated into a desiccator. The sample is received from the oven and placed in a desiccator designed from curved glass with copious silica gel and heated for approximately 15 minutes. it is kept waiting and then the rate of moisture is parameters and complex structures connected to them. Despite the less complex nature of semi-theoretical models, the parameters contained in their equations are also limited in their usefulness to deal only with the products under consideration. There are no complex mathematical equations based on the data obtained in determining the drying rate of a product through experimental studies. The equation, which is the most widely used in semi-theoretical models, is known as the "logarithmic drying" equation [12]. The moisture ratio (MR) is showing the changes of the Ottoman sample as a function of time can be computed by Equation (1). The drying rate (DR) can be computed using Equation (2) as well

$$MR = \frac{M_t - M_d}{M_0 - M_d}, \quad (1)$$

$$DR = \frac{M_{t+dt} - M_t}{dt}. \quad (2)$$

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 (M_0) the initial moisture content, (M_t) the moisture content at the, (M_d) is the balance moisture content. It gives the moisture ratio (MR) values, which can be calculated as a function of the drying moment, the difference and variation of the dimensionless Ottoman Strawberry in the Equations [13]

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^n (MR_{pre,i} - MR_{exp,i})^2 \right]^{1/2} \quad (3)$$

$$X^2 = \frac{\sum_{i=1}^n (MR_{exp} - MR_{pre})^2}{N - z} \quad (4)$$

$$R^2 = 1 - \left[\frac{\sum (MR_{exp} - MR_{pre})^2}{\sum (MR_{pre})^2} \right]. \quad (5)$$

The estimated root mean square error (RMSE) in Equation (3) represents the deviation between the predicted the experimental model and kinetic values. In addition to these, the modeling coefficient of determination (R^2) value in Equation (5) of the model explains the experimental data is an indicator of the usability of the model. According to the statistical calculations results, the coefficients observe in the most suitable model are found using multiple regression method. According to the data obtained, 8 models were applied, and the most suitable drying model was defined from these 8 different models. These determination criteria linked on the R^2 , X^2 , and RMSE values obtained from the models that shown in Table 2. In table

2, R^2 , X^2 and RMSE values and results of 8 kinetic drying models given. As it can be easily seen here, the Page model due to the consideration of R^2 and X^2 amounts, the most suitable drying model with an R^2 value such as 9.998×10^{-1} , which is the closest value to 1, and the closest to zero by 6.993×10^{-5} as X^2 . Further base factor sustaining the suitability of the Page model is that the root means square error (RMSE) value as closest to 0, such as 0.7242×10^{-2} as a supporting factor for the Page model [14].

The drying processes' theoretical model can be determined by its solution, which is shown in the equation given below:

$$\frac{\partial M}{\partial t} = D_{eff} \nabla^2 M \quad (6)$$

$$MR = \frac{8}{\pi^2} \exp\left(\frac{\pi^2 D_{eff} t}{4L^2}\right). \quad (7)$$

Here t defines drying time (s), D_{eff} shows effective diffusivity (m^2/s), n presents a positive integer, and L shows half-thickness of the samples(m). Keeping in view long drying duration with steady diffusion coefficient in a Cartesian coordinate system, we simplified Equations (7) to a limiting form of the diffusion equation. After plotting the experimental drying data for $\ln(MR)$ versus time, we determined effective diffusivity (D_{eff}) values Equations (7) [15]. After plotting the experimental drying data for $\ln(MR)$ versus time, we determined effective diffusivity (D_{eff}) values, as Figure 10 shows.

3. RESULTS AND DISCUSSION

Figure 5 shows the moisture ratio chart of the Ottoman Strawberry sample obtained because of freeze-drying for 14 hours. The moisture content of the product is calculated experimentally and after determining the weight loss of this product depending on time, a chart is created focus on mathematical models. It was ensured that the most suitable model was selected and determined from 8 drying kinetic models applied in our freeze drying study. MATLAB program was used in the process of selecting the mathematical model. Table 1 shows the drying models available in the literature.

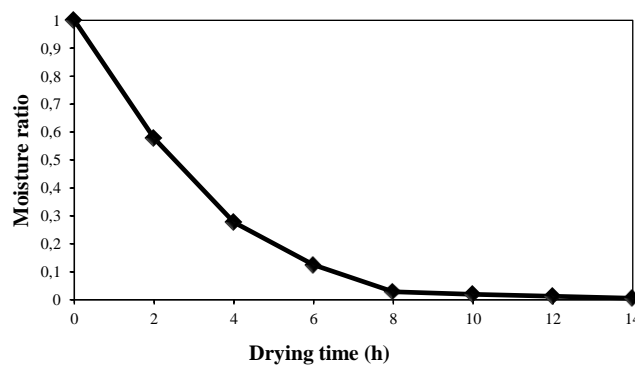


Figure 5. Moisture ratio of Ottoman Strawberry

Table 1. Empirical and semiempirical equations for drying kinetics

Model no	Model name	Model
1	Newton	$MR = \exp(-kt)$
2	Page	$MR = \exp(-kt^n)$
3	Modified Page I	$MR = \exp[-(kt)^n]$
4	Henderson ve Pabis	$MR = a \cdot \exp(-kt)$
5	Logarithmic	$MR = a \cdot \exp(-kt) + c$
6	Two-term eksponential	$MR = a \exp(-kt) + (1 - a) \exp(-kat)$
7	Wang and Singh	$MR = 1 + at + bt^2$
8	Diffusion approach	$MR = a \exp(-kt) + (1-a) \exp(-kbt)$

The RMSE, reduced (X^2) of estimated values, and the coefficient adequacy of the decision (R^2) of kinetic models to prove the harmony and agreement between the moisture ratio of experimentally models and the predicted and guessed moisture and humidity values as statistical approach, can be found with the help of equations [16, 17]. 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 $9,998 \times 10^{-1}$, $6,993 \times 10^{-5}$ and 0.7242×10^{-2} . According to these results in the Table 2, the model of strawberry was determined that the most suitable model is the Page model.

Table 2. The results calculated by 8 kinetic drying models

Model No	Model Name	Model parameters	R^2	X^2	RMSE
1	Newton	k: 0.3223	0.9934	8.49×10^{-4}	0.02725
2	Page	k: 0.229 n: 1.249	0.9998	6.993×10^{-5}	0.007242
3	Modified Page I	k: 0.3064 n: 1.226	0.9995	7.8688×10^{-5}	0.007682
4	Henderson and Papis	a: 1.019 k: 0.3272	0.9939	9.26×10^{-4}	0.026355
5	Logarithmic	a: 1.044 c: -0.03058 k: 0.3008	0.996	7.288×10^{-4}	0.021342
6	Two-term eksponential	a: 1.842 k: 0.4471	0.9994	8.707×10^{-5}	0.08081
7	Wang ve Sing	a: -0.2015 b: 0.009643	0.9781	3.307×10^{-3}	0.049806
8	Diffusion Approach	a: 4.364 b: 0.8945 k: 0.217	0.997	5.347×10^{-4}	0.01828

The comparison of the moisture rates acquired from the calculated page model with the moisture rates acquired from the experiments is shown in Figure 6.

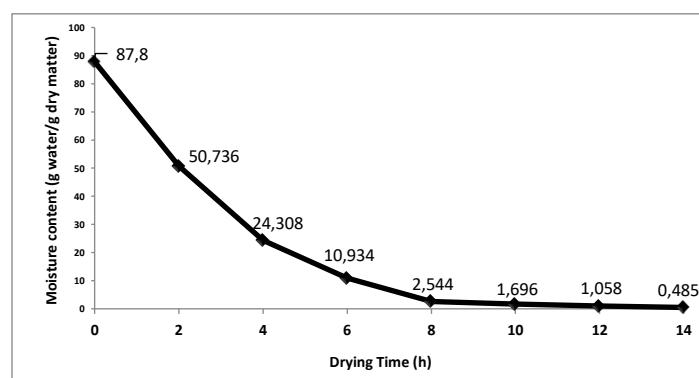


Figure 6. Moisture content of Ottoman Strawberry sample due to time

For food and material drying efficient diffusivity is an important transport characteristic that depends on the moisture content and temperature of a material. Fick's diffusion equation has a second law, which makes it a mass-diffusion equation for drying crop in a fall-rate phase [18]. The moisture content of Ottoman Strawberry decreasing over time is shown in Figure 7.

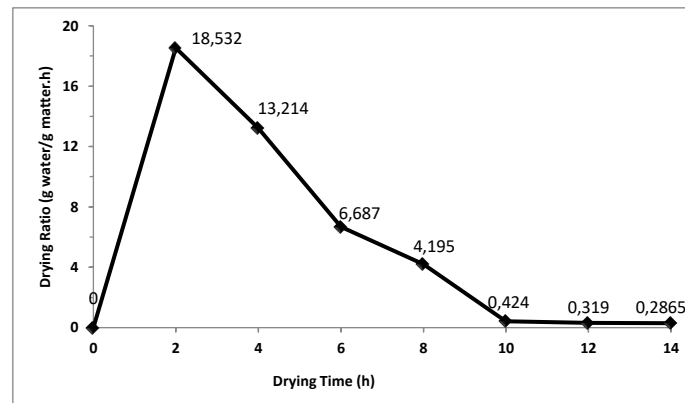


Figure 7. Drying ratio of Ottoman Strawberry sample due to time

The drying rate of the freeze-dried Ottoman Strawberry slices is shown in Figure 7. At the early on the freeze-drying duration, the drying ratio exhibits incline behavior because of the high concentration of the moisture at the face of the product. To the end of the first 2 hours drying period, the drying rate decreased leisurely up to the end of the drying duration because of the increasing temperature of the plate in the freeze-drying device [19]. The freeze-dried Ottoman Strawberry slices is shown in Figure 8.



Figure 8. Dried Ottoman Strawberry

The comparison of the moisture rates acquired from the calculated page model with the moisture rates acquired from the experiments is shown in Figure 5. For food and material drying efficient diffusivity is an important transport characteristic that depends on the moisture content and temperature of a material. Fick's diffusion equation has a second law, which makes it a mass-diffusion equation for drying agricultural products in a fall-rate phase. Comparison between experimental and predicted moisture ratio values applying the Page Model have shown are Figure 9.

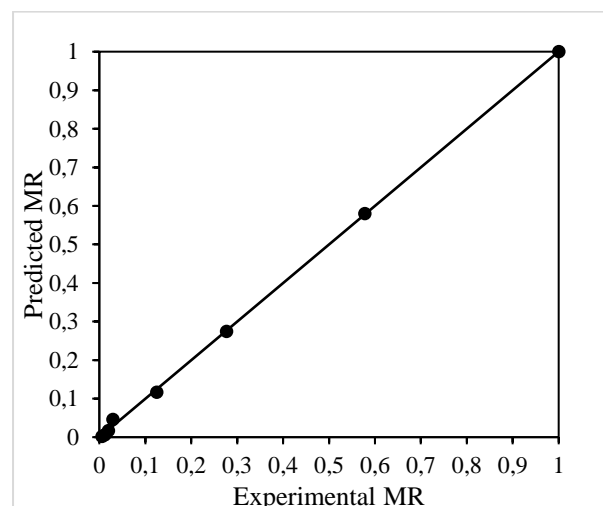


Figure 9. Comparison between experimental and predicted moisture ratio values applying the Page Model

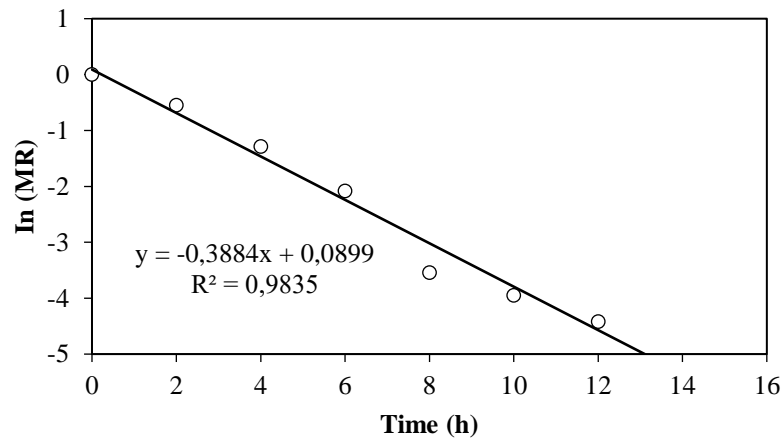


Figure 10. *ln (MR) versus freeze-drying time for Ottoman Strawberry samples*

In Figure 10, we found slope (K) from the graph. For 5mm thick Ottoman Strawberry slices, the effective diffusion value (D_{eff}) was determined using Equation 6, and its value was $2.57665 \times 10^{-12} \text{ m}^2/\text{s}$. From this research, the effective diffusion value was found within the reference range 10^{-12} – $10^{-8} \text{ m}^2/\text{s}$ for drying food materials. According to the literature, no research has been performed so far to establish Ottoman Strawberry's kinetic model, and no attempt has been made to quantify its effective diffusivity or moisture content in the freeze-drying process. We conclude that Ottoman Strawberry's effective diffusivity has good agreement with the general effective diffusivity range for drying food materials [20].

4. CONCLUSION

In the study, strawberries by the weight of 100 g 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 $9,998 \times 10^{-1}$, $6,993 \times 10^{-5}$ and 0.7242×10^{-2} . According to these results, the model of strawberry was determined that the most suitable model is the Page model. Also, the effective diffusivity coefficients for ottoman strawberries were calculated as $2.73286 \times 10^{-10} \text{ m}^2/\text{s}$. It was confirmed that the calculated effective diffusivity value was within the reference range mentioned in the literature ($10^{-12} \text{ m}^2/\text{s} - 10^{-8} \text{ m}^2/\text{s}$) for food products.

Nomenclature

a, b, c, n	The constants of the models
z	Number of parameters in the model
k, k_0, k_1	Drying rate constants (min ⁻¹)
t	Time (min)
M_0	The initial moisture content (g water/g dry matter)
M_t	The moisture content at a time t (g water/g dry matter)
M_d	The final equilibrium moisture content (g water/g dry matter)
M_R	The moisture ratio (dimensionless)
N	Number of observations
MC	Moisture content (g water/g dry matter)
DR	Drying rate (g water/g dry matter)
D_{eff}	The effective diffusivity (m ² s ⁻¹)
L	Half-thickness of samples (m)
R_2	Coefficient of determination
χ^2	Reduced chi-square
$RMSE$	Root mean square error

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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