**Mathematical modelling of ultrasound pretreated kumquat (*Citrus japonica var. margarita*) in freeze dryer**

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| **Abstract** Kumquat (*Citrus japonica var. margarita*) is a citrus fruit that resembles a tiny orange and is rich in flavonoids. Kumquat, which can be consumed raw and processed, was dried in a freeze dryer with ultrasonic pre-treatment and its mathematical modelling were investigated in this study. Ultrasound pretreatment was applied for 30 and 60 seconds and the drying process was proceeded at -68.6 C and 0.9 Pa for control and pretreated samples. The experimental drying data is fitted into Hendersen & Pabis, Jena & Das, Lewis, and Two-Term Exponential drying models, and the data-model compatibilities were compared. The most suitable model was determined as Jena & Das model with the highest *R2*, and the lowest *χ2*, and *RMSE*. It was observed that the *R2* values of all the models applied varied between 0.994740 and 0.998673. |
| Keywords: Kumquats, Exotic fruits, Lyophilisation, Ultrasonication |

1. **Introduction**

Fruits are a food group rich in vitamins and minerals, but also contain high amounts of water. In this case, fruit is one of the food products most prone to spoilage due to its high enzymatic and microbiological activity. Increasing the shelf life of a fruit product is possible by stopping this microbiological activity. Drying is the most popular method for preserving fruits. The main features of this method are to extend shelf life, reduce weight for transportation, minimize storage space, and reduce water activity. With the freeze-drying method, the highest quality product can be obtained compared to other drying methods. When water is added again to the freeze-dried material, it quickly absorbs water in its structure (rehydration) thanks to its wrinkle-free and porous structure and reaches a structure very close to its structure before drying. Another advantage of freeze-dried foods and biological materials is that they experience little loss of taste and aroma during the drying process [1]. There is less antioxidant loss in freeze-dried products than in products dried with other drying methods [2]. In studies conducted for exotic fruits, it has been stated that freeze drying preserves physical properties, minimizes shrinkage, and preserves vitamin C and phenolic content more than other methods [3, 4]. Kumquat is a small, elliptical-shaped fruit which contains high amounts of antioxidant substances. They are used as traditional folk medicine to manage inflammation of the respiratory tract. The flavonoid compositions of kumquats are very different from those of other citrus species [5-7].

In the literature, there are studies on freeze drying of citrus fruits and the effects of ultrasonic pretreatment for many fruits and vegetables. Izli et al. (2018) determined optimal drying conditions for Kumquat in an oven dryer at 70℃ [8]. Igual et al. (2019) focused on freeze-drying grapefruit with high molecular weight solutes. The study included a microwave drying pretreatment, revealing Midilli-Küçük and Page models as suitable for different formulations (F1, F2, F3) with corresponding freeze-drying times. Nutrition and antioxidant capacity were evaluated, showing a protective effect of gum arabic and bamboo fiber [9]. Silva-Espinoza et al. (2021) explored freeze-dried orange snacks, considering freezing rate, shelf temperature, and working pressure. Sensory factors influenced optimal freeze-drying conditions [10]. Dziki (2020) investigated various pretreatment methods on freeze-dried food, highlighting the reduction in drying time for fruits with ultrasound (US) pretreatment. US also enhanced antioxidant properties but caused reduced hardness and shrinkage in quince fruit [11]. Tüfekci et al. (2017) studied ultrasonic pre-treatment on carrot slices before hot air drying, finding increased drying speed and reduced time with longer pre-treatment. Page and Modified Page models explained drying kinetics, and SEM images showed tissue damage with higher amplitude [12]. Turgut (2021) compared freeze drying and hot air drying (50℃, 60℃, 70℃, 1 m/s) effects on Kumquat slices. Freeze-dried slices exhibited superior properties in terms of color, total phenolic, total flavonoid, and ascorbic acid content. The study suggests freeze drying as an alternative for bioactive-rich fruits like kumquat [13].

Despite numerous freeze-drying modeling studies on other citrus fruits, research on kumquat has focused solely on quality characteristics. Furthermore, while ultrasound (US) pretreatment is commonly applied to various fruits before freeze drying, there is a lack of studies on kumquat. Hence, this study aims to develop mathematical models for the freeze-drying process of kumquat slices with ultrasonic pre-treatment.

1. **Materials and Methods**
	1. **Sample Preparation and the Drying Experiments**

Kumquats were obtained from a retail market in Turkiye/Istanbul in September 2023. Kumquat samples was prepared for the study by cutting it in half, each piece weighing approximately 5.0 ± 0.5 g using a Radwag AS 220.R2 Digital Balance (Radwag, Radom, Poland) with an accuracy of 0.0001 g. Ultrasonic pre-treatment (US) was applied to Kumquat samples for 30 and 60 seconds in Isolab Water Bath with 1°C sensitivity and 120 W ultrasonic power (Isolab, Germany). Initial weighing of all samples was taken, and their moisture contents were determined at 105°C for 4 hours using a KH-45 hot air-drying oven (Kenton, Guangzhou, China). The samples were dried in a freeze dryer under conditions of -68.6 ºC and 0.9 Pa. Every 60 minutes, the system's vacuum was switched off to allow for the removal of the samples, which took less than two minutes to weigh and record. Then, the vacuum was activated, and the products were put back into the freeze drier. When the samples' moisture content reached 5%, the drying process was stopped, and the samples were vacuum-packed.

* 1. **Modeling Analyses**

The mass diffusion equation for drying edible products with a falling-rate period is represented by Fick's second law of diffusion. It is observed that the moisture content of the sample is decreased while the drying process continues. To investigate this process moisture content, and the moisture ratio calculations are performed with the following equations (1), (2), and (3).

$M=^{m\_{w}}/\_{m\_{d}}$ (1)

where moisture content (*M*) is calculated by the ratio of water content in the material (kg) to the dry matter content (kg).

$MR=\frac{M\_{t}-M\_{e}}{M\_{i}-M\_{e}}$ (2)

where *Mt* is the moisture content at a specific time, *Me* is the moisture content at equilibrium, and *Mi* is the moisture content of the material initially. Since *Me* value is rather small compared to *Mt* and *Mi* the simplified equation, equation (3) is used for moisture rate calculations [14,15].

$MR= \frac{M\_{t}}{M\_{i}}$ (3)

In this research mathematical modeling of Kumquat is done using different models as shown in Table.

Table 1. Drying models and equations\*

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| --- | --- | --- |
| **Model** | **Equation** |  |
| Hendersen & Pabis | $$MR = aexp(–kt)$$ | [16] |
| Jena & Das | $$MR = aexp(-kt+bt^{1/2}) + c$$ | [17] |
| Lewis | $$MR = exp(–kt) $$ | [18] |
| Two-Term Exponential | $$MR = aexp(-kt)+(1-a)exp(-kat)$$ | [19] |

\*\*In Table 1, a, b and c are the drying exponent coefficients that are defined for each equation separately: k is the drying coefficient that are defined equations separately and the t stands for time.

To find the best suitable model coefficient of determination (*R2*), root-mean-square error (*RMSE*), and reduced chi-squared statistic (*χ2*) are used. Required parameters for given models are estimated using the non-linear regression method with Statistica (Statistica, 2016). Equations for these methods are given below in equations (4), (5), and (6) respectively as follows.

$R^{2}=1- \frac{\sum\_{i=1}^{n}\left(MR\_{exp.i}- MR\_{pre.i}\right)^{2}}{\sum\_{i=1}^{n}\left(MR\_{exp.i}- \left(\frac{1}{n}\right)MR\_{exp.i}\right)^{2}}$ (4)

$RMSE= \left(\frac{1}{n}\sum\_{i=1}^{n}\left(MR\_{exp.i}- MR\_{pre.i}\right)^{2}\right)^{^{1}/\_{2}}$ (5)

$χ^{2}= \frac{\sum\_{i=1}^{n}\left(MR\_{exp.i}- MR\_{pre.i }\right)^{2}}{n-z}$ (6)

where *MRexp* is the experimental moisture ratio values, *MRpre* is the predicted moisture ratio values, n is the total number of the experiments, and z is the number of the constants in the given model. In the selection of best fitted model *R2* values are expected to be closer to 1. On the other hand, *RMSE* and *χ2* values are expected to be closer to 0 [14,15].

1. **Results and Discussion**
	1. **Drying Experiments’ Results**

In the moisture determination study carried out before freeze drying, the moisture contents were determined as 80.10% on wet basis in the control sample, 83.49% on wet basis in 30 seconds US pretreatment, and 81.65% on wet basis in 60 seconds s US pretreatment. Drying of control and pretreated samples was completed at 480 minutes. Kumquats before and after freeze drying are shown in Figure 1.



**Figure 1**. Control (a), 30 s US (b), and 60 s US (c) samples before drying and control (d), 30 s US (e), and 60 s US (f) samples after drying

* 1. **Modeling Analyses Results**

The most suitable model was chosen with non-linear regression by Statistica software. Experimental moisture ratios with respect to drying time were fitted into Hendersen & Pabis, Jena & Das, Lewis, and Two-Term Exponential drying models. Statistical results of drying process at different parameters are given in Table 2. Comparison between the results showed that the lowest *R2* average is seen in Lewis model as 0.994854, 0.996505, and 0.996888 for control, 30 second US, 60 seconds US samples, respectively. Whereas the highest *R2* average is seen in Jena & Das model as 0.997620, 0.997944, and 0.998673 for control, 30 second US, 60 seconds US samples, respectively. In support of these results, the lowest values of *χ2* 0.000802, 0.000638 and 0.000411 and the lowest values of *RMSE* as 0.021106, 0.018820 and 0.015119 are obtained with Jena & Das model for drying of control, 30 second US, 60 seconds US samples, respectively. From the statistical methods, it can be seen that all the drying models are sufficient to define the relation between moisture ratio and the drying time, but Jena & Das model was chosen as the most fitted model.

**Table 2.** Mathematical and statistical parameters for drying models\*\*

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| --- | --- | --- | --- | --- |
| Model | Parameter | Unpretreated | 30 sec - US | 60 sec - US |
| Hendersen & Pabis | *a* | 1.026427 | 1.017758 | 1.020772 |
| *k* | 0.004783 | 0.004353 | 0.004334 |
| *R2* | 0.995460 | 0.996810 | 0.997306 |
| *χ2* | 0.001091 | 0.000706 | 0.000596 |
| *RMSE* | 0.029133 | 0.023437 | 0.021531 |
| Jena & Das | *a* | 15.966409 | 1.616275 | 3.166849 |
| *k* | 0.005854 | 0.005038 | 0.005086 |
| *b* | 0.018107 | 0.012023 | 0.013184 |
| *c* | -2.776722 | -0.485897 | -1.157761 |
| *R2* | 0.997620 | 0.997944 | 0.998673 |
| *χ2* | 0.000802 | 0.000638 | 0.000411 |
| *RMSE* | 0.021106 | 0.018820 | 0.015119 |
| Lewis | *k* | 0.004657 | 0.004271 | 0.004238 |
| *R2* | 0.994854 | 0.996505 | 0.996888 |
| *χ2* | 0.001082 | 0.000677 | 0.000602 |
| *RMSE* | 0.031011 | 0.024530 | 0.023140 |
| Two-Term Exponential | *a* | 0.002413 | 0.001987 | 0.002735 |
| *k* | 1.921299 | 2.141615 | 1.541651 |
| *R2* | 0.994740 | 0.996434 | 0.996773 |
| *χ2* | 0.001264 | 0.000789 | 0.000714 |
| *RMSE* | 0.031353 | 0.024778 | 0.023564 |

\*\*In Table 2, *a*, *b* and *c* are the drying exponent coefficients that are defined for each equation separately: *k* is the drying coefficient that are defined equations separately and the t stands for time.

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| metin, ekran görüntüsü, öykü gelişim çizgisi; kumpas; grafiğini çıkarma, çizgi içeren bir resim  Açıklama otomatik olarak oluşturuldu | metin, ekran görüntüsü, öykü gelişim çizgisi; kumpas; grafiğini çıkarma, çizgi içeren bir resim  Açıklama otomatik olarak oluşturuldu |
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| metin, çizgi, ekran görüntüsü, öykü gelişim çizgisi; kumpas; grafiğini çıkarma içeren bir resim  Açıklama otomatik olarak oluşturuldu |  |

Figure . Graphs of mathematical drying models overlapping with data

1. **Conclusion**

This study was carried out to investigate the freeze-drying kinetics and mathematical modeling of Kumquat. The pretreatment was carried out for two different times, but the drying times for the control and pretreated samples were found to be the same. Different mathematical drying models were applied and Jena & Das drying model was selected as the most appropriate model for all samples considering *R2*, *RMSE* and *χ2*. The experimental and predicted moisture content graphs of the applied models were drawn and data distributions were observed. Accordingly, it was concluded that the US pretreatment showed similar results with the control sample within the applied times and measured parameters.

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