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### Kükürtlenmiş Kayısların Raf Ömrünü Uzatmada Kükürtün Etkisinin Kinetik İncelenmesi

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#### **Öne Çıkanlar:**

- Kayısı
- Raf ömrü
- Ambalaj

#### **Anahtar Kelimeler:**

- Kükürtlenmiş kayısı
- Yarı ömür
- Kinetik
- Kükürt dioksit

#### **ÖZET:**

Bu çalışmada Malatya ilindeki fabrikadan temizlenmiş farklı kükürt değerlerine sahip kükürtlenmiş kayısı alınmıştır. Bu kayısı numuneleri satışa sunulan ambalaj içerisinde market ortamındaki sıcaklık değerlerinde (4, 26 ve 40°C sıcaklık) muhafaza edilerek kükürt dioksit değerleri günlük olarak tayin edilmiştir. Deneysel süreler sonucunda numundeki kükürt dioksitin hesaplanarak azalma hızı ve diğer veriler hesaplanmıştır. Kükürt dioksitin farklı sıcaklıklarda zamanla değişiminden kayıp hızı ve kinetiği belirlenmiştir. Elde edilen sonuçlardan kükürtlü kayısının ambalaj içerisinde farklı sıcaklıklarda raf ömrü, bozulma, kükürt dioksit değerinin raf ömrü üzerine etkisi gibi önemli sonuçlar elde edilmiştir. Farklı oranlarda kükürt içeren kayısının analiz sonuçlarına göre kinetik çalışmada kuru kayısı örneklerinde, rafta kalma süresince meydana gelen; nem ve SO<sub>2</sub> kaybı incelendiğinde 4°C için birinci derece kinetik modele uygun, 26 ve 40°C için de ikinci mertebe kinetik modele uygun olduğu belirlenmiştir. Deneysel sonuçlardan 4°C sıcaklıkta 980 saat süre sonunda, 26°C sıcaklıkta 525 saat süre sonunda satışa sunulan örneklerin kükürt uzaklaşma değerleri oldukça düşük elde edilmiştir. 40°C sıcaklık değerinde yaklaşık 740 saat süre sonunda nem ve SO<sub>2</sub> kayıpları hızlanmıştır. 4°C sıcaklıkta rafta bekleme süresince 3280 ppm düzeyinde kükürt dioksit içeren örnekte 980 saat süre sonunda % 11 oranında kükürt dioksit kaybı olmuştur. Aynı numunelerde 40°C sıcaklıkta 740 saat süre sonunda % 46 oranında kükürt dioksit kaybı belirlenmiştir. Yüksek sıcaklıklarda kükürt dioksit kaybının daha fazla olduğu belirlenmiştir. Örneklerin nem açısından saklama koşulları incelendiğinde 4 ve 40°C sıcaklıklarda 29 gün sonunda kayısı nemini %52-85 aralığında kaybetmektedir. Satışa sunulan ambalajlı kükürtlenmiş kuru kayısının su aktivitesinin %25 olduğu temel alındığında yapılan bu çalışmada bu değere göre yaklaşık ortalama 25 gün raf ömrü saptanmıştır.

### Kinetic Investigation of The Effect of Sulfur on Extending The Shelf Life of Sulfurized Apricots

#### **Highlights:**

- Apricot
- Shelf life
- Packaging

#### **Keywords:**

- Sulphurous apricots,
- Half life,
- Kinetic,
- Sulfur dioxide

#### **ABSTRACT:**

In this study, sulphurized apricots with different sulfur values were obtained from the factory in Malatya province. These apricot samples were kept at market temperature values (4, 26 and 40°C) in the package offered for sale, and their sulfur dioxide values were determined daily. As a result of the experimental periods, reduction rate and other data were determined by calculating the sulfur dioxide in the sample. Also, loss rate and kinetics of sulfur dioxide were determined from its change over time at different temperatures. From the results obtained, important findings such as shelf life of sulphurous apricots at different temperatures in the package, deterioration and effect of the sulfur dioxide value on the shelf life were obtained. According to the analysis results of apricots containing different amounts of sulfur, when the moisture and SO<sub>2</sub> loss in dried apricot samples during their stay on the shelf were examined in the kinetic study, it was determined that it was suitable for the first order kinetic model for 4°C and the second order kinetic model for 26 and 40°C. From the experimental results, quite low sulfur removal values were obtained for the samples offered for sale after 980 hours at 4°C and 525 hours at 26°C. Moisture and SO<sub>2</sub> losses accelerated after approximately 740 hours at a temperature of 40°C. In the sample containing 3280 ppm sulfur dioxide during shelf storage at 4°C, there was an 11% loss of sulfur dioxide after 980 hours. A 46% sulfur dioxide loss was determined in the same samples after 740 hours at 40°C. It has been determined that sulfur dioxide loss is greater at higher temperatures. When the storage conditions of the samples were examined in terms of humidity, it was observed that apricots lost their moisture in the range of 52-85% after 29 days at temperatures of 4 and 40 °C. Based on the fact that the water activity of the packaged sulfurized dried apricots offered for sale is 25%, in this study, an average shelf life of approximately 25 days was determined according to this value.

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Bu çalışma Duygu Gürbüz'ün Yüksek Lisans tezinden üretilmiştir.

## INTRODUCTION

Due to the recent increase in the importance given by developed countries to the agricultural sector, it has led to the development of policies based on the progress of the sector. In the field of agriculture, great efforts are being made in cooperation with the private sector, state sector, universities and other institutions to ensure sustainability and increase productivity in agriculture. When the Common Agricultural Policy implemented by the European Union countries is taken into consideration in this sense, the importance and extent of the work carried out for the development of the sector can be understood. In accordance with the Common Agricultural Policy, the EU spends approximately 40% of its budget (55 billion €) on the agricultural sector every year (Davis, 1972; Davis et al 1975; Davis et al 1973).

Increasing interest in the agricultural sector of countries that can be considered superior to Turkey with their institutional structures and technologies is a situation that should be followed. (Stern et al., 2007). Turkey, like other countries, must quickly adapt to the changing developments and trends in the world and increase its competitiveness.

Agricultural sector has an important place in the Turkish economy. With its geographical location, natural riches and climate, Turkey has suitable conditions for growing many agricultural products. Turkey does not have the place it should be in agriculture due to inadequate policies, technology, research and development activities, and education (Budak and Şan, 2017).

Apricot (*Prunus armeniaca* L.) is in the *Prunus* genus of the Rosaceae family. Apricot, which we can say is a temperate climate fruit, generally grows in places where the vineyard climate prevails in Turkey. However, some varieties and types also grow in subtropical climate conditions. Because it is damaged by excess moisture, it does not grow in many regions of the Black Sea Region (Kocaeli, Zonguldak, Bolu, Ordu, Trabzon and Rize) and in the high plateaus of Eastern Anatolia where severe winter cold is effective (Özçağiran et al., 2004).

Considering that Turkey is the leader in the apricot sector in world production, it should closely follow the developments in the sector and focus on it. With their quality and taste, the apricot varieties grown in Malatya are the most admired apricots in the world. Exporting products as raw materials in the sector and processing these products in foreign countries causes the mistake of increasing their added value (Karaçalı, 2006; Asma et al., 2000). Processing apricots and obtaining added value from the product in this way will be beneficial for producers, industrialists, and Turkey.

Golden yellow dried apricot color has a significant impact on consumer demand. During drying and storage, apricots lose their characteristic golden yellow color due to browning reactions. Nowadays, apricots are sulfurized before drying to prevent both enzymatic and non-enzymatic browning reactions. The sulfurization process, which is an important stage of dried apricot production, is carried out by farmers who do not have the knowledge and sufficient resources. This situation causes excessive sulfuration of the produced apricots and negatively affects our dried apricot exports. Thus, it cannot provide sufficient income, especially for our farmers and then for our country's economy (Salurcan, 2018; Korbel et al 2013; Wedzicha, 1984; WHO Food Additives Series 2008).

The fruits harvested in the sulphurization process with traditional methods are placed on the drying boards (kerevet). Apricots placed on the drying boards are placed in the sulphuring chambers. In one corner of the room, a furnace with powdered sulfur is lit (2 kg of powdered sulfur for 1 ton of fresh apricots) and the door of the room is tightly closed. In order for the fruits to absorb the sulfur gas thoroughly, they are kept in the heating chamber for 6-8 hours. Afterwards, the fruits are taken out of

the warming room and placed in a single row on a cloth in a sunny area and left to dry (Sobutay, 2003; Freedman, 1980).

Aim of the research is to kinetically examine change in sulfur values of sulfurized apricots, which are offered for sale on the shelves, specific to Malatya province, during their stay on the shelves. Malatya apricot is important for the reasons mentioned. Every study and research on apricot is needed. Our aim is to make a small contribution to the apricot industry with the research carried out. The aim of the research is to analyze the enterprises that produce apricots in Malatya province and to reflect it to the whole province of Malatya, and therefore to the Turkish apricot sector

## MATERIALS AND METHODS

In the study, 2000, 3000, 4000, 5000 ppm sulphurous apricots and sun dried apricot samples from Çöloğlu, Hacıhaliloğlu, Kabaası and Karacabey were purchased from the apricot processing factory through BAP. In this study, H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich 7722-84-1), NaOH (Sigma-Aldrich 1310-73-2), HCl (Sigma-Aldrich 7647-01-0), C<sub>19</sub>H<sub>10</sub>Br<sub>4</sub>O<sub>5</sub>S (Sigma-Aldrich 115-39-9) were used as chemicals in the analysis processes. Samples were weighed using Denver Instrument and Precisa 3100 C Balance. In addition, Nüve PN500 oven was used for drying processes and Moulinex HV6 Meat Grinder was used for grinding processes.

### Sulfur analysis method in apricot

In this study, Çöloğlu, Hacıhaliloğlu, Kabaası and Karacabey apricot samples in the packaging at the final sales point were taken from the sales point and some of them were sulfurized and some were used without sulfurization. The sulfurization method of apricots was performed as the 'traditional sulfuration method'.

Sulfur dioxide determinations were carried out in the laboratory at temperature conditions of 4, 26 and 40°C, taking into account features such as apricots, packaging material, temperature and light properties. Analyzes were terminated when the sulfur dioxide value became constant.

In the study, distillation method introduced by Monier Williams (1927), standardized by TSE, and modified by Reith and Willems in 1958, was used to determine sulfur (Gökçe 1966). First of all, ready-to-pack apricot samples containing 2000, 3000, 4000 and 5000 ppm sulfur and sun dried apricots were purchased from the factory through BAP. Apricots were weighed into half-kilo polystyrene containers, which is the most commonly used packaging at sales points, and covered with (PET) stretch film, which is used in food packaging. Apricots were stored at temperatures of 4, 26 and 40°C. Appropriate amounts of samples were taken from the packaging at certain time intervals and prepared for analysis. First of all, the apricots were milled, 5 g of sample was weighed and the experimental setup was prepared before the distillation process. Then, 150 ml of distilled water was placed in a 1 L distillation flask and N<sub>2</sub> gas was sent to the system for 15 minutes, producing 30 bubbles per minute. In this way, oxygen that causes the oxidation of SO<sub>2</sub> to sulfate (SO<sub>4</sub>)<sup>-2</sup> was removed from the medium. Then, 130 ml of distilled water, the weighed apricot sample and 40 ml of 15% HCl solution were added to the distillation flask. 10 ml of 3% H<sub>2</sub>O<sub>2</sub> was added to the distillate collection flask. The relevant mixture was boiled in the heater for approximately 90 minutes (Figure 1) Sulfur dioxide (SO<sub>2</sub>) in dried apricots was liberated with hydrochloric acid (HCl) and distilled in an inert gas atmosphere of nitrogen (N<sub>2</sub>). Then, the distillate was converted to sulfuric acid with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in the collection flask. Amount of SO<sub>2</sub> in apricots was calculated from the amount of base consumed by titrating the acid formed with adjusted NaOH solution. Therefore, the international standard method was used in sulfur dioxide analysis. Also, weighings were performed on analytical precision balances available in our laboratory and, the samples

were analyzed by keeping them in a temperature-controlled oven in the laboratory. Distilled water was used in the all experiments.



Figure 1. Sulfur analysis mechanism

### Drying method in an oven

In this section, apricot types that contain and do not contain sulfur in certain proportions were used. Apricot samples arranged in Petri dishes were weighed more frequently at the first time intervals and then expanded at later time intervals. Then, moisture content was noted. The process continued until the moisture content in the apricots was constant.

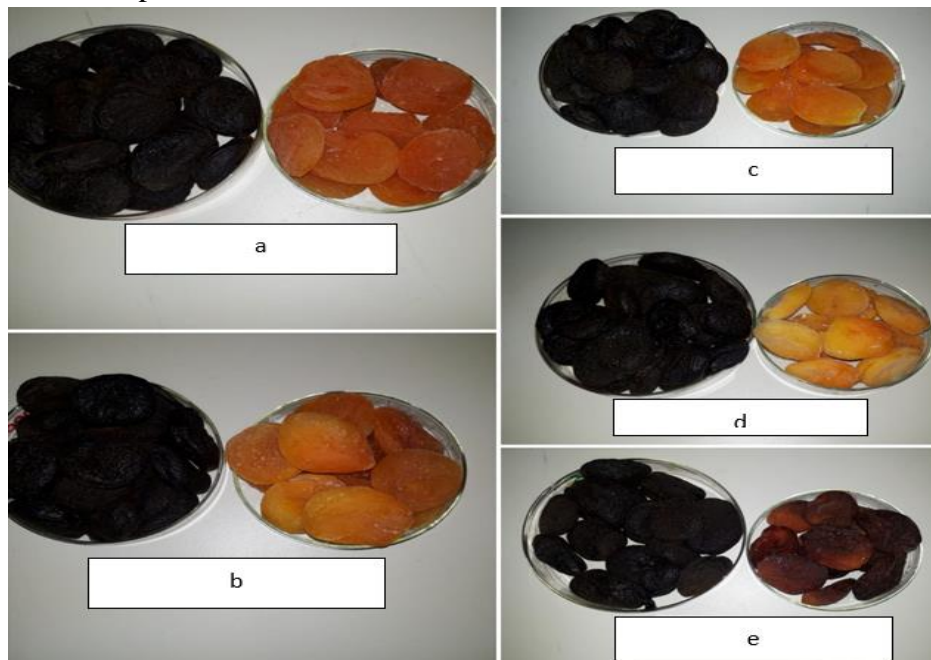


Figure 2. Before and after drying in the oven of (a) 2000 ppm, (b) 3000 ppm, (c) 4000 ppm, (d) 5000 ppm, (e) Sun Dried (Gün Kuru)

As can be seen in the Figure 2, color and odor changes were observed in the apricots dried in the oven as a result of the amount of moisture removed.

## RESULTS AND DISCUSSION

### Change in Free Moisture Value

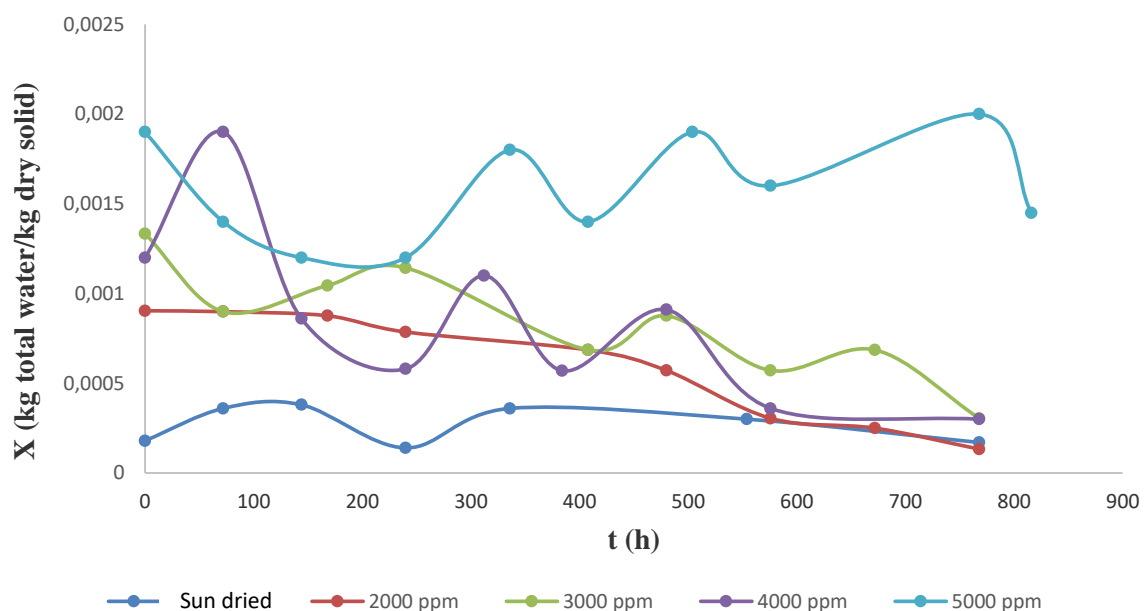
Free moisture-time curves used in the graphical evaluation of the results of the experiments carried out at certain time intervals at 4°C, 26°C and 40°C were examined at different sulfur concentrations (2000, 3000, 4000 and 5000 ppm) and sun dried apricots. The free moisture change over time was examined separately for all temperatures and concentrations and the results were given in Figures 3, 4, 5.

When Figure 3 is examined, results regarding the loss of free moisture at the end of 816 hours for 2000, 3000, 4000 ppm sulfur apricots and sun dried for 4°C operation and at the end of 768 hours for 5000 ppm are as follows:

It can be seen that free moisture decreases over time for a concentration of 2000 ppm. Total change in free moisture is 85.29%. In other words, it is seen that apricots with 2000 ppm sulfur lose a great deal of moisture in storage conditions depending on the packaging material used.

In the experiments carried out at 3000 ppm, change in the free moisture value is in the direction of increasing compared to the 2000 ppm sample. The increase is related to the storage conditions of the sample as well as the ambient humidity. Considering that all experiments were carried out under the same conditions (constant temperature, humidity and pressure), amount of the free moisture at the beginning was 0.003047, while amount of free moisture after drying was found to be 0.001333. Accordingly, approximately 56.35% moisture was removed from the apricot.

When the free moisture change was examined in the experiments performed at 4000 ppm, the amount of free moisture at the beginning was 0.0012, while the amount of free moisture at the end of drying was found to be 0.0003. Accordingly, approximately 75% moisture has been removed from the apricot. Decreases and increases at certain time intervals are associated with opening and closing the package during sampling.



**Figure 3.** Curve of drying versus flow rate of sulfur apricots and sun dried fruits studied at different concentrations under storage conditions at 4°C

When the change in free moisture value was examined in the experiments performed at 5000 ppm, amount of free moisture at the beginning was 0.0019, while amount of free moisture at the end of drying was found to be 0.0015. Accordingly, approximately 21% moisture was removed from the apricot.

Decreases and increases at certain time intervals are associated with opening and closing the packaging during sampling. However, at 5000 ppm concentration, the change in free moisture remained less after a longer period of time compared to others, which can be explained by the fact that sulphurous structures bind more water in the body.

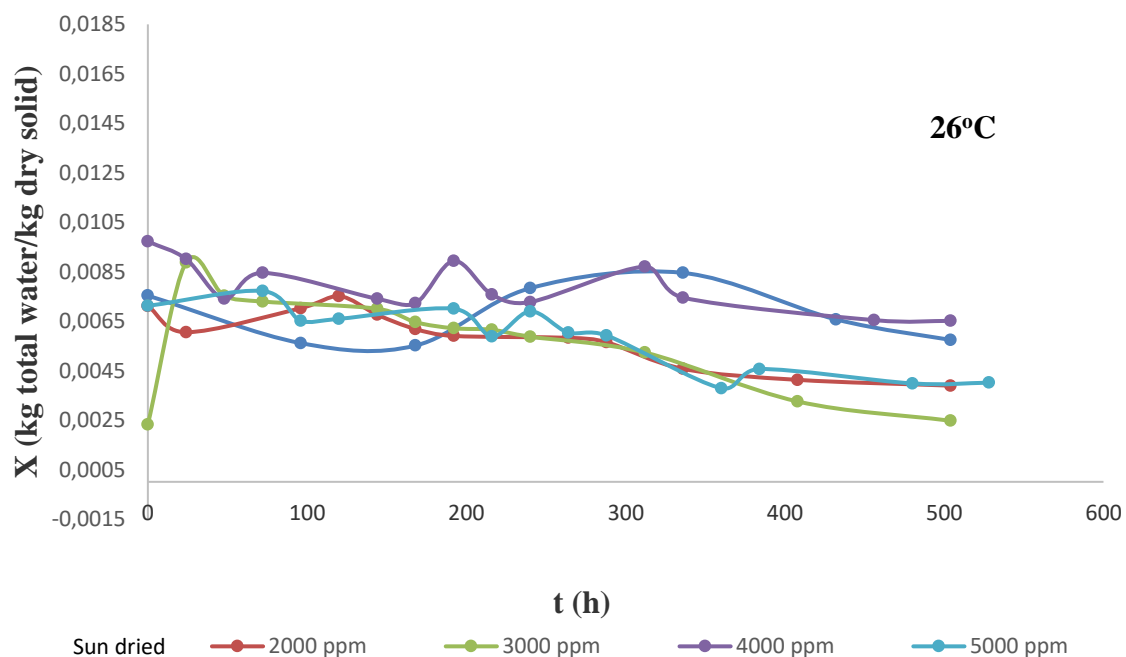
In the experiments performed on sun-dried apricots, change in the free moisture value was at a minimum level compared to the sulphurous samples. While amount of the free moisture at the beginning was 0.00018, amount of the free moisture after drying was found to be 0.00017. Accordingly, approximately 5.6% moisture was removed from the apricot.

In summary, since amount of the moisture in the environment is low under cold storage conditions, water in the material will move away from the environment through evaporation. This is the reason for the decrease in the amount of free moisture. Therefore, in cold storage conditions, it should be taken into account whether environment is fully closed or semi-open.

As can be seen in Figure 4, results regarding the loss of free moisture after certain periods for 2000, 3000, 4000 ppm and sun-dried under the 26°C condition are as follows:

In the experiments carried out at 2000 ppm, change in the free moisture is not much. Reason for this can be explained by the fact that the inside of the package and the ambient humidity are the same. While amount of the free moisture at the beginning was 0.00711, amount of the free moisture after drying was found to be 0.007202. Accordingly, moisture in the apricots increased by approximately 1.29%.

Change in free moisture value in the experiments performed at 3000 ppm is similar to that of 2000 ppm. While amount of the free moisture at the beginning was 0.00232, amount of the free moisture after drying was found to be 0.00247. Accordingly, moisture in the apricots increased by approximately 6.46%.



**Figure 4.** Curve of drying versus flow rate of sulfur apricots and sun dried apricots studied at different concentrations under storage conditions of 26°C

In experiments conducted at 4000 ppm, change in the free moisture is greater, unlike other 2000 and 3000 ppm concentrations. While amount of the free moisture at the beginning was 0.00972, amount

of the free moisture after drying was found to be 0.00651. Accordingly, approximately 33% moisture was removed from the apricot.

In experiments conducted at 5000 ppm, change in the free moisture up to 360 hours is higher, unlike other 2000, 3000 and 4000 ppm concentrations. While amount of the free moisture at the beginning was 0.00711, amount of the free moisture after drying was found to be 0.00378. Accordingly, approximately 47% moisture was removed from the apricot.

Change in the free moisture for sun-dried apricots is not much compared to the sulfur-containing ones. While amount of the free moisture at the beginning was 0.00753, amount of the free moisture after drying was found to be 0.00545. Accordingly, approximately 27% moisture was removed from the apricot.

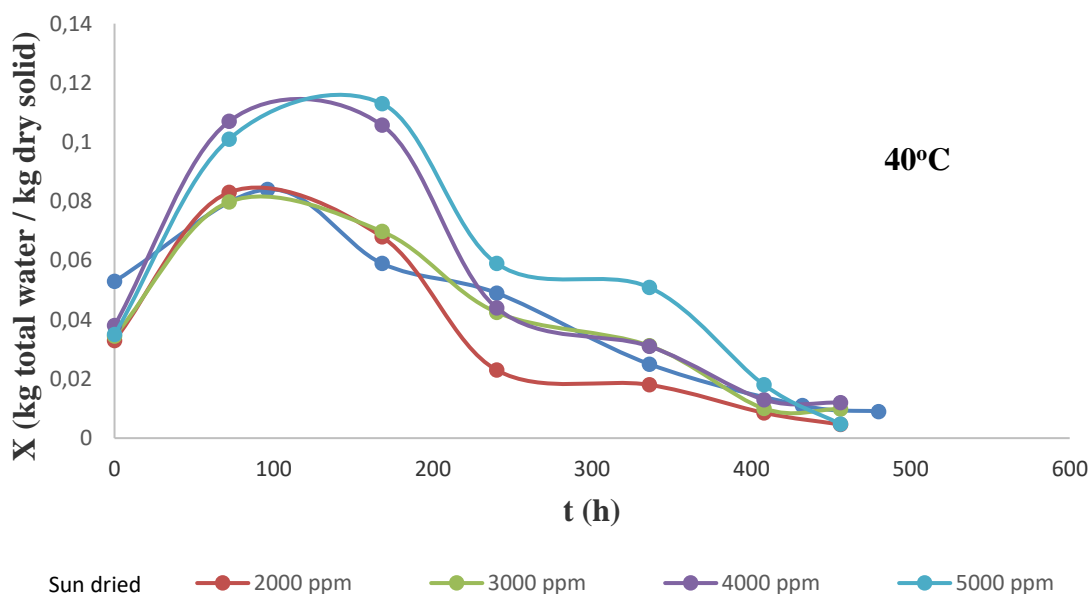
Variation in free moisture at 26°C is lower than that of at 4°C.

As shown in Figure 5, results regarding the loss of free moisture at the end of certain periods for 2000, 4000, 5000 ppm, 3000 ppm and sun dried for 40°C operation are as follows:

In the experiments carried out at 2000 ppm, it was observed that the moisture was rapidly removed at the initial value with the change in the free moisture value. While the amount of free moisture at the beginning was 0.033, the amount of free moisture after drying was found to be 0.00461. Accordingly, approximately 86% moisture was removed from the apricot.

In the experiments carried out at 3000 ppm, it was observed that the moisture was removed rapidly at the initial value when the free moisture value changed. While amount of the free moisture at the beginning was 0.0345, amount of the free moisture after drying was found to be 0.00812. Accordingly, approximately 76% moisture was removed from the apricot.

In the experiments carried out at 4000 ppm, it was observed that the moisture was removed rapidly at the initial value when the free moisture value changed. While amount of the free moisture at the beginning was 0.038, amount of the free moisture after drying was found to be 0.012. Accordingly, approximately 68% moisture was removed from the apricot.



**Figure 5.** Curve of drying versus flow rate of sulfur apricots and sun dried apricots studied at different concentrations under storage conditions of 40°

In the experiments carried out at 5000 ppm, it was observed that the moisture was removed rapidly at the initial value when the free moisture value changed. While amount of the free moisture at the

beginning was 0.035, amount of the free moisture after drying was found to be 0.00472. Accordingly, approximately 87% moisture was removed from the apricot.

In the experiments performed on sun-dried apricots, it was observed that the moisture was removed rapidly at the initial value when the free moisture value changed. While amount of the free moisture at the beginning was 0.053, amount of the free moisture after drying was found to be 0.009. Accordingly, approximately 83% moisture was removed from the apricot.

When the results obtained from the figures are evaluated, the high level of free moisture loss can be explained by the opening of the pores due to the high temperature and the increased tendency of water to evaporate. As a result of the increase in water vapor concentration in the packaging, driving force for mass transfer increased due to both the pressure difference and the concentration difference between the external environment. As a result, moisture loss increased.

In summary, when storage conditions are examined in terms of humidity, apricots lose 52-85% of their moisture after 29 days at temperatures between 4 °C and 40°C. The cold refrigerator environment causes moisture loss just like the warm environment. When the moisture content of ready-to-eat apricots falls below approximately 25%, it becomes hard and difficult to chew. Therefore, ambient humidity conditions, temperature and packaging are of great importance in determining the shelf life. However, shelf life of sulfur apricots may vary depending on the consumption method. Considering that water activity of packaged sulfurized dried apricots offered for sale should be 0.25 (free moisture 25%), an average shelf life of approximately 25 days can be given according to this value in this study. However, when the dried apricots reach the initial moisture value again, they can be put on sale after the necessary tests are carried out.

### Change in Sulfur Amount

Sulfur is of great importance due to its importance in terms of health, both in the shelf life and consumption of apricots. Particularly compared to other fruits, apricot is a type of fruit that is easily spoiled and very difficult to store. Due to this feature, drying and storing of apricots has become important. In addition, short duration of consumption and durability when dried without additives necessitated the use of sulfur in drying and storing apricots. Therefore, drying and storing fresh apricots by sulfur has been used for many years as the most reasonable method

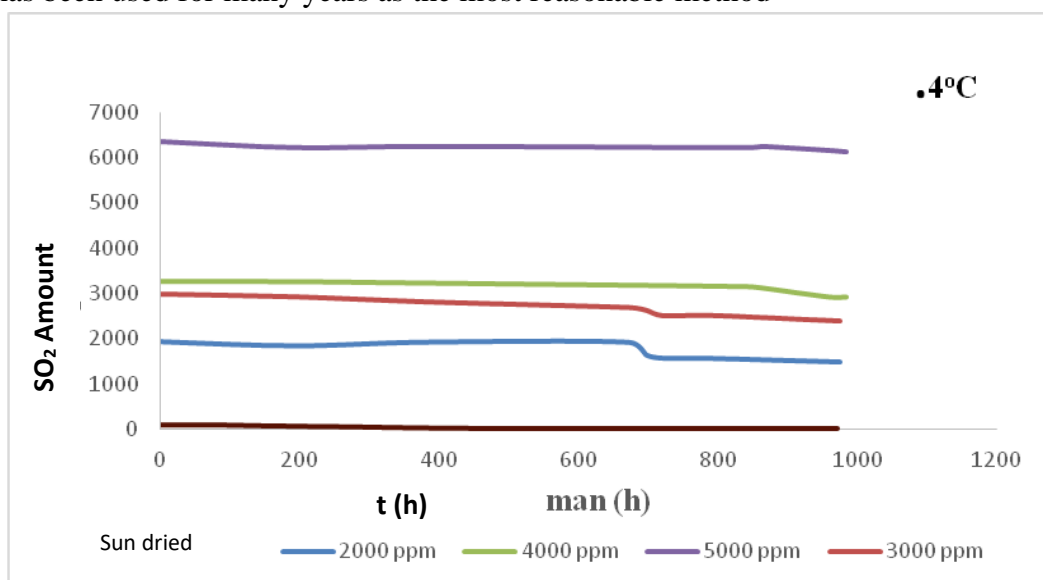


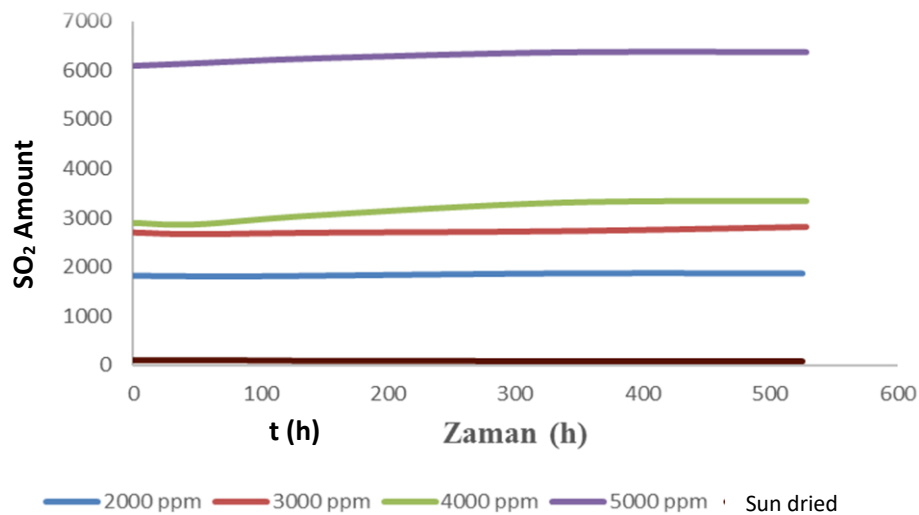
Figure 6. Change of sulfur dioxide amount in apricots over time under storage conditions at 4°C

Therefore, amount of sulfur in sulfurized apricots and their storage conditions have always been questioned. However, its importance has increased with the fact that sulfurized apricot strengthens the



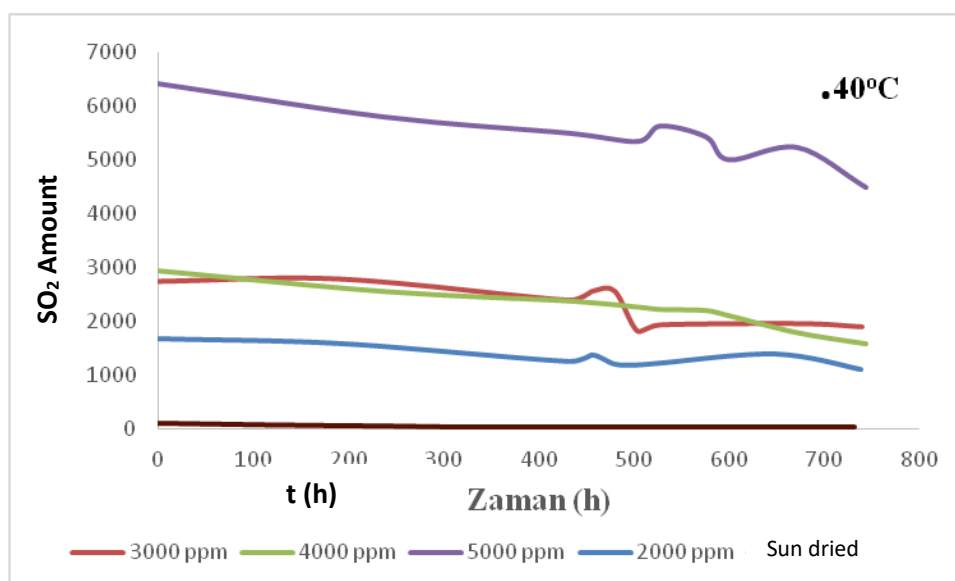
immune system. Shelf life of apricots after their sulfurization is of great importance in putting it on sale. Since darkening of the color of apricots due to the decrease in sulfur in low sulfur rates has a negative effect on sales and appeal, determining decrease in sulfur rate in sales conditions and shelf life has gained importance.

As shown in Figure 6, there is not much change in the sulfur dioxide rates of packaged apricot samples with 2000, 3000, 4000, 5000 ppm sulfur and dried sun dried apricots until approximately 950 hours at 4°C. Mass transfer from outside to inside and from inside to outside was minimal in apricots packaged at 4°C. Based on this, as seen in the graphic, it is the most suitable storage condition. The fact that there is no change in the sulfur rate despite the decrease in free moisture indicates that the sulfur is in the form of an organic compound and not in a form that can interact with water. Moreover, even if free sulfur dioxide forms sulfate acid with water, when the water evaporates, it remains in the structure of the apricot in the form of sulfur sulfate. This is the main reason why apricots are preserved by sulfurization.



**Figure 7.** Change of sulfur dioxide amount in apricots over time under storage conditions at 26°C.

When Figure 7 is examined, it is seen that the amount of sulfur removal in all samples is at a minimum level at 26°C. The situation is similar with storage conditions at 4°C.



**Figure 8.** Change of sulfur dioxide amount in apricots over time under storage conditions at 40°C

As seen in Figure 8, it was observed that the amount of sulfur dioxide removal from sulfurous apricots at 40°C decreased compared to 4°C and 26°C temperatures. The reason for this is that the amount of SO<sub>2</sub> moves away from the apricot as the pores open due to the increase in temperature.

### Variation of Sulfur Concentration with Time

Time-dependent removal of sulfur during drying of sulphurous and sun-dried apricots was investigated. First-order reaction kinetics were investigated according to equation 1 (Gonzalo et al., 2009).

$$-dCA / dt = kCA \quad (1)$$

$$CA / CA_0 = \exp(-kt) \quad (2)$$

$$\ln CA / CA_0 = -kt \quad (3)$$

$$\ln CA = \ln CA_0 - kt \quad (4)$$

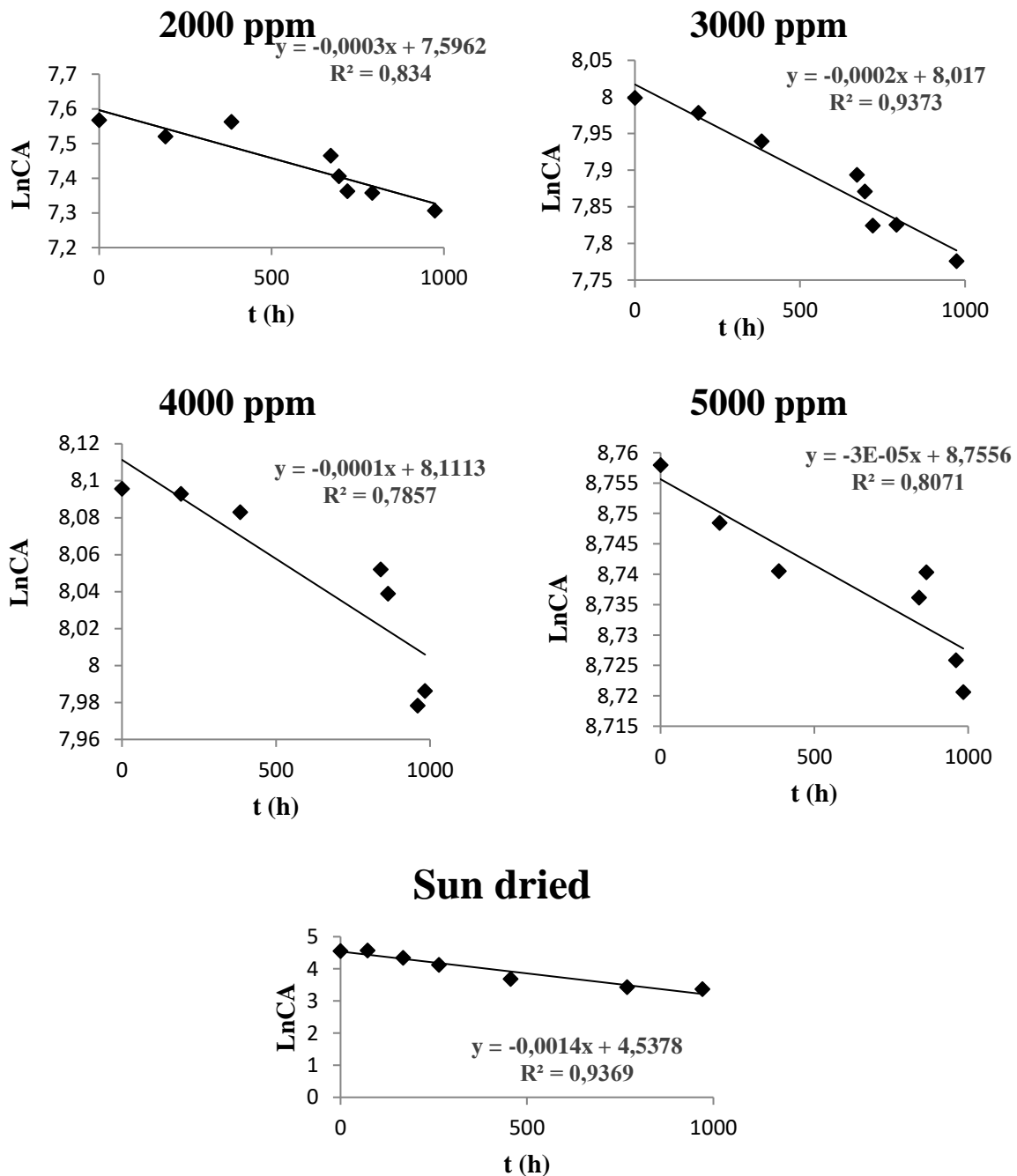


Figure 9. Time-dependent concentration variation graphs of first-order sulphurous and sun-dried apricots at 4°C

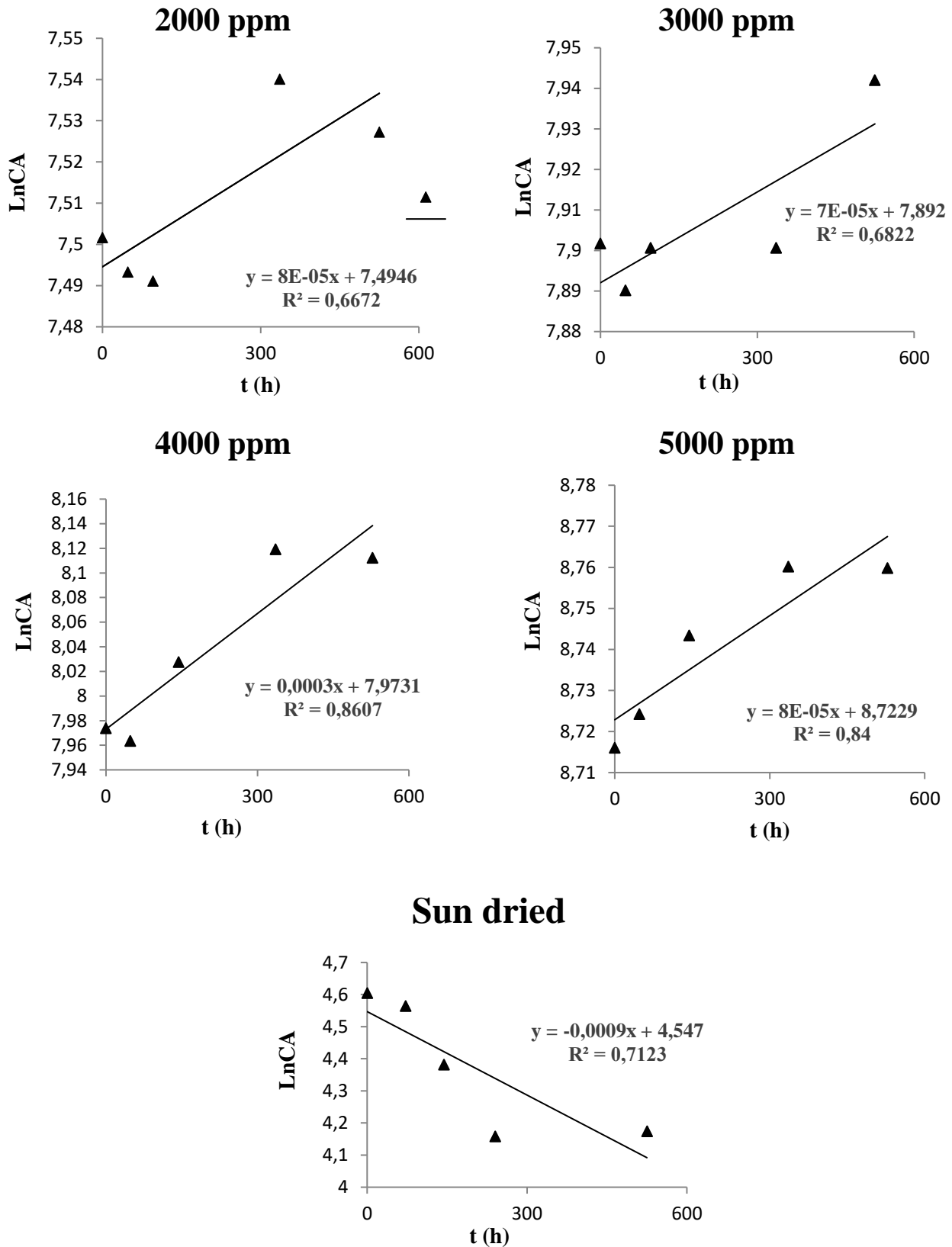
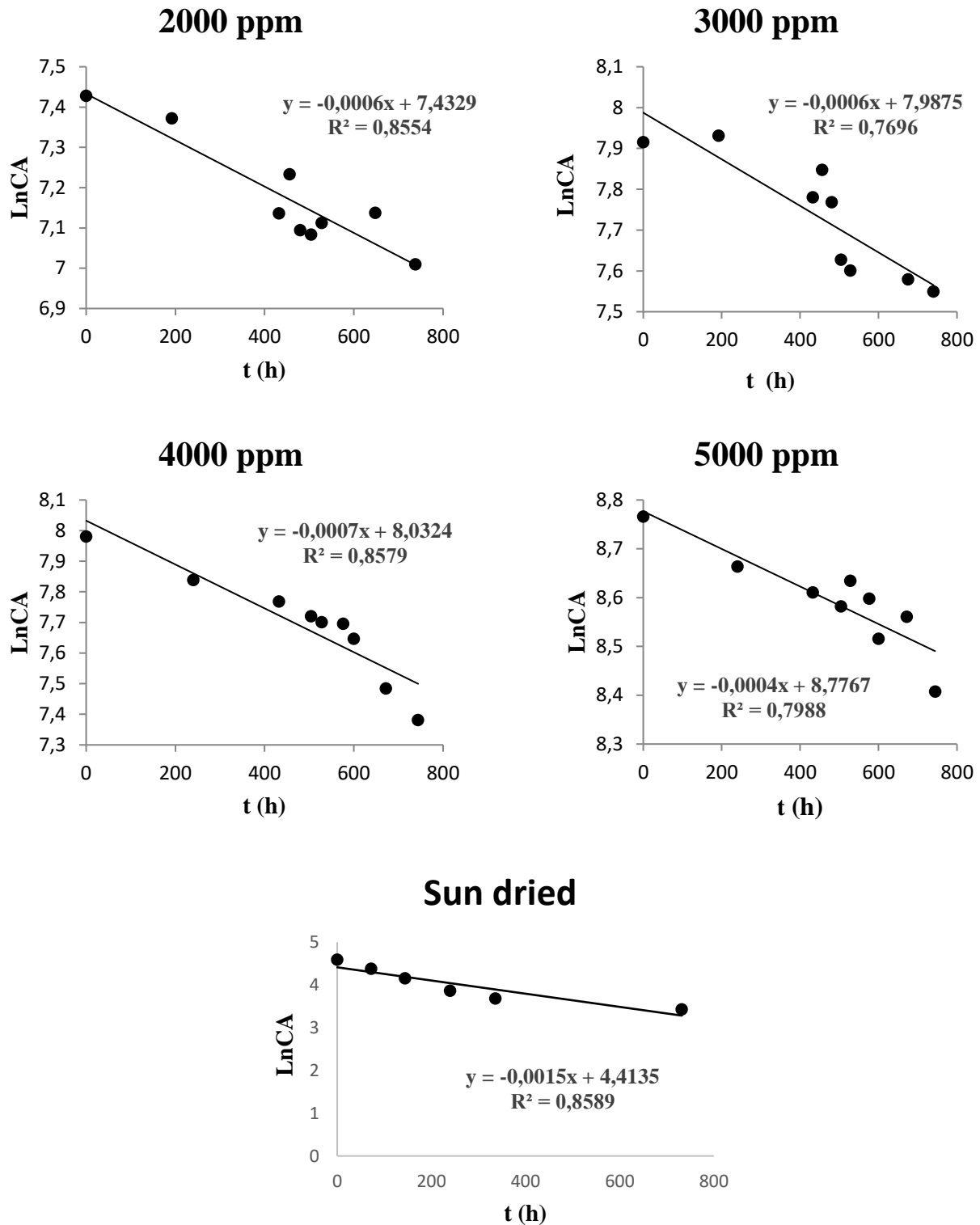


Figure 10. Time-dependent concentration variation graphs of first- order sulphurous and sun dried apricots at 26°C



**Figure 11.** Time-dependent concentration variation graphs of first-order sulphurous and sun-dried apricots at 40°C

Second-order reaction kinetics were investigated according to equation 5.

$$-dCA / dt = kCA^2 \quad (5)$$

$$1/CA - 1/CA_0 = kt \quad (6)$$

$$1/CA = 1/CA_0 + kt \quad (7)$$

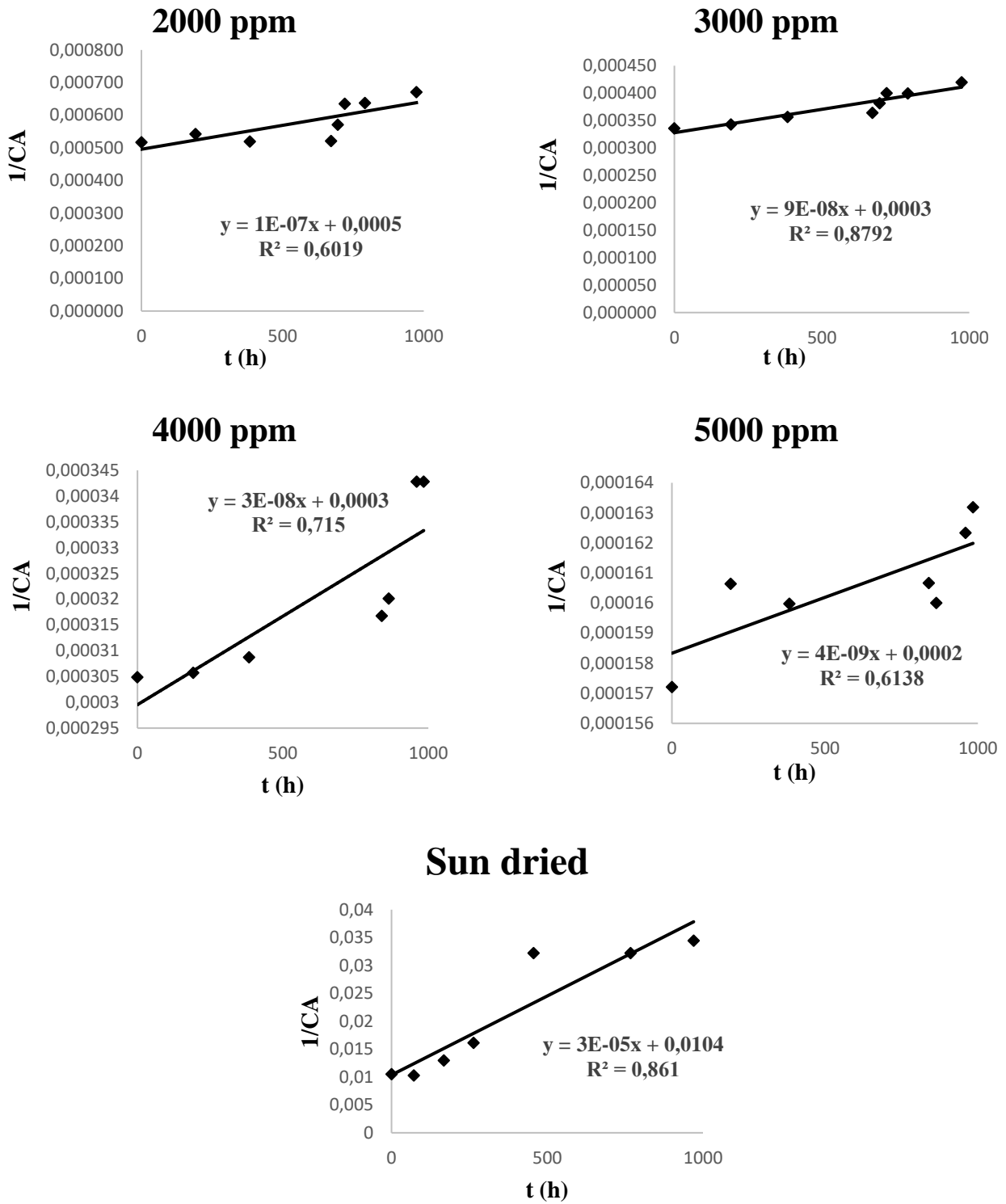


Figure 12. Time-dependent concentration variation graphs of second-order sulphurous and sun-dried apricots at 4°C

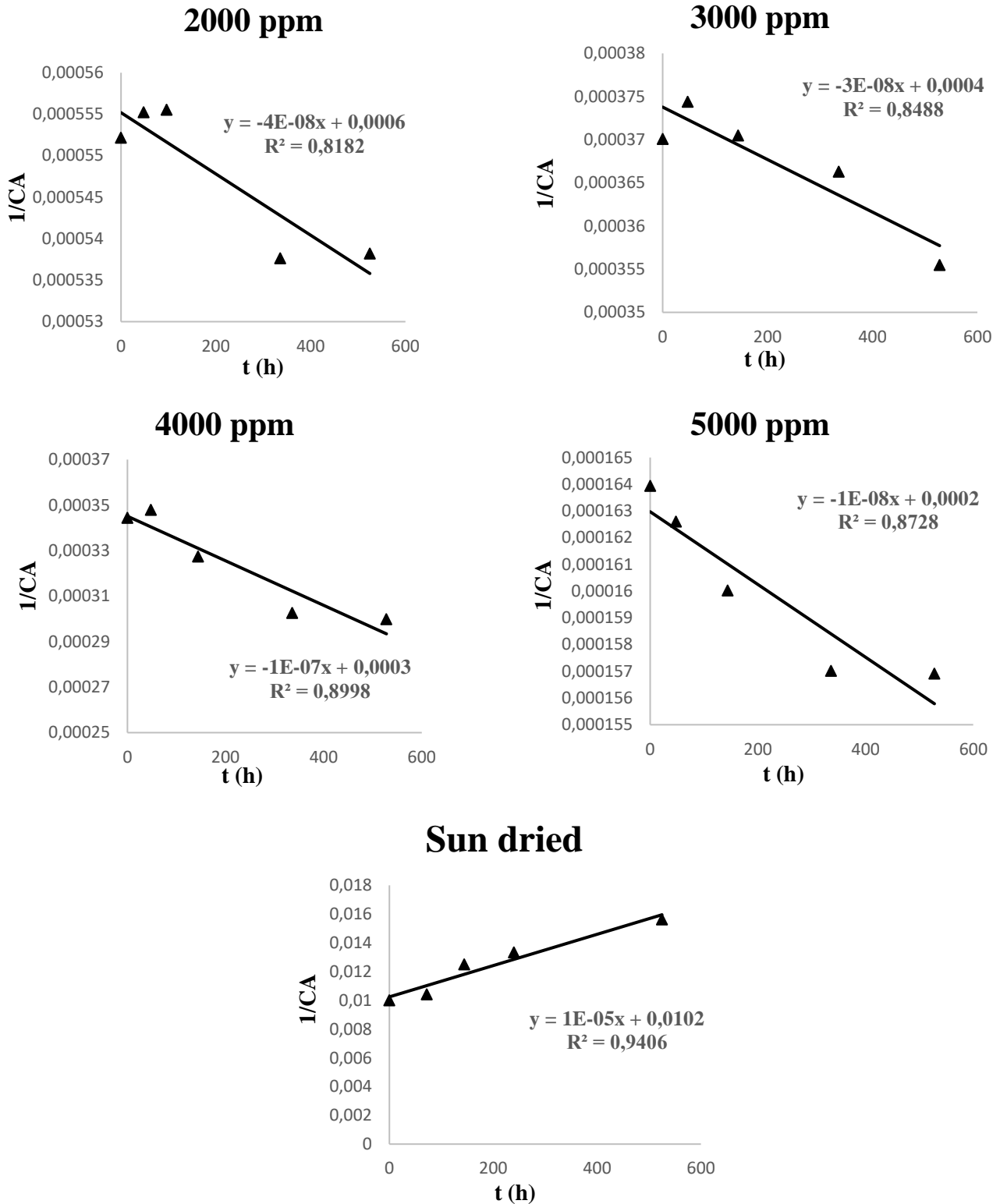


Figure 13. Time-dependent concentration variation graphs of second-order sulphurous and sun-dried apricots at 26°C

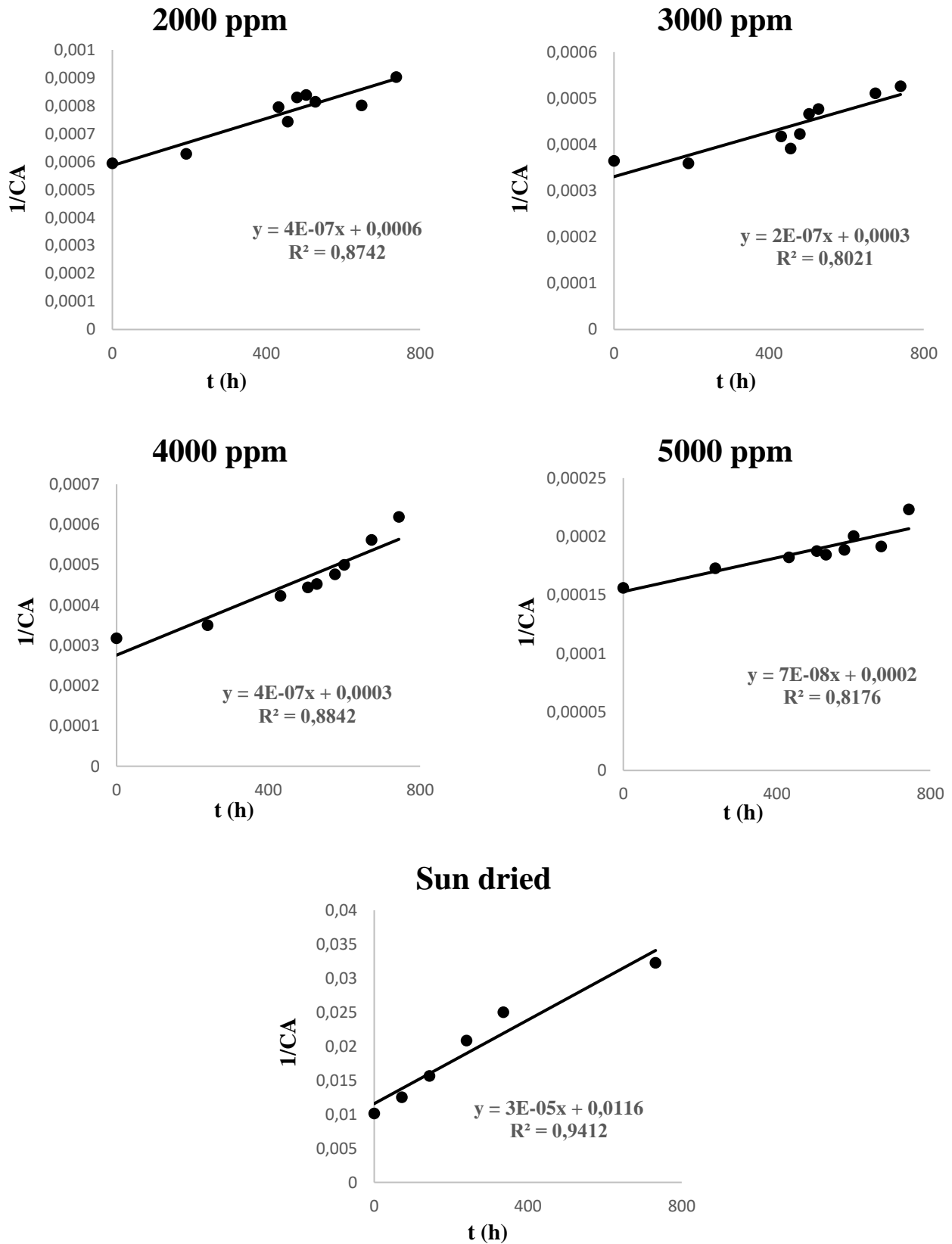


Figure 14. Time-dependent concentration variation graphs of second-order sulphurous and sun-dried apricots at 40°C

**Table 1.** First-order rate constants versus change of concentration at different temperatures

| Concentration | Temperature | k (d <sup>-1</sup> ) | Ea (kJ/mol) |
|---------------|-------------|----------------------|-------------|
| Sun dried     | 4°C         | 1.4*10 <sup>-3</sup> | 1.38        |
|               | 26°C        | 1.1*10 <sup>-3</sup> |             |
|               | 40°C        | 1.5*10 <sup>-3</sup> |             |
| 2000 ppm      | 4°C         | 2*10 <sup>-4</sup>   | 13.88       |
|               | 26°C        | -8*10 <sup>-5</sup>  |             |
|               | 40°C        | 6*10 <sup>-4</sup>   |             |
| 3000 ppm      | 4°C         | 2*10 <sup>-4</sup>   | 21.99       |
|               | 26°C        | -7*10 <sup>-5</sup>  |             |
|               | 40°C        | 6*10 <sup>-4</sup>   |             |
| 4000 ppm      | 4°C         | 1*10 <sup>-4</sup>   | 38.96       |
|               | 26°C        | -3*10 <sup>-4</sup>  |             |
|               | 40°C        | 7*10 <sup>-4</sup>   |             |
| 5000 ppm      | 4°C         | 3*10 <sup>-5</sup>   | 51.86       |
|               | 26°C        | -8*10 <sup>-5</sup>  |             |
|               | 40°C        | 4*10 <sup>-4</sup>   |             |

When the velocity constants calculated according to the 1st and 2nd order velocity data in Tables 1 and 2 are examined, for the first order, positive and increasing values were obtained for the 2000, 3000, 4000 and 5000 ppm sulfur dioxide concentrations for the 4°C temperature at constant drying conditions. The high rate constant at high temperature indicates that sulfur dioxide removal is high. Since the experiments carried out at 26°C were performed under variable ambient conditions, the rate constant was negative. It was concluded that the ambient conditions in the drying process affect the results quite a lot.

**Table 2.** Second-order rate constants versus change of concentration at different temperatures

| Concentration | Temperature | k (d <sup>-1</sup> ) | Ea(kJ/mol) |
|---------------|-------------|----------------------|------------|
| Sun dried     | 4°C         | 3*10 <sup>-5</sup>   | -1.47      |
|               | 26°C        | 2*10 <sup>-5</sup>   |            |
|               | 40°C        | 3*10 <sup>-5</sup>   |            |
| 2000 ppm      | 4°C         | 1*10 <sup>-7</sup>   | 27.75      |
|               | 26°C        | -4*10 <sup>-8</sup>  |            |
|               | 40°C        | 4*10 <sup>-7</sup>   |            |
| 3000 ppm      | 4°C         | 9*10 <sup>-8</sup>   | 15.98      |
|               | 26°C        | -3*10 <sup>-8</sup>  |            |
|               | 40°C        | 2*10 <sup>-7</sup>   |            |
| 4000 ppm      | 4°C         | 3*10 <sup>-8</sup>   | 51.86      |
|               | 26°C        | -1*10 <sup>-7</sup>  |            |
|               | 40°C        | 4*10 <sup>-7</sup>   |            |
| 5000 ppm      | 4°C         | 4*10 <sup>-9</sup>   | 57.34      |
|               | 26°C        | -1*10 <sup>-8</sup>  |            |
|               | 40°C        | 7*10 <sup>-8</sup>   |            |

When the rate constants found for the 2nd order velocity are examined, the rate constants show a decrease at the 40°C temperature condition.



## CONCLUSION

Free moisture change of the samples increases as temperature increases depending on the packaging. Equilibrium conditions in terms of evaporation and mass transfer inside the package will also be at different times. While evaporation will be less at low temperatures, it will be more at high temperatures. As a result, more steam will be formed at high temperatures and pressure will be created inside. Therefore, driving force for mass transfer from the package to the outside will increase. When the kinetic data on sulfur dioxide removal were examined, it was determined that it was suitable for the first-order kinetic model for 4°C, and suitable for the second-order kinetic model for 26 and 40°C, considering the temperature and based on the correlation coefficients.

Based on the change of sulfur dioxide amount, it was determined that average change in SO<sub>2</sub> amount is approximately 15% for 4°C and 36% for 40°C.

According to the kinetic data of sulfur dioxide removal, it is not notable for 4°C and 26°C temperatures. However, it can be explained by the presence of sulfur dioxide in different chemical forms at 40°C. Reason for this can be explained by the bonding of sulfur with organic compounds in the structure at low temperatures. This is explained by the fact that water forms sulfate acid even when moisture is removed and sulfate has no tendency to evaporate. As a result of the decomposition of the structure with HCl in the determination of sulfur, sulfur in the organic structure is separated from the structure as sulfur dioxide.

In terms of time, sulfur removal values of the samples stored at 4°C for approximately 980 hours and at 26°C for approximately 525 hours were found to be low. It was determined that moisture and SO<sub>2</sub> losses accelerated after approximately 740 hours at 40°C.

During storage at 4°C, the sample containing 3280 mg/kg SO<sub>2</sub> lost 11% of SO<sub>2</sub> after 980 hours and in the same example, 46% SO<sub>2</sub> loss occurred after 740 hours at 40°C. Moreover, it was observed that SO<sub>2</sub> loss increases rapidly at high temperatures.

When storage conditions were examined in terms of humidity, it was determined that apricot lost 52-85% of its moisture at the end of 29 days and 4°C and 40°C temperatures. Based on the 25% water activity of packaged sulphurized dried apricots offered for sale, in this study, an average shelf life of 25 days was determined according to this value. The k values of sulfur removal vary according to the temperatures.

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## Conflict of Interest

The article authors declare that there is no conflict of interest between them.

## Author's Contributions

The authors declare that they have contributed equally to the article.

## REFERENCES

- Asma, B. M. (2000) Kayısı Yetiştiriciliği. Türkiye, Malatya: Evin Ofset
- Budak, M. M & Şan, B. (2017). Hasat Öncesi Giberellik Asit ve Oksalik Asit Uygulamalarının 'Kosiu' ve 'Hakko' Asya Armut Çeşitlerinde Meyve Kalitesi Üzerine Etkileri, *SDÜ Ziraat Fakültesi Dergisi*; 12 (2): 73-80.

- Davis, E. G., McBean, D. McG., & Rooney, M. L. (1975). Packaging foods that contain sulphur dioxide. *CSIRO Food Research Quarterly*, 35, 57–62.
- Davis, P. H. (1972). *Flora of Turkey and the East Aegean Islands*. Edinburgh University Press, Vol.3. ISBN: 9780852241547, 0852241542
- Davis, E. G., McBean, D. McG., Rooney, M. L., & Gipps, P. G. (1973). Mechanisms of sulphur dioxide loss from dried fruits in flexible films. *Journal of Food Technology*, 8, 391–405.
- Freedman, B. J. (1980). Sulphur dioxide in foods and beverages: its use as a preservative and its effect on asthma. *British Journal of Diseases of the Chest*, 74, 128–134.
- Gonzalo, M., Angel, B., Domingo, S. & Antonio, M. (2009). Sulphur dioxide evolution during dried apricot storage. *LWT - Food Science and Technology*, 42, 531–533.
- Gökçe K. (1966). Malatya kayısılarının kükürtlenmeleri üzerine teknik çalışmalar. Ankara Üniversitesi Ziraat Fakültesi Yayınları, No: 261, 87 s., Ankara.
- Karaçalı, İ. (2006). *Bahçe Ürünlerinin Muhafaza ve Pazarlanması*. (5. Baskı). Ege Üniversitesi, Ziraat Fakültesi Yayınları, (494).
- Korbel, E., Attal, E., Grabulos, J., Lluberas, E., Durand, N., Morel, G., Goli, T. & Brat, P. (2013). Impact of temperature and water activity on enzymatic and non-enzymatic reactions in reconstituted dried mango model system, *European Food Research and Technology*, 237(1), 39–46.
- Özçağırın, R, Ünal, A & Özeker, E, (2004). İsfendiyaroğlu M. Ilıman İklim Meyve Türleri, Sert Çekirdekli Meyveler, Ege Üniversitesi Basımevi, Bornova İzmir
- Salurcan, A. (2018). *Farklı Düzeylerde Kükürtlenen Kuru Kayısıların Organik Asit Ve Karotenoid Miktarlarında Depolama Boyunca Meydana Gelen Değişimin, Kayısının Rengi Ve Duyusal Özellikleri Üzerine Etkisi*, (Yüksek Lisans Tezi). Ankara Üniversitesi Fen Bilimleri Enstitüsü, Ankara. TEZ NO: 508060
- Sobutay, T. (2003). Erişim: 05.06.2015. Kayısı sektör araştırması. İstanbul Ticaret Odası Dış Ticaret Şubesi Araştırma Servisi. <http://www.ito.org.tr/Dokuman/Sektor/1-54.pdf>.
- Stern, A. R, Flaishman, M. A & Ben-Arie, R. (2007). Effect of Synthetic Auxins on Fruit Size of Five Cultivars of Japanese Plum (*Prunus salicina Lindl.*) *Scientia Horticulture*, 112, 304-309.
- Türk Standartları Enstitüsü TSE 485 Kuru Kayısı Dried Apricot 2009 ICS 67.080.10
- Wedzicha, B. L. (1984). *Chemistry of sulphur dioxide in foods*. London, England: Elsevier App. Sci. Pu.
- WHO Food Additives Series. (2008). Available from: <http://www.inchem.org/documents/jecfa/jecmono/v21je15.htm>.