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EFFECT OF DRYING PROCESS ON PESTICIDE RESIDUES IN GRAPES

Ayşe Özbey[1*], Şeyda Karagöz[2], Ali Cingöz[3]

[1]Department of Food Engineering, Faculty of Engineering, Ömer Halisdemir University, Niğde, Turkey
[2]Department of Food Tecnology Zile Vocational High School, Food Technology, Gaziosmanpaşa University, Zile, Tokat, Turkey
[3]Department of Food Engineering, Faculty of Engineering and Natural Sciences, Gaziosmanpaşa University, Tokat, Turkey

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Abstract

In this study, drying kinetics of chlorpyrifos, diazinon, dimethoate and methidathion pesticides on grape samples were determined. Grapes were dried under two conditions: by sunlight (for 21 days) and in a ventilated oven at different temperatures (at 50 °C for 72 hrs, at 60 °C for 60 hrs, at 70 °C for 48 hrs, at 80°C for 36 hrs). During sun drying, half-lives of chlorpyrifos, diazinon and methidathion were 5.64, 6.42 and 5.25 days, respectively. The data for dimethoate did not fit 0^{th},, 1^{st} and 2^{nd} order kinetics. During oven-drying, the pesticides followed the first order kinetic model. When the temperature increased, degradation of pesticides raised. The activation energies of dimethoate, diazinon, chlorpyrifos and methidathion were calculated as 42.02, 42.18, 42.01 and 41.08 J/mol, respectively.

Keywords: Grape, oven-drying, pesticides, sun-drying

KURUTMA İŞLEMİNİN ÜZÜMLERDE BULUNAN PESTİSİTLER ÜZERİNE ETKİSİ

Öz

Bu çalışmada üzümlerde bulunan chlorpyrifos, diazinon, dimethoate ve methidathion pestisitlerinin kurutma kinetikleri belirlenmiştir. Güneşte ve farklı sıcaklılarda (50°C'de 72 saat, 60°C'de 60 saat, 70°C'de 48 saat, 80°C'de 36 saat süre ile) hava akımlı etüvde kurutma işlemi olmak üzere iki farklı kurutma işlemi uygulanmıştır. Güneşte kurutma işleminde chlorpyrifos, diazinon ve methidathion pestisitlerinin yarılanma ömürleri sırasıyla 5.64, 6.42 ve 5.25 gün olarak bulunmuştur. Dimethoate verileri 0., 1. ve 2. derece kinetik uyumu göstermemiştir. Sıcaklık yükseldikçe pestisitlerin parçalanması artmıştır. Dimethoate, diazinon, chlorpyrifos ve methidathionun aktivasyon enerjileri sırasıyla 42.02, 42.18, 42.01 ve 41.08 J/mol olarak hesaplanmıştır.

Anahtar kelimeler: Üzüm, fırında kurutma, pestisit, güneşte kurutma

* Yazışmalardan sorumlu yazar / *Corresponding author;*
ayse.ozbey@ohu.edu.tr, ✆ (+90) 388 225 4305, (+90) 388 225 0110

INTRODUCTION

Grapes are one of the most popular and the widespread cultural fruit in the world. World's fresh grape production is about the 65 million tons per year and the 7.5 million hectares of the world are dedicated to grapes (1, 2). Grapes are nutritionally important fruit crops of international trade significance and consumed both as fresh and processed products. The use of pesticides can be beneficial in protecting crops, thereby increasing agriculture production. However multiple applications of a variety of pesticides can lead to residues within the food product (3, 4). Since there is need for pesticide treatments on grapes as near as possible to harvest, high residues could be present on grapes at harvest time (5). Raisins are dehydrated grapes manufactured by exposure to sunlight or oven-drying. It is one of the most important and popular dried fruits in the world because of their high nutrition value (6). The different drying processes have different effects on pesticide residues on raw commodity since sun light may additionally photodegrade pesticide residues (7).

Food processing usually causes a decrease in pesticide levels. However, in some cases, residue levels may increase in the final product due to concentration factors of raw commodities in the process of the final product. This concentration effect can be related with water removal for example in the production of dry fruit such as raisins and prunes. Processing factors assist in the dietary-intake assessment of processed commodities (8). They are also used in recommending MRLs for processed products with an existing Codex commodity code, but only if the processing leads to an increase of the residue level (7, 9, 10).

The objectives of this work were to determine the effects of sun-drying and oven-drying on chlorpyrifos, diazinon, dimethoate and methidathion residues on grapes.

MATERIAL AND METHODS

Materials

The Sultana grape samples were supplied from Manisa (Turkey) in September 2012. Chlorpyrifos (98.5%), diazinon (99.0%), dimethoate (98.5%) and methidathion (98.5%) standarts were purchased from the Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Apparatus and Chromatography

Analysis of pesticides was performed using a Perkin Elmer Clarus 500 GC-MS. The separation was conducted on a CP-Sil 8-ms capillary column (30 m, 0.25 mm id, 0.25 µm film thickness). Helium was used as the carrier gas at the flow rate of 1.3 mL min^{-1}, and the injection volume was 5.0 µL. The injection port temperature was held at 250 °C at the split mode with the split ratio of 1:5. The oven temperature was programmed as follows: 75 °C held for 3.0 min, and then the temperature was increased to 180 °C at a rate of 25 °C min^{-1} and then the temperature was raised to 300 °C at a rate of 5 °C min^{-1} and maintained for 3 min. Dedector was operated on the EI (70 eV) ionization mode. Scan mode was fullscan (40 m/z–360 m/z), interface temperature and ion source temperature were 250°C. Processing data was performed using NIST 2008 and Wiley 2002 libraries.

Drying Processes

To evaluate the effect of drying process on pesticide residues, Sultana grape treated with pesticides (chlorpyrifos 45µL/kg, diazinon 50µL/kg, dimethoate 50µL/kg, methidathion 45µL/ kg) through spraying onto surface. To maintain the penetration of pesticides, the grapes were kept in a closed container for 12 hours at room temperature. Then grapes were separated from stems and dried. Grapes were dried under two conditions: by sunlight (for 21 days) and in a ventilated oven at different temperatures (at 50 °C for 72 hrs, at 60 °C for 60 hrs, at 70 °C for 48 hrs, at 80°C for 36 hrs). Moisture content and pesticide analyses were conducted at equal time intervals. Moisture content was determined according to AOAC (11).

Pesticide Analysis

QuECHERS method (12) was used to extract pesticides residues from grapes. Grape samples were homogenized and 15 g of each homogenate was weighed into a 50 mL centrifuge tube. Then 15 mL MeCN was added into tube. Tubes were capped well and shaken vigorously by hand for 45 s. 6 g anhydrous $MgSO_4$ and 1.5 g NaCl were added and shaken. Tubes were centrifuged at 3000 rpm for 1 min. Extracts were decanted into the dispersive-SPE tubes containing 0.3 g PSA + 1.8 g anhydrous $MgSO_4$. Tubes were capped well, shaken by hand for 20 s and centrifuged for 1 min at 3000 rpm. Supernatant were then analysed by GC/MS.

The recoveries were ranged from 88 to 98%. Detection limit was 0.02 mg/kg for all pesticides.

Drying Kinetics

Food processing studies often results in transfer factors or food processing factors (PF) of the pesticide residue in the transition from raw agriculture commodity to the processed product. Processing factors are calculated and considered by JMPR (13) as follows:

$$\text{Processing factors} = \frac{\text{residue level in processed commodity}}{\text{residue level in raw commodity}} \quad (1)$$

In order to determine degradation kinetics, the obtained data were evaluated with zero-order, first–order and second–order kinetic models. All pesticides obey first order kinetic model during drying. The experimental data were fitted according to simple first–order rate:

$$\frac{C}{C_0} \; e^{-kt}$$

In this equation, C_0 is the initial concentration of the pesticides, k is the rate constant. Half-lives ($t_{1/2}$) were calculated from the equation:

$t_{1/2} = \ln(2) / k$

The temperature dependence of rate constants was described by the Arrhenius equation. Activation energy of pesticides during oven drying was calculated according to Arrhenius equation:

$k = Ae^{-Ea/RT}$

E_a: Activation energy

R: Gas constant (8.3145 J mol^{-1} K^{-1})

T: Absolute temperature

A: Frequency factor

Since rate constants were determined at two temperatures, the following formula derived from the Arrhenius equation was used to calculate activation energy.

$\ln (k_1 / k_2) = -E_a/R\,(1/T_1 - 1/T_2)$

RESULTS AND DISCUSSION

Sun Drying

The moisture content of the fruits reduced to ~10-12%. Chlorpyrifos, diazinon, methidathion and dimethoate disappeared 73, 92, 82 and 39%, respectively. Processing factors of pesticides are given in Table 1. All pesticides decreased during all drying processes. These results supported by previous work (14).

Figure 1 shows the first order kinetic behaviours of chlorpyrifos, diazinon and methidathion during sun-drying. Half-lives of chlorpyrifos, diazinon and methidathion were 5.64, 6.42 and 5.25 days, respectively. The data for dimethoate did not fit zero, first and second order kinetics.

During sun-drying dimethoate decreased by 39% probably due to not having chromophores in the molecules (15). Chlorpyrifos, diazinon and methidathion reduced considerably because of their chromophores. Table 2 shows the physical-chemical characteristics of pesticides. As seen from the Table 2, hydrolysis and photolysis are the main mechanisms for the decrease during sun drying. We found that diazinon level mostly decreased because it was very sensitive to photodegradation. Chlorpyrifos level was higher than methidation level after drying although chlorpyrifos more sensitive to photodegradation. However chlorpyrifos was least water soluble pesticide and hydrolysis rate was slower than methidation.

Table 1. Processing factors of pesticides

Process	Dimethoate	Diazinon	Chlorpyriphos	Methidathion
80 °C	0	0	0.09	0.02
70 °C	0.01	0	0.04	0.06
60 °C	0.03	0.01	0.12	0.13
50 °C	0.64	0.02	0.22	0.35
Sun-drying	0.60	0.08	0.26	0.18

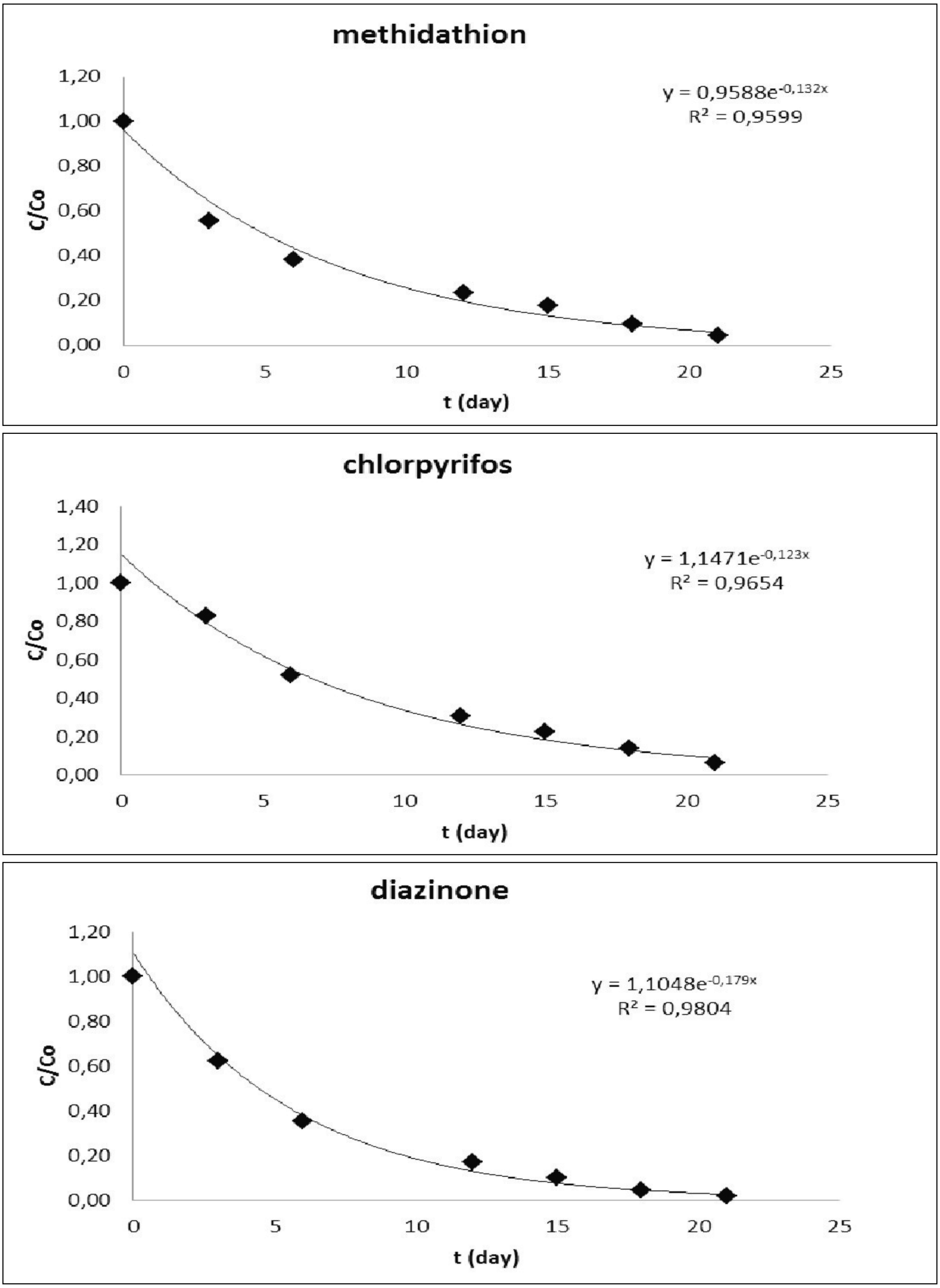

Figure 1. The first order kinetic behaviours of methidathion, chlorpyrifos and diazinon during sun-drying

Table 2. Physico-chemical properties of pesticides

Parameter	[a]Dimethoate	[b]Diazinon	[c]Chlorpyriphos	[d]Methidathion
Solubility in water	39.8 g/L	40 mg/L	0.39 mg/L	221 mg/L
Octanol/water partition coefficient	0.704	3.30	5.0	2.22
Photolysis characteristics t1/2 (summer)	-	4 days	4.2 days	8.2 days
Hydrolysis characteristics t1/2 at pH5	72 days	156 days	38 days	37 days

([a]18, [b]16, [c]17, [d]19)

Table 3. Kinetic models of pesticides at 50 °C and 60 °C

Pesticides	50 °C	60 °C
Dimethoate	$y = 16.635e^{-0.067x}$ $R^2 = 0.975$	$y = 1.4105e^{-0.11x}$ $R^2 = 0.949$
Diazinon	$y = 1.763e^{-0.078x}$ $R^2 = 0.9506$	$y = 0.8564e^{-0.153x}$ $R^2 = 0.9689$
Chlorpyriphos	$y = 1.2039e^{-0.044x}$ $R^2 = 0.9395$	$y = 0.8424e^{-0.072x}$ $R^2 = 0.9607$
Methidathion	$y = 1.1394e^{-0.035x}$ $R^2 = 0.9344$	$y = 0.9539e^{-0.064x}$ $R^2 = 0.9736$

Oven Drying

When the temperature increased, degradation of pesticides raised (Table 1). Drying in the oven at 70 °C and 80 °C cause drastic reduction (above 90%) in short time. Therefore those data were not convenient for kinetic evaluation.

During oven-drying, the pesticides followed the first order kinetic model. Table 3 summarizes the pesticide degradation rate constants and regression coefficients obtained. Half-lives of chlorpyrifos, diazinon, methidathion and dimethoate were respectively 15.75, 8.89, 19.8, 10.35 hours at 50°C and 9.63, 4.53, 10.83, 6.3 hours at 60 °C.

The activation energies of dimethoate, diazinon, chlorpyrifos and methidathion were calculated as 42.02, 42.18, 42.01 and 41.08 J/mol, respectively. There was no information related to activation energies of pesticides for grapes in the literature.

CONCLUSION

As a result, this study showed that the higher the temperature, the fastest the degradation of pesticides in drying processes of grapes. Physical-chemical characteristics of pesticides were not effective on pesticide residues during oven drying. Thermal degradation was the determinative mechanism for oven drying.

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