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Photodegradation of phytosanitary molecules present in virgin olive oil

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ABSTRACT

In recent years, traces of active ingredients from phytosanitary products and other products used in treating olive trees have been found in some olive oils because production systems are unable to separate and/or eliminate these chemical residues. Degradation of five phytosanitary chemicals (methyl parathion, ethyl parathion, chlorpyrifos, methyl chlorpyrifos and oxyfluorfen) in virgin olive oil exposed to ultraviolet light at different temperatures has been studied. The influence on the quality parameters of treated virgin olive oil and its composition has been analyzed. The photodegradation kinetics can be described by a first-order degradation curve. The half-life values determined at the end of a 150-min UV irradiation (T = 288 K) were as follows: methyl parathion 60.3 min, ethyl parathion 73.0 min, chlorpyrifos 110 min, methyl chlorpyrifos 86.6 min and oxyfluorfen 239.0 min. After the treatment, the phytosanitary chemicals were still present at 19.6, 24.1, 39.1, 32.8, and 67.3% of their initial concentration, respectively. The activation energy for each pesticide was calculated obtaining the following values under the experimental conditions: methyl parathion 15.5 kJ mol^{-1}, ethyl parathion 29.7 kJ mol^{-1}, chlorpyrifos 23.5 kJ mol^{-1}, methyl chlorpyrifos 16.0 kJ mol^{-1}, and oxyfluorfen 157.9 kJ mol^{-1}. These results reinforce photodegradation as an effective tool for the degradation of pesticides in olive oil.

1. Introduction

Spain is the world's leading olive oil producer. Olive oil production has long been a tradition in Mediterranean countries and in recent years these countries have sought to increase its value [1]. The introduction of irrigation, together with the improvement and development of production techniques has tremendously boosted olive-oil production in the past few years. The greater output has led to the development of modern systems for olive harvest and transport and also systems for olive-oil extraction.

The use of machines (sweepers, blowers) that facilitate the collection of the fallen olives from the ground is the most frequent harvesting practice. However, this system augments the amount of earth accompanying the olives to the mill and thus oil quality seriously declines. In addition, phytosanitary products as insecticides, fungicides, and herbicides, are widely used to control pests, diseases, and weeds. It should be noted that each of the active ingredients has a safety period (minimum number of days that should elapse between the final application and harvest). Therefore, non-degraded chemical products (phytosanitary not degraded during the safety period) can be persist and pollute not just the water but also the soil at harvest time, contaminating the olives that reach the ground. On the other hand, some of the active ingredients of the phytosanitary products are degraded through hydrolytic degradation or photolytic degradation mediated by sunlight. As a result, harmless or harmful residues (phytosanitary residues) can be retained by the ground or leach into the surface water or groundwater.

This problem has been discussed during the last decade and was first addressed by analytical studies followed by elaboration of techniques aimed at elimination of phytosanitary contaminants from the water. Nevertheless, this remains a matter of study for researchers worldwide [2] as it is a major problem in many countries. Due to the toxicity of these compounds, the European Union has established guidelines stipulating the acceptable limits for drinking water. The maximum concentrations of phytosanitary residues in drinking water accepted by the European Parliament for the countries of the European Union are 0.1 μg L^{-1} for a given chemical and 0.5 μg L^{-1} for the total amount of pesticides [3]. In recent years, there has been remarkable progress in photodegradation of pesticides (as a part of tertiary treatment) since conventional techniques of contaminated water treatment were found ineffective. Research results have demonstrated the feasibility of photodegradation with UV light on atrazine, isoproturon and mecoprop [4]. The degradation of pentachlorophenol (PCP) has also been studied. Used as fungicide, PCP contains polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran impurities, which are

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even more toxic than the main product. Further research has been made in the field of photodegradation of other pesticides, but all publications mainly deal with treatments in plant, soils [4], aqueous solutions [5], and no research is available on treatment of phytosanitary-contaminated extra virgin olive oil (EVOO). Chemical treatment is completely forbidden in the production process of EVOO. Only research in refined olive oil is known [6].

Investigation has shifted from the contamination detected in drinking water to the pesticide residues found in foods such as grapes and wines of many wine producing countries [7–9]. In the last 3 years, traces of phytosanitary products have also been detected in olive oil. This fact caused increasing concerns within the sector which resulted in regular administrative controls established on at least 20 different pesticides. It is important to note that the water used to wash the olives frequently comes from a closed circuit so that olives free of phytosanitary residues could be easily contaminated. For this reason, some authors recommend not to wash olives harvested directly from a tree and to limit the washing of olives that have been in direct contact with the ground.

In this paper, the feasibility of a controlled process of photodegradation of phytosanitary residues present in virgin olive oil is reported using UV light and five phytosanitary chemicals (methyl parathion, chlorpyrifos, ethyl parathion, oxyfluorfen and methyl chlorpyrifos).

2. Materials and methods

2.1. Experimental device

The experiments were carried out in an experimental photoreactor (Fig. 1) composed of a 1 L reactor tank with a UV lamp covered with a quartz immersion tube and a quartz cooling jacket, a magnetic stirrer inside the reactor for blending the olive oil with the phytosanitary chemicals, cryorefrigeration equipment with an Frigiterm 30 ultra-thermostat to eliminate the heat created by the UV lamp and controlling the temperature of olive oil in the reactor. A thermometer was located in the interior of the reactor to indicate the operating temperature.

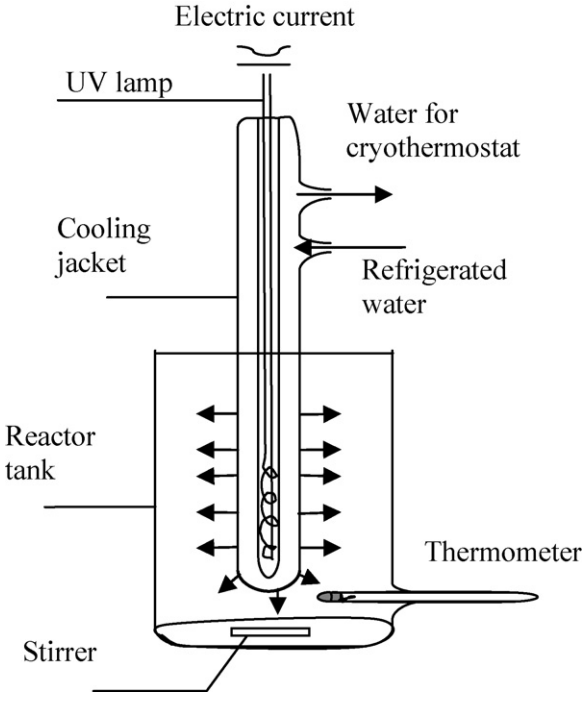

Fig. 1. Configuration of the photoreactor used.

The UV lamp used has the following characteristics: UV Immersion lamp (model TQ 150; no. 5600 1725; brand HNG Germany G4) with a length of total immersion 384 mm, length of the luminous part of the immersion 303 mm, position of the emission centre of the lamp 44 mm, power of the lamp 150 W and nominal level of emission intensity 200–280 nm.

2.2. Experimental conditions and procedure

Commercial extra virgin olive oil from the province of Jaén (Spain) was used as solvent to study the influence of UV radiation on photodegradation of the phytosanitary residues. First the influence of UV light on the quality parameters of the olive oil has been studied. Thus, we analysed the usual parameters: acidity, peroxide index, the values of absorption coefficients K_{270}, K_{232}, and ΔK, and the stability to oxidation determined by the Rancimat method [10].

To study the photodegradation and degradation kinetics of the phytosanitary residues in the olive oil, after analysing several olive oil samples, we introduced a 'doped mixture' containing active phytosanitary components with concentrations higher than those usually registered in olive oils (to detect the exact amount of degraded pesticides).

Once the olive oil and active ingredients were prepared, the mixture was placed in the reactor, where each active phytosanitary has been mixed with olive oil. Different experiments have been conducted to study the five phytosanitary molecules (one for each phytosanitary investigated). All the experiments carried out under air atmosphere. The average concentration for each phytosanitary in olive oil was 1841 $\mu g\,L^{-1}$ with a standard deviation of 244.

The circulation of water refrigerated by the quartz cooling jacket around the lamp was activated, the UV lamp was switched on and the oil temperature was controlled. Once the desired temperature was reached (within few minutes), the time was started from zero. Over the course of the experiment samples were taken at different times during the approximately 2.5 h of operation.

A series of experiments were carried out at different temperatures and with different operation times, in order to determine the effect of temperature and time on the photodegradation of phytosanitaries and on the quality parameters of olive oil.

2.3. Analytical methods

2.3.1. Quality parameters of extra virgin olive oil

Olive oil quality parameters such as: acidity, peroxide index, the values of absorption coefficients K_{270}, K_{232}, and ΔK have been determined using methods of analysis published in the official bulletin of the European Communities [11].

2.3.2. Rancimat stability

The olive oil was oxidized to its possible maximum through an air flow at 100 °C, determining the oil conductivity with Metrohn 679 Rancimat stability equipment [10].

2.3.3. Extraction and determination of residues from phytosanitary products

These were determined by gas chromatography with a capillary column and a Varian Saturn 2000 mass detector with GPC purification clean-up (Waters 717 Plus Autosampler equipment, Water-Fraction Collector III, and Envirogel GPC clean-up columns of 19 mm × 300 mm and 19 mm × 150 mm). The principle of measurement was based on the extraction of the pesticide fraction in oil to which an internal standard, anhydrous sodium sulphate, *n*-hexane with acetonitrile had been added. Afterwards, the extracted fraction was purified through chromatography of gel permeability separation and finally the direct analysis was carried out through gas chromatography in a capillary column and mass detector. The

Table 1
The injector and oven conditions.

	T (K)	Rate (K/min)	Hold (min)	Total time (min)
Injector	343	–	0.50	0.50
	573	373	15.0	17.8
Oven	343	–	3.50	3.50
	453	298	10.0	17.90
	573	277	10.0	57.90

quantitative measurements of pesticides (MS/MS) have been done using different calibration lines for each pesticide where the concentration of pesticides has varied between 10 and 500 $\mu g\,L^{-1}$. The purity pesticide standards were purchased from Dr. Erhenstorfer (Pomochem, Wesel, Germany) and used without further purification. Varian CP3800 Gas chromatography equipment was used with detector Saturn 2200 GC with a sample of 10 μL injected. The injector and oven conditions are shown in Table 1. The helium flow in the column was 1 $mL\,min^{-1}$.

2.4. Calculation methods and reproducibility

The experiments were made at least in duplicate and the analytical methods were applied at least in triplicate. The calculation and statistical methods used are available in the program OriginPro 8.0.

3. Results and discussion

3.1. Influence of UV light exposure on the quality of virgin olive oil

To ensure the quality of EVOO during the process of exposure to ultraviolet light, the main quality parameters were analyzed with a frequency of 10 min during 150 min. Table 2 shows the initial parameters of EVOO quality (without exposition to UV light) and after treatment for 16, 30, 60 and 150 min, and different temperatures. Treatments at higher temperature values have not been reported as far. The quality parameters of the oil were not affected significantly by ultraviolet light during the time period tested (150 min). Acidity (≤0.52%), peroxide index (≤12.6 meq. O_2 kg^{-1}), UV absorbency: K_{270} (≤0.200), K_{232} (≤2.18), and ΔK (≤0.001) have not exceeded the maximum values of the quality parameters allowed according the official legislation (Table 2).

A tasting panel did not registered significant differences from sensorial standpoint that might be attributed to temperature or oxidation reactions.

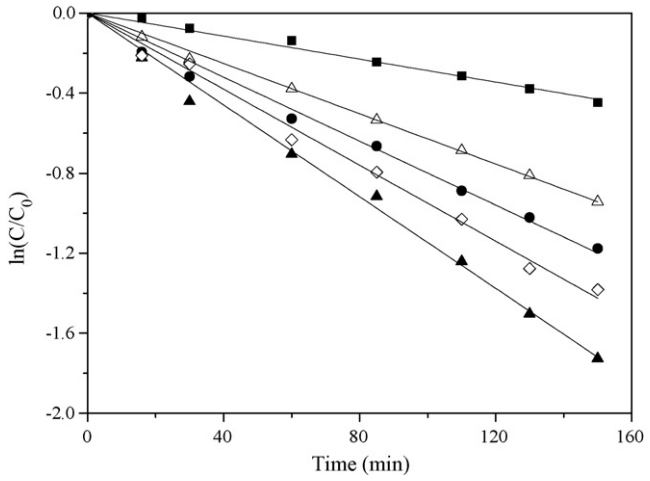

Fig. 2. Kinetics of the photodegradation of pesticides (T = 288 K): (▲) methyl parathion, (△) chlorpyrifos, (◊) ethyl parathion, (■) oxyfluorfen, and (●) methyl chlorpyrifos.

3.2. Photodegradation kinetic

The reactions of photodegradation of pesticides in water can be described by kinetics of different orders. However, with reactions of first-order kinetics fit well to these processes and were successfully used [5,7,8].

Since similar behaviour has been observed in the photodegradation of pesticides in the EVOO, the graphical representation of napierian logarithm of the concentration versus time gives a straight line (Fig. 2), where the slope of the line gives the constant of the reaction of photodegradation (Eq. (1)).

$$\ln\left(\frac{C}{C_0}\right) = -k_b t \quad (1)$$

Table 2
Variation of the quality parameters of virgin olive oil exposed to UV light at different periods of time and different temperatures.

T (K)	t (min)	Acidity (%)	Peroxide index (meq. O_2 kg^{-1})	K_{270}	K_{232}	ΔK	Rancimat stability (h)
288	0	0.28	11.5	0.139	1.991	0.001	33.0
	16	0.33	12.1	0.129	1.766	0.001	36.0
	30	0.44	10.8	0.154	1.987	0.001	36.1
	60	0.52	8.3	0.126	1.732	0.001	36.2
	150	0.52	13.0	0.193	2.182	0.001	36.3
293	0	0.28	11.5	0.139	1.991	0.001	33.0
	16	0.31	12.6	0.131	1.766	0.001	36.0
	30	0.35	11.5	0.152	2.014	0.001	35.6
	60	0.44	10.1	0.142	1.912	0.001	34.9
	150	0.52	8.9	0.178	2.006	0.001	35.0
289	0	0.28	11.5	0.139	1.991	0.001	33.0
	16	0.32	12.1	0.147	1.791	0.001	37.7
	30	0.39	8.8	0.150	1.912	0.001	38.4
	60	0.42	10.0	0.140	1.735	0.001	35.0
	150	0.49	7.5	0.184	2.010	0.001	36.0
303	0	0.28	11.5	0.139	1.991	0.001	33.0
	16	0.33	12.4	0.161	2.008	0.001	35.7
	30	0.43	10.6	0.161	1.984	0.001	36.2
	60	0.43	9.1	0.183	1.989	0.001	36.0
	150	0.51	10.4	0.200	2.036	0.001	36.1

Maximum values allowed according the Commission Regulation (CEE) no. 2568/91: acidity ≤ 0.8, peroxide index ≤ 20, K_{270} ≤ 0.20, K_{232} ≤ 2.50, ΔK ≤ 0.01. Rancimat stability: the value of this parameter varies largely depending on the variety of olives and their value varies from 20 to 200 h roughly. (Officially no value given.)

Table 3
The apparent first-order photodegradation rate constant of five pesticides at different temperatures.

T (K)	$k_b \times 10^3$ (min^{-1})				
	Methyl parathion	Ethyl parathion	Methyl Chlorpyrifos	Chlorpyrifos	Oxyfluorfen
288	11.5	9.50	8.00	6.30	2.90
293	9.64	7.25	7.00	5.32	1.53
298	9.50	6.61	6.48	4.58	0.401
303	8.09	4.95	5.69	3.86	0.120

where C and C_0 are the concentrations of pesticide at time t and time 0, respectively, and k_b is the apparent first-order photodegradation rate constant.

Table 3 shows the values obtained for the apparent first-order photodegradation rate constant of the five pesticides studied at different temperatures (in a previous study, the best results of the photodegradation with direct use of UV have been obtained using methyl parathion, chlorpyrifos, ethyl parathion, oxyfluorfen and methyl chlorpyrifos [10]). It can be seen that the constant of the reaction in all experiments of photodegradation decreases with increasing the temperature. Particularly in the temperature range from 288 to 298 K, the rate of the photodegradation of pesticides decreases in the following order (highest to lowest): methyl parathion, ethyl parathion, methyl chlorpyrifos, chlorpyrifos, and oxyfluorfen. However, at 303 K methyl chlorpyrifos recorded a higher value for k_b than ethyl parathion. In addition, the photodegradation of oxyfluorfen is much slower than the rest of the pesticides studied. For this reason, the photodegradation rate constant of methyl parathion 4 and is 67 times higher than of oxyfluorfen at 288 and 303 K, respectively.

The half-life ($t_{1/2}$) of pesticide indicates that the stability of the compound over time can be calculated by Eq. (2):

$$t_{1/2} = \frac{0.693}{k_b} \tag{2}$$

Fig. 3 shows the half-lives of the photodegradation of the pesticides. In all experiments the half-life of each pesticide increases with increasing the temperature. The photodegradation half-life of methyl parathion, ethyl parathion, methyl chlorpyrifos, chlorpyrifos and oxyfluorfen varies in the range between 60.3 and 85.7, 73 and 140, 86.6 and 121.8, 110.0 and 179.6, and 239.0 and 5776.2 min, respectively.

The half-life values show that oxyfluorfen demonstrates the longest dissipation half-life (between 4 and 32 times higher) than the rest of pesticides studied. Moreover, while the half-life of the other pesticides do not exceed 3 h, that of oxyfluorfen can reach up to 97 h. The persistence or dissipation of a chemical is mainly controlled by its physico-chemical properties and environment conditions including (in this case) olive oil as a solvent [12].

Moreover, the order of magnitude of the constant of the reaction of photodegradation and half-life of the pesticide obtained is similar to values registered in the literature, for example in aqueous solutions the kinetics parameters of methyl parathion is $k_b = 8.46 \times 10^{-3}$ min^{-1} and $t_{1/2} = 82.0$ min ($T = 303$ K, pH 12) [13], for ethyl parathion is equal to 9.6×10^{-3} min^{-1} and $t_{1/2} = 72.2$ min ($\lambda_{irradiation} = 350$ nm) [14], for the organophosphorus compounds (chlorpyrifos) $k_b = 52.1 \times 10^{-3}$ min^{-1} and $t_{1/2} = 13.3$ min ($\lambda_{irradiation} < 410$ nm) [15] and for oxyfluorfen in n-hexane ($T = 294.0$ K) $k_b = 0.415$ 10^{-3} min^{-1} and $t_{1/2} = 1673.3$ min [16]. All the photodegradation reactions fit a first kinetic order. No significant reaction was observed in the dark.

The rate of degradation is affected by the temperature dependence of k_b and the temperature is given by the Arrhenius equation:

$$k_b = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the frequency factor (min^{-1}), E_a the activation energy (kJ mol^{-1}), T the temperature (K) and R the gas constant. This equation can be expressed with the napierian logarithm:

$$\ln(k_b) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \tag{4}$$

Eq. (4) represents a lineal equation, where the slope of the line gives the activation energy for each pesticide (Fig. 4). The activation energy provides information about the dependence of photodegradation reaction on temperature: the greater the activation energy value, the more temperature affects photodegradation.

The dependence of the photodegradation rate of pesticides on temperature is well pronounced within the range 288–303 K. It is observed that the reaction rate decreased with increasing

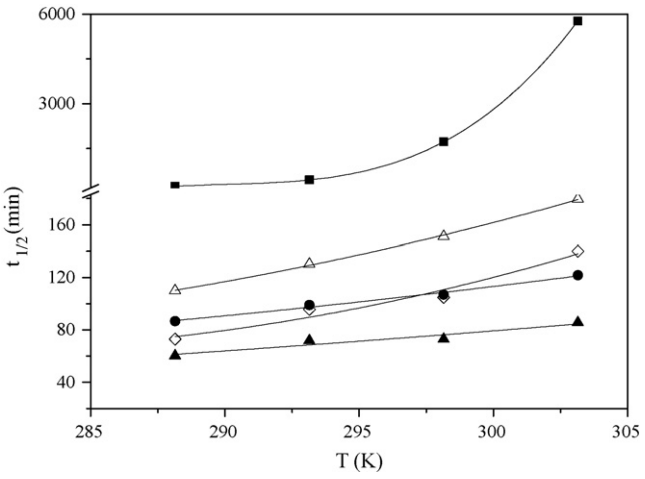

Fig. 3. Variation of the half-lives of pesticides with temperature: (▲) methyl parathion, (△) chlorpyrifos, (◊) ethyl parathion, (■) oxyfluorfen, and (●) methyl chlorpyrifos.

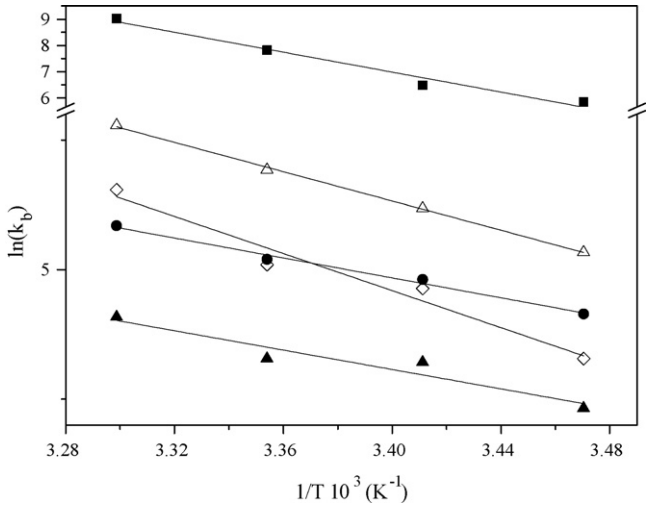

Fig. 4. Arrhenius graphic and calculation of activation energy: (▲) methyl parathion, (△) chlorpyrifos, (◊) ethyl parathion, (■) oxyfluorfen, and (●) methyl chlorpyrifos.

Table 4
Activation energy calculated for each pesticide at the experimental conditions.

Pesticide	A (min^{-1})	E_a (kJ mol^{-1})
Methyl parathion	5.83×10^4	15.5
Ethyl parathion	2.62×10^7	29.7
Methyl chlorpyrifos	9.89×10^4	16.0
Chlorpyrifos	2.89×10^6	23.5
Oxyfluorfen	1.32×10^{31}	157.9

the temperature. The Arrhenius plot yields a straight line from which the overall apparent activation energy varies between 15 and 157.9 kJ mol^{-1} (Table 4). Obviously, this value is smaller than that of ordinary thermal reactions and it appears that the photodegradation reaction is less temperature dependent. The rate decrease is most probably due to decreasing collision frequency of molecules in the olive oil at higher temperatures (more viscosity at low temperature).

The activation energy values reported in literature at pH 7.1 for seven organophosphorous pesticides are in the range between 58.6 and 92.1 kJ mol^{-1} [17]. In more recent studies [18], lower values, in the range between 0.46 and 40.6 kJ mol^{-1}, were found for 14 organophosphorous pesticides at pH 7.3. Badawi and El-Dib [19] reported the activation energy for methyl parathion at pH 11 equal to 41.5 kJ mol^{-1}. Accordingly, Di Palma [20] reported that the phosalone activation energy values varied in the range between 11.5 and 22.1 kJ mol^{-1} (pH 10–12 and room temperature).

3.3. Photodegradation of pesticide

In real samples without the addition of pesticides (samples collected directly from the market) have been detected trichlorfon 99 μg L^{-1}, diuron 12 μg L^{-1}, carbaryl 43 μg L^{-1}, dimethoate 15 μg L^{-1}, terbuthylazine 19 μg L^{-1}, terbutryn 8 μg L^{-1}, oxifluorfen 12 μg L^{-1}, endosulfan II 8 μg L^{-1}, endosulfan sulphate 19 μg L^{-1}, diflufenican 9 μg L^{-1}, and phosmet 7 μg L^{-1}. In any case, these values exceeded allowed. There is currently no specific legislation in Spain as regards maximum residue limits (MRLs) for pesticides in olive oil, but only in olives. However, levels five times higher than those set for olives are commonly accepted for oil [21].

Fig. 5 presents the results of the photodegradation treatment at different times for the pesticides tested in virgin olive oil, obtained under UV light (T = 303 K). The values of the percentages of pesticides degraded (PD) over time (t) has been adjusted by nonlinear regression using the OriginPro 8.0 program to the mathematical Eq. (5):

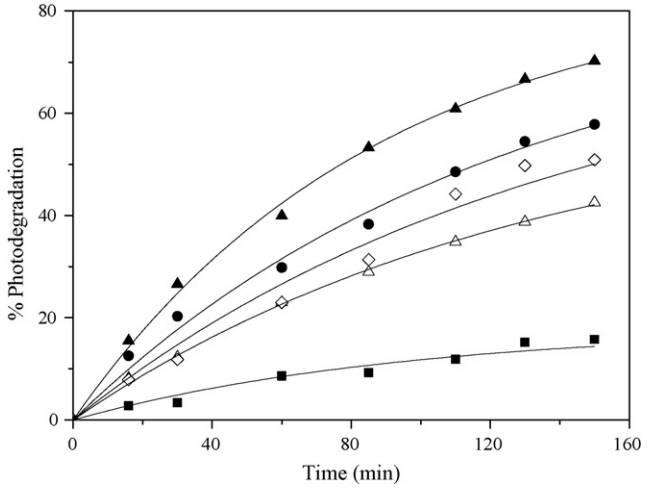

Fig. 5. Photodegradation of pesticides (T = 303 K): (▲) methyl parathion, (△) chlorpyrifos, (◊) ethyl parathion, (■) oxyfluorfen, and (●) methyl chlorpyrifos.

Table 5
The maximum photodegradation for each pesticide at different temperatures.

	% Photodegradation (150 min) T (K)			
	288	293	298	303
Methyl parathion	80.4	78.8	73.7	70.1
Ethyl parathion	75.1	50.9	60.8	50.1
Methyl chlorpyrifos	67.2	55.8	60.7	57.6
Chlorpyrifos	60.2	40.1	48.9	42.1
Oxyfluorfen	32.7	12.9	5.42	14.4

$$PD = PD_{max}(1 - \exp^{-\alpha t}) \quad (5)$$

where PD and PD_{max} are the percentage of photodegradation of pesticide at time t and the maximum percentage of photodegradation of pesticide at infinite time, α is the constant of equation.

Fig. 5 shows that the process of photodegradation with UV light consists of two stages. In the first stage, photodegradation is very fast and then reach a second stage where degradation rate is much slower. At infinite time, a maximum value of the photodegradation of the pesticide is reached. In this study, with the objective to preserve the quality of EVOO, the maximum values of the photodegradation were considered once a period equal to 150 min was reached.

Table 5 lists the percentages of the maximum photodegradation reached by each chemical at t = 150 min. In any experiment photodegradation did not exceeded 80.4%. Methyl parathion, ethyl parathion, chlorpyrifos, methyl chlorpyrifos registered a photodegradation percentage above 40%. However, the percentage of photodegradation of oxyfluorfen under the optimal experimental conditions did not exceeded 33%. The highest decreases were registered after 150 min of operation time. In terms of operating temperature, the highest degradation rates were detected at 288 K (Table 5). Also, the photochemical degradation over extra virgin olive oil only with residual pesticide detected was carried out. The degradation yields of trichlorfon recorded equal to 98% at 16 min and 96% at 30 min (T = 298 K). The experiments with mixed oil with terbuthylazine recorded values of 38% and 55% at 16 and 30 min (T = 298 K), respectively. Dzyadevych and Chovelon [22] reported a percentage equal to 90% (160 min) for the photodegradation of methyl parathion similar to that obtained in this work (Table 5). On the other hand, Scrano et al. [16] reported that 3000 min were necessary to achieve a percentage of photodegradation of oxyflurfen equal to 70% (T = 294 K using methanol, acetonitrile, n-hexane).

In general, the photodegradation of a pesticide with UV light in EVOO decreases with increasing temperature. This can be explained considering that increasing the temperature decreases the viscosity of olive oil (oxygen solubility in olive oil is almost refractory to temperature change, varying less than 1% over a range of 30 °C [23]) and therefore, molecular collisions decrease with increasing temperature until 303 K. While temperatures above 303 K can increase photodegradacion of pesticides in olive oil, high temperatures adversely affect the quality of olive oil. Therefore, operations aimed at photodegradation at temperatures above 303 K should be restricted. Compared with the available literature, results obtained in this study do not comply with what has been observed in aqueous solutions where photodegradation increases with increasing temperature [13,20]. Such a process behaviour depends on the chemical structure of the pesticide and chemical environment where it conducts its degradation.

4. Conclusions

As shown by these results, the photodegradation of residues of pesticide (methyl parathion, ethyl parathion, chlorpyrifos, methyl chlorpyrifos and oxyfluorfen) in the virgin olive oil is possible in

the wavelength range between 200 and 280 nm. The photodegradation of residues of pesticides in extra virgin olive oil in the range between 288 and 303 K follows a first-order kinetic degradation curve. The half-lives were as follows: methyl parathion 60.3 min, ethyl parathion 73.0 min, chlorpyrifos 110 min, methyl chlorpyrifos 86.6 min, and oxyfluorfen 239.0 min, which, at the end of 150 min irradiation (T = 288 K), were still present at 19.6%, 24.1%, 39.1%, 32.8%, 67.3%, respectively, of the initial concentration. Also, the activation energy for each pesticide above mentioned has been calculated obtaining the following values at the experimental conditions: 15.5, 29.7, 23.5, 16.0, and 157.9 kJ mol^{-1}.

Even though the values presented are preliminary results, we can conclude that this work proposes a new approach for eliminating phytosanitary products found in oils, applying a physical procedure which does not alter the quality standards established by the regulations within the intervals analyzed. As mentioned in the Section 1, most research to date has been focused on pesticides treated individually and in an aqueous environment.

Acknowledgements

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References

[1] A. De Benedetto, A. Jacoboni, L. Venzi, G. Pannelli, Evaluación económica de un olivar moderno en Italia central, Olivae 95 (2003) 10–17.
[2] J. Prousek, Advanced oxidation processes for water treatment. Chemical processes, Chem. Listy 90 (1996) 229–237.
[3] D.J. Hamilton, Á. Ambrus, R.M. Dieterle, A.S. Felsot, C.A. Harris, P.T. Holland, A. Katayama, N. Kurihara, J. Linders, J. Uunsworth, S.S. Wong, Regulatory limits for pesticide residues in water (IUPAC Technical Report), Pure Appl. Chem. 75 (8) (2003) 1123–1155.
[4] T. Katagi, Photodegradation of pesticide on plant and soil surfaces, Rev. Environ. Contam. Toxicol. 182 (2004) 1–195.
[5] E. Gal, P. Aires, E. Chamarro, S. Espulgas, Photochemical degradation of parathion in aqueous solutions, Water Res. 26 (1992) 911–915.
[6] M.V.R. Méndez, I.P. De la Rosa, A.J. Márquez, M.U. Ojeda, Elimination of pesticides in olive oil by refining using bleaching and deodorization, Food Addit. Contam. 22 (1) (2005) 23–30.
[7] P. Cabras, M. Meloni, F.M. Pirisi, Pesticides fate from vine to wine, Rev. Environ. Contam. Toxicol. 99 (1987) 84–117.
[8] P. Cabras, V.L. Garau, M. Melis, F.M. Pirisi, L. Spanedda, Pesticide residues in Italian wines, Ital. J. Food Sci. 2 (1995) 133–145.
[9] A. Watterson, Pesticides and Your Food, Green Print, London, 1991.
[10] L.M. Nieto, G. Hodaifa, S.V. Rodríguez, J.A.C. Jiménez, M.S. Casanova, J.L.P. Lozano, Fotodegradación de restos de residuos fitosanitarios presentes en el aceite de oliva virgen, International Expoliva Symposium, Jaén, España, 2005.
[11] Official bulletin of the European Communities (no. L248/1 from 5.9.91 Commission Regulation (CEE), no. 2568/91) on the characteristics of olive oils and olive-residue oil (July 11, 1991 updated with the change to date in May 1999).
[12] G.G. Ying, B. Williams, Dissipation of herbicides in soil and grapes in a South Australian vineyard, Agric. Ecosyst. Environ. 78 (2000) 283–289.
[13] J. Manzanilla, M. Barceló, O. Reyes, Cinética de la hidrólisis del metilparatión en medio acuoso, Rev. Int. Contam. Ambient 13 (1997) 35–40.
[14] M. Nowakowska, M. Sterzel, S. Zapotoczny, E. Kot, Photosensitized degradation of ethyl parathion pesticide in aqueous solution of anthracene modified photoactive dextran, Appl. Catal. B Environ. 57 (2005) 1–8.
[15] M.B. Kralj, M. Franko, P. Trebše, Photodegradation of organphosphorus insecticides-Investigations of products and their toxicity using gas chromatography-mass spectrometry and AChE-thermal lens spectrometric bioassay, Chemosphere 67 (2007) 99–107.
[16] L. Scrano, S.A. Bufo, M. Auria, C. Emmelin, Photochemical behaviour of oxyfluorfen: a diphenyl-ether herbicide, J. Photochem. Photobiol. A 129 (1999) 65–70.
[17] V.H. Freed, C.T. Chiou, D.W. Schmedding, Degradation selected organophosphate pesticides in water and soil, J. Agric. Food Chem. 27 (1979) 706–708.
[18] S.B. Lartiges, P.P. Guarrigues, Degradation kinetics of organophosphorous and organonitrogen pesticides in different waters under various environmental conditions, Environ. Sci. Technol. 29 (1995) 1246–1254.
[19] M.I. Badawi, M.A. El-Dib, Persistence and fate of methyl parathion in sea water, Bull. Environ. Contam. Toxicol. 33 (1984) 40–49.
[20] L. Di Palma, Experimental assessment of a process for the remediation of organophosphorous pesticides contaminated soils through in situ soil flushing and hydrolysis, Water Air Soil Pollut. 143 (2003) 301–314.
[21] M.A. Aramendía, V. Borau, F. Lafont, A. Marinas, J.M. Marinas, J.M. Moreno, F.J. Urbano, Determination of herbicide residues in olive oil by gas chromatography-tandem mass spectrometry, Food Chem. 105 (2007) 855–861.
[22] S.V. Dzyadevych, J.M. Chovenlon, A comparative photodegradation studies of methyl parathion by using Lumistox test and conductometric biosensor technique, Mater. Sci. Eng. C 21 (2002) 55–60.
[23] R. Battino, F.D. Evans, W.F. Danforth, The solubilities of seven gases in olive oil with reference to theories of transport through the cell membrane, J. Am. Oil Chem. Soc. 45 (1968) 830–833.