



Short communication

Elimination of pesticide residues from virgin olive oil by ultraviolet light: Preliminary results

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ABSTRACT

Virgin olive oil is one of the essential products for the economy of Mediterranean countries. The possible residues of pesticides that can reach the oil may be a risk to public health, thus causing the prohibition of its marketing by the health authorities. This paper is a preliminary study on photochemical degradation of pesticide residues using a small-scale prototype (1 L capacity). The method presents an effective alternative for the complete photodegradation or reduction of these chemicals using ultraviolet light without harming the quality parameters of the virgin olive oil. The photodegradation yields have varied within the range 7–80% depending on the time and temperature applied.

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1. Introduction

Olive oil extraction is one of the most traditional agricultural industries in the Mediterranean region, and is still of primary importance for the economies of most of the countries in this area [1]. The oil has beneficial effects on consumer's health because of its composition rich in monounsaturated fatty acids and antioxidants. However, undesirable pesticide residues are sometimes present. Innovations to improve the technology used in the extraction process have been developed over the years, while at the same time the introduction of irrigation and increasing development of production techniques, etc., have led to a dramatic boost in olive production in recent years. This increased production has resulted in the concomitant development of better systems for fruit collection and transportation as well as oil extraction.

Today the use of machines (sweepers, blowers) that facilitate the collection of the fallen olives from the ground is the most frequent harvesting method. However, this system increases the amount of earth accompanying the olives to the mill and thus oil quality seriously declines.

Moreover, the control of pests, diseases, and weeds requires the use of such products as insecticides, fungicides, and herbicides. Some of these chemicals, after completing their mission, degrade via hydrolysis or photolysis. For that reason, each pesti-

cide has a specific security term (the minimum time in days that must elapse between the last application and fruit harvest) to determine whether the final products are safe or not. However, the toxic form of the pesticide may be retained by the soil, may penetrate partly to surface water, or may be filtered to groundwater, causing pollution [2]. This same phenomenon occurs with non-degraded products that can be retained and contaminate not only water but also the soil which at the time of harvest is mixed with the olives, thereby contaminating the harvested crop [3].

The problem has arisen in the past decade and began first with the analytical study and then with the elimination of these products from drinking water [4,5]. This problem is being studied by researchers around the world [6], an issue of prime importance in many countries. The toxicity of these compounds has led the European Union to establish guidelines that determine the health limits for drinking water. The maximum allowable concentrations in potable water adopted by the European Parliament for European Union countries are $0.1 \mu\text{g L}^{-1}$ for each species and $0.5 \mu\text{g L}^{-1}$ for total pesticides [7].

The conventional means of water treatment do not seem to be adequate for removing pesticides, according to the photodegradation that is being studied and successfully implemented as a complement to the tertiary treatment. Photochemical degradation of herbicides (atrazine, propazine, and prometryne) has been investigated in different types of natural waters (ground, river, lake, and marine) as well as in soils [8–12]. The degradation kinetics was monitored and the impact of humic substances on decomposition was examined [13]. Brun et al., [14] studied the aqueous

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phototransformations of atrazine by 254 nm and polychromatic light. The authors propose a complex mechanism, including oxidations, dealkylations, and hydrolyses, and also suggest a significant involvement of radicals in these processes. The degradation of pentachlorophenol (PCP), which is used as a fungicide was also studied. The formation of PCP leads to the by-products polychlorodibenzo-dioxins and polychlorobenzofurano (as impurities), which are even more toxic than PCP itself. It presents another possible application of photochemical degradation. However, all the current literature refers to treatments in aqueous or organic solution. No research is available on the photochemical degradation of pesticides in extra-virgin olive oil (where chemical treatment is prohibited). Only research in refined olive oil is known [15].

Among the problems found in the drinking water has led to the investigation of pesticide residues in food [16,17] and in olive oil. In the last 3 years, worrisome traces of pesticides have been detected [18–21], resulting in the establishment of routine administrative controls on at least 20 different pesticides. Finally, it is often the wash water of the olives from a closed circuit, which can contaminate batches of pesticide-free oil (therefore, some authors do not recommend washing fruits collected directly from the tree and restrict this operation to olives that have been in direct contact with the ground).

The present paper seeks to identify and quantify the effect of ultraviolet light on the possible pesticide products that are found in extra-virgin olive oil produced by olive oil extraction industries. The aim is to develop a simple system that will eliminate or reduce the amount of pesticides present in virgin olive oil as a result of cultivation, harvesting, and extraction practices.

2. Experimental

2.1. Installation

The experiments were performed in a photoreactor composed of a 1 L reactor tank with a UV lamp covered by a quartz immersion tube and a quartz cooling jacket, a magnetic stirrer inside the reactor for blending the olive oil with the pesticide 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.

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 to study the influence of UV radiation on photodegradation of the pesticide residues. First, the influence of UV light on the quality parameters of the olive oil has been studied. Thus, the usual parameters were analysed: acidity, peroxide index, the values of absorption coefficients K_{270} , K_{232} , and ΔK , and the stability to oxidation determined by the Rancimat method [22,23].

For the study of the photodegradation of the pesticide residues in the olive oil, after analysing several olive oil samples, a 'doped mixture' was introduced, this contains active pesticide components with concentrations higher than those usually registered in olive oils (to detect the exact amount of degraded pesticides).

Table 1

The new concentration of pesticides in commercial virgin olive oil after the addition and mixing of the active molecules.

	Virgin olive oil after mixed with pesticides Pesticide concentration ($\mu\text{g L}^{-1}$)
Trichlorfon	2576
Diuron	4268
Carbaryl	552
Dimethoate	1500
Simazine	2808
Terbutylazine	1524
Chlorpyrifos methyl	1944
Parathion methyl	2248
Pirimiphos methyl	1800
Fenitrothion	1908
Terbutryn	1228
Malathion	1528
Chlorpyrifos	1688
Parathion ethyl	1792
Metidathion	4232
Endosulfan I	2020
Oxifluorfen	1532
Endosulfan II	1436
Endosulfan sulphate	1108
Diflufenican	1096
Phosmet	1216
Fenoxicarb	1156
Alpha-cypermethrin	524
Deltamethrin	340

Once the olive oil and active ingredients were prepared, the mixture was placed in the reactor; where there were 24 active pesticides mixed with olive oil (Table 1).

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 a few minutes), the time was started from zero. Over the course of the experiment samples were taken at different times 16, 30, and 150 min of operation.

A series of experiments was carried out at different temperatures (15, 20, 25, and 30 °C) and at different operation times, in order to determine the effect of temperature and time on the photodegradation of pesticides and on the quality parameters of the 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 , were determined using analysis methods published in the official EU bulletin [24]. In the case of 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.

2.3.2. Extraction and determination of residues from pesticides

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 × 300 mm and 19 × 150 mm). The extraction of the pesticide fraction from oil was based on the addition of the internal standard (bromophos-methyl), anhydrous sodium sulphate, *n*-hexane and acetonitrile. Afterwards, the extracted fraction was purified by chromatography of gel-permeability separation and finally the direct analysis was made by gas chromatography in a capillary column and mass detector. The quantitative measurements of pesticides (MS/MS) were made using different calibration lines for each pesticide where the concentration of pesticides had varied

Table 2
Influence of ultraviolet light on the quality parameters of virgin olive oil ($T=20^{\circ}\text{C}$).

t (min)	Acidity (%)	Peroxide index (meq $\text{O}_2 \text{ kg}^{-1}$)	K_{270}	K_{232}	ΔK	Rancimat stability (h)
0	0.28	11.5	0.139	1.991	0.001	33.0
2	0.28	12.2	0.140	2.009	0.001	–
4	0.29	12.1	0.140	2.009	0.001	–
8	0.29	12.5	0.139	1.999	0.001	33.4
12	0.29	12.7	0.140	2.020	0.001	34.1
16	0.28	13.2	0.143	2.026	0.002	33.4
20	0.29	12.7	0.144	2.007	0.002	–
25	0.28	12.1	0.145	1.981	0.003	33.6
30	0.29	12.1	0.144	1.949	0.003	–
49	0.29	12.1	0.150	1.948	0.005	–
60	0.29	12.0	0.156	1.942	0.005	34.0
150	0.52	8.90	0.178	2.006	0.001	35.0

Maximum values allowed according the Commission Regulation (CEE) no. 2568/91: acidity ≤ 1.0 , peroxide index ≤ 20 , $K_{270} \leq 0.20$, $K_{232} \leq 2.50$, $\Delta K \leq 0.01$. 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).

between 10 and $500 \mu\text{g L}^{-1}$. The pesticide-purity standards were purchased from Dr. Erhenstorfer (Pomochem, Wesel, Germany) and used without further purification. Varian CP3800 Gas chromatography equipment was combined with the detector Saturn 2200 GC, using a sample of $10 \mu\text{L}$ injected. The starting temperature of the oven, 70°C , was maintained for 3.5 min. Afterwards, the temperature was raised at $25^{\circ}\text{C min}^{-1}$ intervals up to 180°C and held at this temperature for 10 min. Finally, the temperature was raised to $4^{\circ}\text{C min}^{-1}$ intervals up to 300°C and kept at 300°C for another 10 min. Thus, the total time to heat the oven was 57.9 min. The helium flow in the column was 1 mL min^{-1} .

3. Results and conclusions

In the sample without the addition of pesticides (sample collected directly from the market), the following were detected: trichlorfon $99 \mu\text{g L}^{-1}$, diuron $12 \mu\text{g L}^{-1}$, carbaryl $43 \mu\text{g L}^{-1}$, dimethoate $15 \mu\text{g L}^{-1}$, terbuthylazine $19 \mu\text{g L}^{-1}$, terbutryn $8 \mu\text{g L}^{-1}$, oxifluorfen $12 \mu\text{g L}^{-1}$, endosulfan II $8 \mu\text{g L}^{-1}$, endosulfan sulphate $19 \mu\text{g L}^{-1}$, diflufenican $9 \mu\text{g L}^{-1}$, and phosmet $7 \mu\text{g L}^{-1}$. In any case, these values exceeded permitted limits. There is currently no specific legislation in Spain regarding 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. With this rule of thumb, the maximum acceptable contamination levels for some of the more commonly used pesticides would be $500 \mu\text{g L}^{-1}$ for atrazine and simazine, $250 \mu\text{g L}^{-1}$ for terbuthylazine, $100 \mu\text{g L}^{-1}$ for oxyfluorfen and diflufenican, $250 \mu\text{g L}^{-1}$ for norflurazone and $1000 \mu\text{g L}^{-1}$ for diuron [18].

Table 1 shows the pesticide residues identified in the commercial olive oil after spiking with different chemical compounds.

In Table 2 shows the values ($T=20^{\circ}\text{C}$) of different quality parameters studied with the increased operating time. The values of quality parameters of the olive oil were not affected significantly by ultraviolet light during the time period tested (150 min maximum). Acidity (≤ 0.59), peroxide index ($\leq 12.7 \text{ meq O}_2 \text{ kg}^{-1}$), UV absorbency: K_{270} (≤ 0.200), K_{232} (≤ 2.03), and ΔK (≤ 0.005) have not exceeded the maximum values of the quality parameters allowed according to the official legislation (Table 2). The values of the official quality parameters studied are not heavily affected by the impact of ultraviolet light on oil. Finally, olive oil was considered by a panel of sensory analysis, which did not detect changes in odour or taste.

Tables 3–5 show the photodegradation yields of each of the active ingredients contained in the pesticides most commonly found in oil, and after a time exposure to ultraviolet light of 16, 30, and 150 min, respectively. These yields were determined to four different temperatures: 15, 20, 25 and 30°C .

Table 3
Photochemical degradation yields of pesticide residues at different temperatures, after 16 min.

Photodegradation yields (%)	Temperature ($^{\circ}\text{C}$)			
	15	20	25	30
Trichlorfon	65.9	64.5	61.5	62.2
Diuron	47.4	45.3	40.6	45.6
Dimethoate	18.3	2.1	–	–
Simazine	42.3	42.9	14.6	21.9
Terbuthylazine	6.8	–	–	–
Chlorpyrifos methyl	30.3	29.9	26.2	32.7
Parathion methyl	37.3	31.9	34.1	35.1
Pirimiphos methyl	20.1	20.5	13.7	5.3
Fenitrothion	35.0	27.1	33.4	33.9
Terbutryn	2.4	2.2	2.9	9.5
Malathion	34.6	28.0	53.1	51.0
Chlorpyrifos	25.9	29.8	29.7	28.6
Parathion Ethyl	21.0	17.5	29.0	19.8
Metidathion	29.7	7.3	21.9	14.2
Endosulfan I	4.2	11.4	–	–
Fenoxicarb	2.8	1.6	8.6	–

For the initial concentration see Table 1.

From Table 3 it can be deduced that 16 pesticides decreased in content between 8.6% and 66.0% (between 6.8% and 65.4%, between 7.6% and 79.1% at 30, and 150 min, respectively). Notably, 14 of them (trichlorfon, diuron, carbaryl, dimethoate, simazine, terbuthylazine, chlorpyrifos methyl, parathion methyl, fenitrothion, malathion, chlorpyrifos, parathion ethyl, methidathion and oxifluorfen) were found to have decreased more than 30% (Table 6). The photochemical degradation of oxifluorfen, diflufenican, phosmet,

Table 4
Photochemical degradation yields of pesticide residues at different temperatures, after 30 min.

Photodegradation yields (%)	Temperature ($^{\circ}\text{C}$)			
	15	20	25	30
Trichlorfon	62.7	65.4	62.3	64.6
Diuron	39.4	37.1	31.9	57.0
Dimethoate	6.8	–	–	–
Simazine	32.8	28.5	18.8	40.5
Terbuthylazine	2.2	–	–	–
Chlorpyrifos Methyl	27.2	43.0	33.4	34.0
Parathion Methyl	35.7	40.6	36.3	42.8
Pirimiphos Methyl	–	9.3	7.7	3.2
Fenitrothion	17.6	22.7	28.5	32.4
Malathion	31.9	43.8	26.9	44.3
Chlorpyrifos	20.5	37.3	27.1	31.9
Parathion Ethyl	18.5	31.0	26.0	25.7
Metidathion	5.6	19.9	–	20.5

For the initial concentration see Table 1.

Table 5
Photochemical degradation yields of pesticide residues at different temperatures, after 150 min.

Photodegradation yields (%)	Temperature (°C)			
	15	20	25	30
Trichlorfon	18.0	78.1	73.6	66.9
Diuron	28.2	75.4	63.1	76.6
Carbaryl	–	33.0	8.9	–
Dimethoate	–	48.4	33.4	–
Simazine	15.2	63.9	52.0	43.4
Terbuthylazine	–	39.9	23.6	–
Chlorpyrifos methyl	65.2	68.7	53.3	61.3
Parathion methyl	67.9	73.8	74.9	79.1
Pirimiphos methyl	4.4	10.9	–	9.2
Fenitrothion	31.6	48.2	38.2	44.6
Terbutryn	3.2	25.7	–	8.6
Malathion	–	–	–	49.3
Chlorpyrifos	61.0	63.4	48.6	65.2
Parathion Ethyl	55.6	64.1	61.3	74.0
Metidathion	14.3	3.6	–	29.8
Oxifluorfen	44.5	20.3	6.1	29.5
Diflufenican	14.5	–	–	–
Phosmet	7.6	–	–	–
Fenoxicarb	–	1.4	–	13.0
Alpha-cypermethrin	9.0	–	–	–
Deltamethrin	20.3	–	–	–

For the initial concentration see Table 1.

alpha-cypermethrin and deltamethrin was detected only in the experiments with operation times of 150 min.

Table 6 shows the maximum photochemical degradation yields recorded for each pesticide, regardless of the temperature and time of operation. On the other hand, all chemical compounds studied were reduced in content after being submitted to ultraviolet light [25]. Also, photochemical degradation experiments made with extra-virgin olive oil without mixing in any pesticides (only with the residual pesticides detected) were the photochemical degradation yields of trichlorfon recorded equal to 96% at 16 min and 98% at 30 min ($T = 20^\circ\text{C}$). Other experiments with oil mixed only with terbuthylazine registered values of photodegradation yields ($T = 20^\circ\text{C}$) equal to 38% and 55% at 16 and 30 min, respectively.

Table 6
The maximum photochemical degradation yields of pesticides and its corresponding temperature and operating time.

Pesticide	t (min)	T_{opt} (°C)	% Maximum photodegradation yields
Trichlorfon	150	20	78.1
Diuron	150	30	76.6
Carbaryl	150	20	33.0
Dimethoate	150	20	48.4
Simazine	150	20	63.9
Terbuthylazine	150	20	39.9
Chlorpyrifos methyl	150	20	68.7
Parathion Methyl	150	30	79.1
Pirimiphos Methyl	16	20	20.5
Fenitrothion	150	20	48.2
Terbutryn	150	20	25.7
Malathion	16	25	53.1
Chlorpyrifos	150	30	65.2
Parathion Ethyl	150	30	74.0
Metidathion	150	30	29.8
Endosulfan I	16	20	11.4
Oxifluorfen	150	15	44.5
Endosulfan II	150	15	0.7
Endosulfan sulphate	150	15	1.8
Diflufenican	150	15	14.5
Phosmet	150	15	7.6
Fenoxicarb	150	30	13.0
Alpha-cypermethrin	150	15	9.0
Deltamethrin	150	15	20.3

Although some degradation products of the pesticides can be less toxic and harmless, it is not uncommon for them to be more toxic than the parent pesticides. Indeed, the evaluation of the degradation products is important from the standpoint of human health and environmental protection [26]. Toxic effects associated with exposure of phosmet are related to its irreversible inhibition of the acetylcholinesterase enzyme, which causes acute effects in humans [27]. In recent years strong research effort has been made to identify the products arising from photodegradation of phosmet. Tanabe et al., [28] irradiated phosmet in diethyl ether and have identified *N*-methylphthalimide and *N*-methoxymethylphthalimide as its main degradation products.

Photodegradation of diuron by the Photo-Fenton or TiO_2 system has recently been studied with the aim of reducing the diuron concentration in water [29]. Total mineralisation (i.e., complete disappearance of TOC) can be achieved after a long irradiation (more than 200 min). However, it appears that 90% of the initial TOC could be mineralised in approximately 125 and 159 min, respectively. The carbaryl photodegradation products in the absence and presence of the AgY zeolites were quantified using the technique of GC-MS. In the absence of the catalysts, only α -naphthol was produced after a solution of carbaryl was irradiated for up to 12 h. However, in the presence of the AgY catalysts, α -naphthol and phthalic acid were the major photodegradation products that were produced [30]. The degradation curve of chlorpyrifos, with a half life of 13.3 min, indicates the complete degradation of the parent compound within 120 min of irradiation. The GC-MS identification of chlorpyrifos photodegradation products suggested the formation of only one product, i.e., chlorpyrifos-oxon A1. The degradation curve of malathion was similar to that of chlorpyrifos, with the calculated half life of 11.6 min. The complete degradation of the starting compound was achieved within 60 min of irradiation. The GC-MS chromatograms of irradiated samples indicate the formation of several photoinduced by-products. The majority of these belong to a family of bute(a)ne diethyl esters. The other three identified photoproducts belong to the family of toxic compounds, all members of the phosphate ester group: phosphorodithioic O,O,S-trimethyl ester (C4) and phosphorothioic O,O,S-trimethyl ester (C1) as major compounds and diethyl (dimethoxy-phosphoryl) succinate in traces (C9) [31]. Photochemical degradation of endosulfan in controlled aqueous systems was performed by ultraviolet light irradiation at $\lambda = 254 \text{ nm}$. The photolysis of ($\alpha + \beta$: 2 + 1) endosulfan, α -endosulfan and β -endosulfan were first-order kinetics. The observed rate constants determined from linear least-squares analysis of the data were 1×10^{-4} ; 1×10^{-4} ; and $2 \times 10^{-5} \text{ s}^{-1}$, respectively, and the calculated quantum yields were 1, 1 and 1.6, respectively. Preliminary differential pulse polarographic (DPP) analysis indicated the possible endosulfan photochemical degradation pathway. This degradation route involves the formation of the endosulfan diol, its transformation to endosulfan ether and finally the ether's complete degradation by observing the potential shifts [32].

In relationship to the operation time, the largest decreases, except pirimiphos methyl, malathion, and endosulfan I, were recorded after an operation time equal to 150 min. With regard to operating temperature, maximum reductions have been detected within a temperature range of 15–20°C. 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 [33]) and, therefore, molecular collisions decline with rising temperatures. Such a behavioural trend depends on the chemical structure of the pesticide and chemical environment where it undergoes degradation.

These initial results open the possibility of using ultraviolet light as an effective and low-cost physical process (without harming the

official quality parameters of virgin olive oil) for the elimination or reduction of the pesticide content in virgin olive oil. Also, it should be noted that the use of a tubular reactor exposed to ultraviolet light may be the most appropriate application to carry out such treatment at an industrial level.

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