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Influence of uv radiation on the degration of ethion in pistachio

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Abstract

Ethion is a broad-spectrum pesticide commonly used for control of insects on pistachio (Pistacia vera L.). The extensive use of pesticides on pistachio fruits has raised concerns about pesticide residues. In this study, used UV radiation and TiO2 photocatalyst as decomposing agent to evaluate the rate of ethion degradation . The experiment in two modes,ethion spray on filter paper and pistachio fruit was conducted. Based on a series of pre-tests, the Filter papers were treated with ethion,they were exposed to radiation inside the reactor at appropriate time(5,10 and 20 hour).then pesticide residues were determinded on them.ethion degradation percentage respectively were(9.29,24.77and33.49%)at desired time.Additionally, two UV lamps in absence or presence of TiO2(200 mg/mL) were used to degradade ethion residue from pistachio fruits. All treatments had moderate efficiency for ethion removal from both filter papers and pistachio fruits. The efficiency was positively affected by time of exposure, number of UV light sources, and presence of TiO2. Although, this study showed the potential of UV radiation and TiO2 for ethion degradation from pistachio fruits, further studies are needed to optimize the experimental condition for enhancing the degradation efficiency

Keywords: ethion, uv radiation, pistachio

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Introduction

Iran is the world's largest producer and exporter of pistachio (Pistacia vera L.), more than 48% of the world pistachio production in 2014 (FAO, 2017). Kerman province, especially the Rafsanjan region of Iran is the main center of pistachio production. Accounting for 57% of the country production (97000 tones) in 2015 (Iran Pistachio Association, 2016). Pistachio production in Iran is largely affected by a variety of pests and diseases. The wide use of pesticides for control of these pests has emerged serious concerns about environmental pollutions and human health. Although, several procedures, including incineration, biological treatment, and adsorption process have been developed in order to remove pesticide residues, the efficiency of these methods are questionable due to a variety of reasons (see Barros et al., 2013).

A partial elimination of the pesticide residues through oxidation technichs has been proposed to produce intermediate compounds that are more readily degradable and can be further removed by the conventional methods mentioned above (Scott & Ollis, 1995). Earlier studies have argued that organic contaminants can be partially removed from the environment by the help of the powerful oxidization potential of several agents such as ozone, uv radiation, and Fenton's reagent (Masten & Davies, 1994; Benitez et al., 2002; Wu et al., 2007). However, the resistant characters of some compounds to these oxidative agents necessitate stronger oxidant agents or advanced oxidation processes (AOPs) (Benitez et al., 2002). AOPs are a set of chemical procedures through which, the organic materials are oxidized by combined effects of conventional reagents (such as ozone, hydrogen peroxide, and oxygen), radiation sources and specific catalysts and converted into water, carbon dioxide, and nontoxic or less toxic reaction products (Barros et al., 2013). During the last two decades, a large volume of studies has evaluated the efficiency of UV radiation and AOPs for degradation of organic materials from wastewater, and to a lesser extent, from vegetables and fruits (Benitez et al., 2002; Wu et al., 2007; Lin et al., 2012; Barros et al., 2013; Hassarangsee et al., 2015; Thao et al., 2017).

The pistachio oyster shell scale, Lepidosaphes pistaciae (Archangelskaya) (Hem: Diaspididae), is an important pest of both cultivated and wild pistachio trees in Iran (Mehrnejad, 2001). Adult females occur in two or three distinct forms, each developing on a specific part of pistachio trees (Masjedian &Seyedoleslami, 2003). Under severe infestation, the pest causes delayed fruit ripening, fully undeveloped kernels, decreased nut production and twig death (Mehrnejad, 2001). Growers use the pesticide ethion (0,0,0',0'-Tetraethyl s,s'-methylene) in mixture with oil to control L. pistaciae in pistachio orchards (Desouky et al.,2013). Ethion is an organophosphate pesticide widely used to control aphids, mites, scales, thrips, and leafhoppers on fruits and foliage (Desouky et al., 2013) The objectives of this study was to evaluate the degradation rate of ethion on pistachio surfaces by means of either single oxidant (UV radiation) or the advanced oxidation processes constituted by combinations of titanium dioxide (TiO2) plus UV radiation. selected TiO2 as photocatalyst due to its high photoactivity, photocorrosion resistance, thermal stability, non-toxicity, cost effectiveness, and potential applications under UV light (254 nm).

Material and methods

Chemicals

Certified reference pesticide, ethion (99%), was purchased from Fluka, (Germany). The commercial pesticide ethion (47%) was obtained from Kavosh Kimia Kerman (Kerman, Iran). Analytical grade ethyl acetate and acetone were obtained from Merck (Darmstadt, Germany) and Dr. Mojallali industrial chemical complex company (Tehran, Iran), respectively. Titanium dioxide (TiO2) was purchased from Mehregan Shimi (Tehran, Iran).

Photocatalytic reactor

The photocatalytic reactor consisted of a transparent glass container (35.35.48 cm) covered with aluminum foil. Four UV high-pressure mercury vapor quartz lamp radiation source, with a monochromatic radiation at 254 nm, and a nominal power of 12 Watt were positioned side by side at the ceiling of the container to ensure maximum energy exchange between the irradiation source and the reaction mixture.

Ethion photodegradation on filter paper

To determine the time of the UV ray effect on the product and as a pre-stage to the experiment, irradiation was investigated on a filtering paper within 5h, 10h and 20h time periods so as to make it clear whether decomposition occurs during these times or not(table1). Photodegradation of ethion residue on filter paper, was evaluated using a laboratory-scale photocatalytic reactor. The commercial formulation of ethion was diluted using conditioned water as 10 ppm. Filter papers (Schleicher & Schuell MicroScience, GmbH, Germany) were immersed into the pesticide solution for 10 min, then left in room temperature to air-dry for 12 hours. After drying, the treated filter papers were put inside the reactor containing four and two UV lamps for 5, 10 and 20 hours. In control, the treated filter papers were maintained outside the reactor without UV irradiation. This experiment was carried out in triplicate.

Table 1- The rate of photodegradation of ethion from filter papers at different times of exposure to two UV lamps

Exposure time (hour)	Photodegradation(%) ±SD
5	9.29±5.20
10	24.77±1.17
20	33.49±4.29

In order to extract the insecticide residue, the filter papers were placed inside Petri dishes containing 5 ml of ethyl acetate as solvent. The Petri dishes were then placed on a rotary shaker with low revolutions per minute (RPM). After 30 min of rotation, the filter papers were removed and the solvent containing insecticide residue were transferred into glass vials. The samples were stored at 4 °C for further analysis of pesticide residue using GC-MS analysis. As for pistachio products, irradiation for 10h and 20h was not found causing much of a change in the protein content in comparison to 5h but burns and changes of color and taste were evidenced in the product. Thus, the time of UV irradiation on the product was decreased to below 5 hours and 30min, 60min, 120min and 300min were taken into account for the main experiment. Furthermore, UV irradiation intensity was investigated during the aforementioned times in such a manner that 2 lamps were applied in one experiment and 4 lamps were used in another. Higher UV intensities, to wit the simultaneous use of 4 lamps, caused change of color and burns in the filtering paper. Thus, the main experiment was designed using 2 UV lamps for 30min, 60min, 120min and 300min times

Ethion photodegradation from pistachio

About 500 g of pistachio fruits were randomly collected from growing areas in Rafsanjan County The samples were obtained from organic orchards with no insecticide application during the growing season to ensure that they do not already contain insecticide residue. The pistachios were placed in a net bag and submerged in ethion solution (100 ppm) for 30 min. After treatment, the fruits were left for 24 hours in ambient temperature to air-dry and then allocated to one of the three following treatments: 1) the fruits were put in Tio2 solution (200 µg/L) and then put inside the reactor with two UV lamps for 30, 60, 120, and 300 min. 2) the treated fruits without Tio2 exposed to UV irradiation.3)in control , the treated fruits were maintained outside the reactor This experiment was performed with three replicates.

To analyze insecticide residue, the treated pistachios were ground into a uniform powder using an electric grinder. Twenty g of each sample was transferred into glass vials containing ethyl acetate solvent. The vials were then placed on a rotary shaker for 30 min. The extract was transferred into new vials and a rotary dryer was used to concentrate the extract. The vials were maintained at 4 °C until being used for analysis of pesticide residue.

A GC–MS system (HP7890/MSD 5975C, Agilent, CA, USA) equipped with a capillary column DB-5MS (5% phenyl methylpolysiloxane, 30 m × 0.25 mm id × 0.25 µL film thickness, J&W Scientific, Folsom, CA, USA) was used for analysis of ethion residue in extracts taken from either treated filter papers and pistachio fruits. Helium was used as carrier gas with a velocity of 20 cm/s. The temperature program for the GC column consisted of a 2-min hold at 80 °C, a 20 °C/min raise to 160 °C, a 10 °C/min raise to 210 °C, and a final raise to 260 °C at 5 °C/min. The injector temperature was set at 200 °C.

Data analysis

Chromatographic data were analyzed using Chemstation software.Data were analyzed using SPSS computer software. Duncan's test was conducted to analyzed the difference between various treatments.

Results and Discussion

To investigate the efficiency of UV irradiation and titanium dioxide, filter papers were used within the format of a pretest so that the experiments could be conducted on the product in the later stages. The results of photodegradation of ethion on filter papers by use of two UV lamps, four UV lamps, and TiO2/two UV lamps have been summarized in Tables2. In all treatments, removal of the pesticide residue increased by time (Fig. 1). The least rate of pesticide degradation was recorded for papers exposed to two UV lamps (Table 2), while papers treated with TiO2 and two UV lamps retained the least pesticide residues (Table2, Fig. 1). Titanium dioxide was used as a catalyst in experiment environment for accelerating the chemical destruction reactions. Besides reducing the time, titanium dioxide enhances the chemical decomposition percentage. So, it can be stated that it effectively contributes to the efficiency elevation.

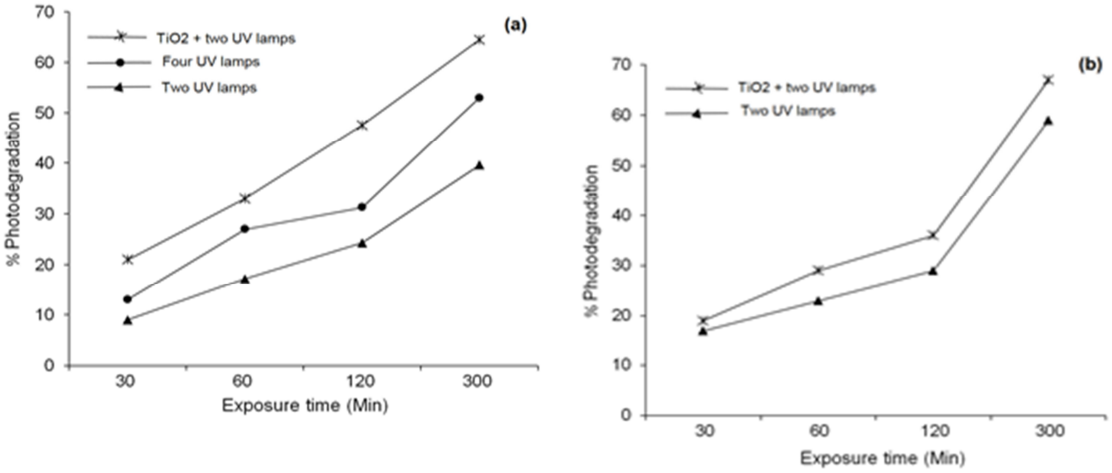

Fig. 1- The rate of ethion photodegradation from filter paper (a) and pistachio fruits (b) by different treatments and in different exposure times

Table 2- The rate of photodegradation of ethion from filter papers at different times of exposure to two UV lamps/four UVlamps/Tio2/ two uv lamps.

two UV lamps		four UV lamps		TiO2/two UV lamps	
Exposure time (min)	Photodegradation (%) ± SD	Exposure time (min)	Photodegradation (%) ± SD	Exposure time (min)	Photodegradation (%) ± SD
30	9 ± 1.5	30	13 ± 2.85	30	21 ± 1.43
60	17.2 ± 0.17	60	27 ± 2.68	60	33 ± 1.12
120	24.3 ± 4.42	120	31.3 ± 5.66	120	47.6 ± 2.71
300	39.6 ± 2.22	300	53 ± 6.5	300	64.5 ± 2.29

According to the study objective, i.e. investigation of the effect of UV irradiation in chemical decomposition, it remains to be answered that could the results be changed if UV is directly applied on the product and whether the product will be damaged or not? And, as it is known, damaged products lose their market agreeableness. In the next stage, the experiment was carried out on dried pistachio products and, similar to the first stage, the products were subjected to various dosages of UV irradiation. The results indicated that the increase in dosage causes increase in the decomposition of the pesticide but the critical point of the study was determination of an appropriate UV irradiation dosage without imposing serious damage on the product. Thus, the results indicated that burning effects appear on the product in 10h and 20 h times as well as when there are used four UV lamps. Of course, this was proved in brief experiments. Therefore, exposure time beyond 300 minutes and a dosage of 4 UV lamps were not taken into account in the primary experiments.

In addition, the results of ethion photodegradation from pistachio fruits by the two treatments (two UV lamps vs. TiO2/two UV lamps) have been shown in Table 3. Like the previous experiment on filter paper, the rate of pesticide removal increased by time, with the highest rates of photodegradation were recorded in samples treated for 300 min. Treatment of pistachio fruits with TiO2 resulted in significant increase in pesticide photodegradation by UV lamps in all studied times (Table 3).

Table 3- The rate of photodegradation of ethion from pistachio fruits at different times of exposure to two UV lamps, TiO2/two UV lamps

two UV lamps		TiO2/two UV lamps	
Exposure time (min)	Photodegradation (%) ± SD	Exposure time (min)	Photodegradation (%) ± SD
30	17 ± 3.77	30	19 ± 2.71
60	23 ± 1.9	60	29 ± 1.68
120	29 ± 4.2	120	36 ± 5.16
300	59 ± 7.5	300	67±4.82

Pesticides have long been used as the cheapest, easiest and the most effective methods for pest management (Fields & White, 2002). Indiscriminate use of broad-spectrum pesticides can results in environmental pollutions, besides leaving residues on crops that threats human health (Stanley &Preetha, 2016). Although a variety of methods have been developed for pesticide degradation from surface and underground waters, soil, and plant tissues, recent advances in technology have provided new insights into the combined use of conventional reagents (such as ozone, hydrogen peroxide, and oxygen), radiation sources and specific catalysts for efficient degradation of notorious compounds, a techniques commonly known as advanced oxidation process (Barros et al., 2013). The efficiency of several photocatalytist has been investigated for the degradation of notorious compounds, including TiO2, CdS, ZnS and active carbon. However, studies involving TiO2 has been more extensive because of its low cost, stable nature and high photocatalytic activity when exposed to UV radiation (Pera-Titus et al., 2004). Barros et al. (2013) exposed two concentrations of the organophosphate pesticide, chlorpyrifos to thermal effect of microwave, microwave + UV radiation, and microwave + hydrogen peroxide (H2O2) and reported efficient removal of the pesticide especially when the time of exposure and the power of microwave were increased. Consistent with our results, Laoufi and Bentahar (2014) showed that removal of the commonly used herbicide linuron by photocatalytic process (UV radiation in presence of TiO2) was significantly more efficient than degradation by each of photolysis (i.e. UV radiation in absence of TiO2) or absorption (physical absorption by TiO2). In another study, Wu et al. (2007) showed that 1.4 mg/l of ozonated water was sufficient to oxidize 60–99% of the four broad-spectrum pesticides, methyl-parathion, cypermethrin, parathion and diazinon, in aqueous solution within 30 min and the degradation was mostly completed in the first 5 min. Schulman and Throop (2013) used two reactors to test the efficiency of UV radiation and TiO2 for photodegradation of chlorpyrifos and reported a degradation efficiency of 80% and 89.17% for these reactors, respectively. In another study, removal of 80% of cypermethrin and 78% of malathion from tea fresh leaves was reported when the leaves were treated with O3/UV/TiO2 (Lin et al., 2012).

Altogether, results of the current study indicate that advanced oxidation process using UV radiation in absence or presence of TiO2 has the potential to remove ethion from both filter paper and pistachio fruits. Higher efficiency was obtained when TiO2 was used as photocatalyst. However, the rate of pesticide removal was lower than those reported for other pesticides (e.g. Lin et al., 2012; Schulman & Throop, 2013; Laoufi & Bentahar, 2014). Apparently, the efficiency of pesticide degradation is affected by a variety of factors such as the type of reactor, the power of light source, the time of exposure, and the concentration of photocatalyst. Therefore, further studies are needed to optimize these conditions for more efficient degradation of ethion and other pesticides from this economically valuable nut.

Experiments indicated that it is possible to decompose ethion using UV irradiation and the destructive effect of UV in braking down of the chemicals' structures has been documented in the experiments. Therefore, the results obtained in the other studies conform to what has been found herein. These studies have been conducted with the objective of optimizing UV application for decomposition of chemicals so that, besides easing the UV irradiation, the dangers and burns that might come about in the product could be avoided.

According to the fact that UV breaks double bonds, it seems that it can be effective when used on pesticides in the structures of which there are double bonds and this incorporates a great many of the pesticides. But, in order to avoid the various problems, it is necessary to perform more studies

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References

Barros, F.C.F; Barros, A.L; Silva, M.A.A.and do Nascimento, R.F .2013. Use of m-Assisted oxidation for removal of the pesticide chlorpyrifos from aqueous media. International Journal of Civil & Environmental Engineering, 13: 16–27.

Benitez, F.J; Acero, J.L.and Real F.J. 2002. Degradation of carbofuran by using ozone, UV radiation and advanced oxidation processes. Journal of Hazardous Materials, 89: 51–65.

Desouky, M.M.A; Abdel-Gawad, H.and Hegazi, B .2013. Distribution, Fate and histopathological effects of ethion insecticide on selected organs of the crayfish. Procambarus clarkia. Food and Chemical Toxicology, 52: 42–52.

FAOSTAT .2017. Pistachio production in 2014. Food and Agricultural Organization of the United Nations, Statistics Division (FAOSTAT). Retrieved 5 April 2017**.**

Fields, P.G. and White, N.D.G .2002. Alternatives to methyl bromide treatments for stored-product and quarantine insects. Annual Review of Entomology, 47: 331–359.

Hassarangsee, S; Whangchai, K; Uthaibutra, J.and Chantara, S .2015. Photocatalysis of titanium dioxide to decompose ethion in tangerine fruit. Acta Horticulturae, 1088: 359–362.

Iran Pistachio Association (IPA) .2016. Prediction of Iran pistachio production for 2016, 5: 8.

Johnson, W.Wand Finley, M.T .1980. Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. Resource Publication 137. U.S. Department of Interior, Fish and Wildlife Service, Washington, DC. 5-1.

Kidd, H.and James, D.R.1991. The Agrochemicals Handbook, Third Edition. Royal Society of Chemistry Information Services, Cambridge, UK. 5–14.

Laoufi, N.A.and Bentahar, F .2014. Pesticide removal from water suspension by UV/TiO2 process: a parametric study. Desalination and Water Treatment, 52: 1947–1955.

Lin, L; Xie, M; Liang, Y; He ,Y; Chan, G.Y.S.and Luan T .2012. Degradation of cypermethrin, malathion and dichlorovos in water and on tea leaves with O3/UV/TiO2 treatment. Food Control, 28: 374–379.

Masjedian, H.and Seyedoleslami, H .2003. Bioecology of Pistachio Oyster Shell Scale, Lepidosaphes pistaciae Archangelskaya (Homoptera: Diaspididae) in Isfahan. Journal of Science and Technology in Agriculture and Natural Resources, 6: 181–194 .

Masten, S.J.and Davies, SH .1994. The use of ozonation to degrade organic contaminants in wastewaters. Environmental Science and Technology, 28: 180A–185A.

Mehrnejad, M.R .2001. The current status of pistachio pests in Iran,315-322. In : Ak BE (ed.). XI GREMPA Seminar on Pistachios and Almonds, Zaragoza , CIHEAM.

Pera-Titus, M; Garcia-Molina, V; Banos, M.A; Giménez, J.and Esplugas, S .2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. Applied Catalysis B: Environmental, 47: 219–256.

Schulman, I.and Throop, D .2013. Photocatalytic oxidation for the removal of chlorpyrifos from aqueous solution. BSc project. University of Nova Gorica.

Scott, J.P.and Ollis, D.F .1995. Integration of chemical and biological oxidation processes for water treatment: Review and recommendations. Environmental Progress and Sustainable Energy, 14: 88–103.

Stanley, J.and Preetha, G .2016. Pesticide Toxicity to Non-target Organisms: Exposure, Toxicity and Risk Assessment Methodologies. Dordrecht : Springer Netherlands.

Wu, J; Luan, T; Lan, C; Lo, T.W.H. and Chan, G.Y.S .2007. Removal of residual pesticides on vegetable using ozonated water. Food Control, 18: 466–472.

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تاثیر تشعشعات فرابنفش بر تجزیه تدریجی اتیون در پسته

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چکیده

اتیون یک حشره‌کش طیف وسیع است که معمولا برای کنترل آفات پسته(*Pistacia Vera L.*)مورد استفاده قرار می گیرد. استفاده گسترده از آفتکشها روی میوه پسته نگرانی زیادی را در مورد باقیمانده آفتکش‌ها به وجود آورده است.در این مطالعه اشعه UV و فوتوکاتالیست TIO2 به عنوان عوامل تجزیه کننده ، جهت تجزیه تدریجی اتیون مورد استفاده قرار گرفتند.آزمایش در دو حالت اسپری آفتکش بر کاغذ صافی و میوه پسته انجام شد.براساس یکسری پیش آزمایش ،کاغذهای صافی آغشته به اتیون در زمانهای مناسب (٥ ، ١٠ و ٢٠ ساعت)داخل راکتور در معرض اشعه یو وی قرار گرفتند و پس از خارج شدن باقیمانده آفتکش روی انها اندازه گیری شد.درصد تجزیه اتیون در زمانهای یادشده به ترتیب (٩.٢٩، ٢٤.٧٧ و ٣٣.٤٩ درصد) تعیین گردید.در نهایت ٢ لامپ UV در حضور و عدم حضور TIO2(200mg/ml) برای تجزیه تدریجی اتیون در میوه پسته استفاده شدند.همه تیمارها بازده متعادلی برای حذف اتیون از کاغذ صافی و میوه پسته داشتند. بازده به‌طور مثبت متاثر از تعداد لامپ uv و حضور TIO2 بود.اگر چه این آزمایش پتانسیل مثبت اشعه UV و TIO2را در تجزیه تدریجی اتیون در پسته نشان داد لذا مطالعات آتی برای بهینه سازی شرایط تجربی در تجزیه تدریجی لازم است.

واژه‌های کلیدی :اتیون،اشعه فرابنفش،پسته

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