Ecotoxicology and Environmental Safety 108 (2014) 84–88

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Photodegradation of organophosphorus pesticides in honey medium

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ARTICLE INFO

Article history:
Received 25 February 2014
Received in revised form
25 June 2014
Accepted 26 June 2014
Available online 18 July 2014

Keywords:
Coumaphos
Methyl parathion
Fenitrothion
Photodegradation
Pseudo-first order kinetics
Pseudo-second order kinetics

ABSTRACT

Honey can be polluted due to environmental pollution and misuse of beekeeping practices. In the present study, photodegradation experiments of organophosphorus pesticides (coumaphos, methyl parathion and fenitrothion) in honey medium were conducted using Atlas Suntest simulator CPS+ as a sunlight producer. Photodegradation experiments were conducted under three different intensities as 250 W/m^2, 500 W/m^2 and 750 W/m^2 to evaluate the impact of sunlight intensity on removal of OPs in honey medium. Significant decreases of three OPs' concentrations were observed. Coumaphos showed the highest degradability, reaching a degradation percentage of 90 percent within 15 min. After 1 h irradiation, residual percentages of coumaphos were 6.62 percent for 250 W/m^2, 3.48 percent for 500 W/m^2 and 2.98 percent for 750 W/m^2, respectively. Methyl parathion and fenitrothion also could be removed through photodegradation efficiently. After 1 h irradiation, the residual percentages of methyl parathion and fenitrothion under 750 W/m^2 sunlight irradiation were 26.89 percent and 16.70 percent, respectively. Intensity of sunlight showed a positive impact on removal of OPs in honey medium. The higher intensity, the lower residual percentage. Photodegradation of three OPs fitted well with pseudo-first order kinetics. Half-lives calculated from pseudo-first order kinetics were 17.61 min (250 W/m^2), 16.67 min (500 W/m^2) and 17.58 min (750 W/m^2) for coumaphos, 57.62 min (250 W/m^2), 34.13 min (500 W/m^2) and 31.69 min (750 W/m^2) for methyl parathion and 144.70 min (250 W/m^2), 95.47 min (500 W/m^2) and 22.57 min (750 W/m^2) for fenitrothion, respectively. Most of the three OPs could dissipate in a short time under sunlight irradiation. Photodegradation could be accepted as an appropriate method for the removal of OPs in honey medium.

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1. Introduction

Honey is a natural product of bees and is recognized as a food with nutritional properties and is known like a food with valuable therapeutic applications. Honey produced by honey bees (*Apis mellifiera*) from pollen, plant nectars, and/or honeydew is composed of over 300 chemical substances which belong to different chemical compound groups. These are mainly carbohydrates, water, polysaccharides, fatty acids, proteins, minerals, dyes, fragrances, enzymes, hormones and vitamins in amounts depending on the plant from which the honey was made (Bargańska et al., 2013; Kujawski and Namieśnik, 2008).

However, honey can also be a source of toxic substances, such as antibiotics, pesticides and heavy metals due to environmental pollution and misuse of beekeeping practices. Honey bees collect pollen and nectar from the surrounding flowers (over very large areas) and then they may return to hives collecting significant amounts of toxic contaminants, therefore their hives and products can result contaminated with many different kinds of pollutants (López et al., 2014; Morgano et al., 2010; vanEngelsdorp and Meixner, 2010). In addition the honeybees are also exposed to pesticides and antibiotics administered by beekeepers as part of the hive to control some infestations such as *Varroa destructor*, *Acarapis wood* and *Paenibacillus larvae* (Fell and Cobb, 2009; Genersch et al., 2010); unfortunately the conventional commercial beekeepers frequently apply agrochemicals whether there are healthy or sick bees (Blacquiere et al., 2012; López et al., 2014), therefore, the presence of pesticides and antibiotics in bees' products has become commonplace.

Several researchers have studied the pesticides contamination in various honey samples collected from different regions of the world and different pesticide residues were found in honey produced from France, Jordan, Italy, Portugal, Spain and Switzerland (Bogdanov et al., 2003; Raghunandan and Basavarajappa, 2013). The organophosphorus pesticides (OPs) and acaricides are the most common pesticides detected in honey samples. The pesticide levels found in honey samples collected from different countries varied considerably. Coumaphos, methyl parathion and fenitrothion are the common detectable OPs in honey samples (Wang et al., 2011).

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http://dx.doi.org/10.1016/j.ecoenv.2014.06.032
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Honey with contamination would cause a potential risk for human health, because of the sub acute and chronic toxicity of contaminations (Raghunandan and Basavarajappa, 2013).

Due to this situation, the European Union has established maximum residue limits (MRLs) for a large number of pesticides used in agricultural and beekeeping practices, through the Regulation (EC) 396/2005 (Leu and Stenstrom, 2010). Since September 1st 2008, the European Commission set new MRLs of some pesticides in honey, which are in range of 10 ng/g and 50 ng/g (Bargańska et al., 2013).

Generally, the contaminated honey should be disused if the residue levels of pesticides exceed the maximum residue limits (MRLs). Yet this way may cause a large amount of wastes which remain lots of beneficial substances underutilized (Cheng et al., 2012; Xu et al., 2012). As the pesticide residues in honey are reduced to the level below MRLs, the unqualified honey can be reused as a sweetener in food industry (Xu et al., 2012). Therefore, it is necessary to establish reliable, efficient and economical methods for the removal of pesticides in honey.

Atlas Suntest CPS+ sunlight simulator has widely been used as a nature sunlight producer for irradiation experiments (Abrusci et al., 2013; Hou et al., 2013; Rosado-Lausell et al., 2013; Seto et al., 2013). Three different intensities (250 W/m^2, 500 W/m^2 and 750 W/m^2) were used in the present study to evaluate the impact of sunlight intensity on photodegradation of coumaphos, methyl parathion and fenitrothion.

The objectives of the study were (1) to study the feasibility of photodegradation of three OPs in honey medium under sunlight irradiation, (2) to evaluate the impact of sunlight intensity on photodegradation of OPs and (3) to evaluate the photodegradation models of three OPs.

2. Materials and methods

2.1. Chemicals

Coumaphos, methyl parathion and fenitrothion were purchased from Pestanal, Riedel de Haen. Detailed information of three organophospuorus pesticides (OPs) was shown in Table 1. Sodium sulfate Na_2SO_4 (99 percent) was purchased from Riedel de Haen; ethyl acetate (99.8 percent) from Carlo Erba.

The water used in this experiment was prepared using a Milli-Q water ion-exchange system (Millipore Co.) to give a resistivity of 18.2 MΩ cm at 25 °C.

Commercial honey (Purchased from a local supermarket) was used in this experiment as the medium of OPs.

2.2. Experiment set-up

The photodegradation experiments were conducted in a Suntest CPS+ simulator (Atlas, Germany) equipped with a Xenon lamp and temperature sensor. The device emitted radiation in the wave-length range of 300–800 nm to simulate natural sunlight.

During the experiments the irradiation intensity was maintained at 250 W/m^2, 500 W/m^2 and 750 W/m^2, respectively and the reaction temperature was kept at (25 ± 2) °C.

50 μL of stock solution was added into 5 g of commercialized honey in culture dish to make spiked honey sample. After evaporation of the solvent, the culture dish was covered with culture dish and then putted into the stimulator for photodegradation experiment. Photodegradation experiments were run for 5 min, 10 min, 15 min, 30 min and 60 min under each irradiation intensity.

After the experiments, spiked honey samples were used for extraction of OPs. All experiments were carried out in triplicates.

2.3. Extraction of OPs

Honey sample in culture dish was dissolved into 25 mL flask using Milli-Q water. 2 mL of honey solution was put into a 10 mL centrifugal tube for extraction of OPs. 2 mL of ethyl acetate was added into the tube and the tube was stirred for 2 min and then centrifuged at 2000 × g for 5 min. Upper organic phase was transferred into another 10 mL tube and the residues were extracted twice using the same method mentioned above. All organic phase was collected and dried using Na_2SO_4. Solvent was evaporated using rotary evaporator and residues were dissolved using 1 mL of ethyl acetate for GC analysis.

2.4. Determination of OPs

Determination of pesticides was performed with gas chromatograph (GC) HP-6890 fitted with tritium-electron capture detector (^{3}H-ECD). Megborecolumn HP-608 proprietary polysiloxane (30 m × 0.53 mm id × 0.5 μm film thickness) was used.

Gas chromatographic conditions applied were: splitless injection and the injector temperature was 220 °C. The carrier gas used was helium at a flow rate of 2.5 mL/min. Nitrogen was used as the makeup gas for ECD detector at a flow rate of 4 mL/min and the detector temperature was 280 °C. For coumaphos, the initial oven temperature was 60 °C (hold for 1 min), ramps: 30 °C/min to 200 °C (hold for 1 min), 5 °C/min to 250 °C, final temperature 250 °C (hold for 14 min). Under this condition, the retention time of coumaphos was 21.28 min. For methyl parathion and fenitrothion, the initial oven temperature was 60 °C (hold for 2 min), ramps: 10 °C/min to 140 °C, 5 °C/min to 180 °C, 10 °C/min to 250 °C, final temperature 250 °C (hold for 5 min). Under this condition, the retention time of methyl parathion and fenitrothion were 21.18 min and 21.85 min, respectively.

2.5. Data analysis

All data shown in the present study were given in mean value of three replicates. Data were collated and analyzed using Microsoft Excel. Graphs were prepared using Origin 8.5 (OriginLab, MA, USA). Linear fitting was conducted using Origin 8.5 and results were collated in Excel.

Residual percentage (D) was calculated using the following formula:

$$D = \frac{C_t}{C_0} \times 100 \quad (1)$$

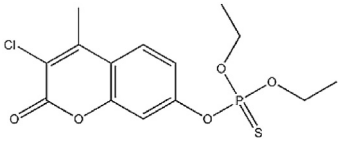
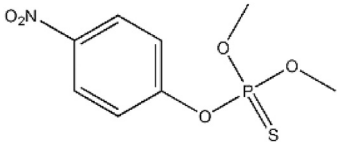
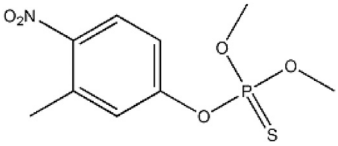
where C_0 and C_t are the initial and residual OPs concentrations, respectively.

3. Results and discussion

3.1. Recovery efficiency of extraction

In order to ensure the progress of the experiment and determine the appropriate concentration for reaction, recovery efficiency of extraction was detected before sunlight irradiation experiments. Spiked honey sample with three different concentrations of OPs was

Table 1
Physical and chemical properties of coumaphos, methyl parathion and fenitrothion.

Property	Coumaphos	Methyl parathion	Fenitrothion
Chemical abstracts service no.	56-72-4	298-00-0	122-14-5
Molecular formula	$C_{14}H_{16}ClO_5PS$	$C_8H_{10}NO_5PS$	$C_9H_{12}NO_5PS$
Chemical structure			
Molecular weight (g/mol)	362.77	263.21	277.23
Density (g/ml at 20 °C)	1.47	1.36	1.32
Water solubility (mg/L at 20 °C)	1.5	50.0	38.0

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