

Photodegradation of several triazidic and organophosphorus pesticides in water by pulsed light technology



Ana Beatriz Baranda^{a,*}, Olatz Fundazuri^b, Iñigo Martínez de Marañón^a

^a Food Research Division, AZTI-Tecnalia, Parque Tecnológico de Bizkaia, Astondo Bidea, Edificio 609, 48160 Derio, Bizkaia, Spain

^b BIOFUNGITEK S.L., Parque Tecnológico de Bizkaia, Ibaizabal bidea, Edificio 800-2°, 48170 Derio, Bizkaia, Spain

ARTICLE INFO

Article history:

Received 18 November 2013
Received in revised form 27 February 2014
Accepted 29 March 2014
Available online 8 April 2014

Keywords:

Pesticide
Decontamination
Water
UV
Pulsed light
Photoproducts

ABSTRACT

Pulsed light technology consists of a successive repetition of short duration (325 μ s) and high power flashes emitted by xenon lamps. These flashlamps radiate a broadband emission light (approximately 200–1000 nm) with a considerable amount of light in the short-wave UV spectrum. In the present work, this technology was tested as a new tool for the degradation of several herbicides in water: simazine, atrazine, phosmet, azinphos-methyl, methyl-parathion, pirimiphos-methyl and chlorpyrifos-ethyl. To evaluate the presence and evolution with time of these herbicides, as well as the formation of derivatives, liquid chromatography–mass spectrometry (atmospheric pressure chemical ionization) ion trap operating in positive mode was used. The degradation process followed first-order kinetics for all studied compounds except for parathion. Fluences about 4.65 J/cm² induced 50% reduction of simazine, atrazine, phosmet, azinphos-ethyl and pirimiphos-ethyl, independently of these compounds were PL treated separately or mixed in an aqueous solution. A higher fluence (9.81 J/cm²) was needed to induce 50% reduction for chlorpyrifos-ethyl, being more difficult to degrade it in presence of other pesticides in the same solution. While simazine and atrazine were degraded, no chlorinated photoproducts were formed. Partial dechlorination was also observed for chlorpyrifos-ethyl. For the rest of organophosphorus pesticides different kinds of reactions could be suggested such as oxidative desulfuration, oxidation of ethyl groups or N-dealkylations. The molecular structures for some of derivatives could be proposed. The different formation profiles of photoproducts suggested that the degradation pathway may include several successive and competitive steps, with subsequent degradation processes taking part from the already formed degradation products. According to the degradation efficiency, the short treatment time and the type of derivatives, this new technology could be considered as an alternative for water treatment.

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1. Introduction

The increasing interest in the fate of the persistence of pesticides in the natural media and possible toxic effects on human health and

environment has led to the development of different remediation methods.

Artificial degradation and purification treatments of polluted waters include ozonation [1], oxidation [2], carbon adsorption [3], ultrafiltration, nanofiltration [4] or homogeneous photodecomposition [5]. The destruction or inactivation of contaminants without producing toxic or carcinogenic residues in the final product is expected for those processes. However, not always this goal is reached.

Direct photodecomposition processes can be used whenever organic molecules absorb enough UV light, to be decomposed [6]. In general, direct processes such as continuous light or UV rays emission by artificial sources (e.g. xenon arc lamps, mercury lamps, etc.) require high-energy photons. Photodegradation by those processes usually exhibits very slow rates and does not totally degrade pesticides [7]. The degradation efficiency can be improved using indirect

Abbreviations: LC-DAD-MS, liquid chromatography diode array mass spectrometry; MSD, mass selective detector; APCI, atmospheric pressure chemical ionization; SIM, single ion monitoring; BPC, base peak chromatogram; P, product; PL, pulsed light; PVDF, polyvinylidene fluoride; H, total fluence; C₀, initial concentration; C_t, concentration at a given fluence; k, degradation rate constant; H_{1/2}, half fluence; UV, ultraviolet; t₀, before wash treatment of fruits or vegetables; t_f, after wash treatment of fruits or vegetables.

* Corresponding author. Tel.: +34 94 657 4000; fax: +34 94 657 2555.

E-mail addresses: abaranda@azti.es (A.B. Baranda), ofundazuri@biofungitek.com (O. Fundazuri), imaranon@azti.es (I. Martínez de Marañón).

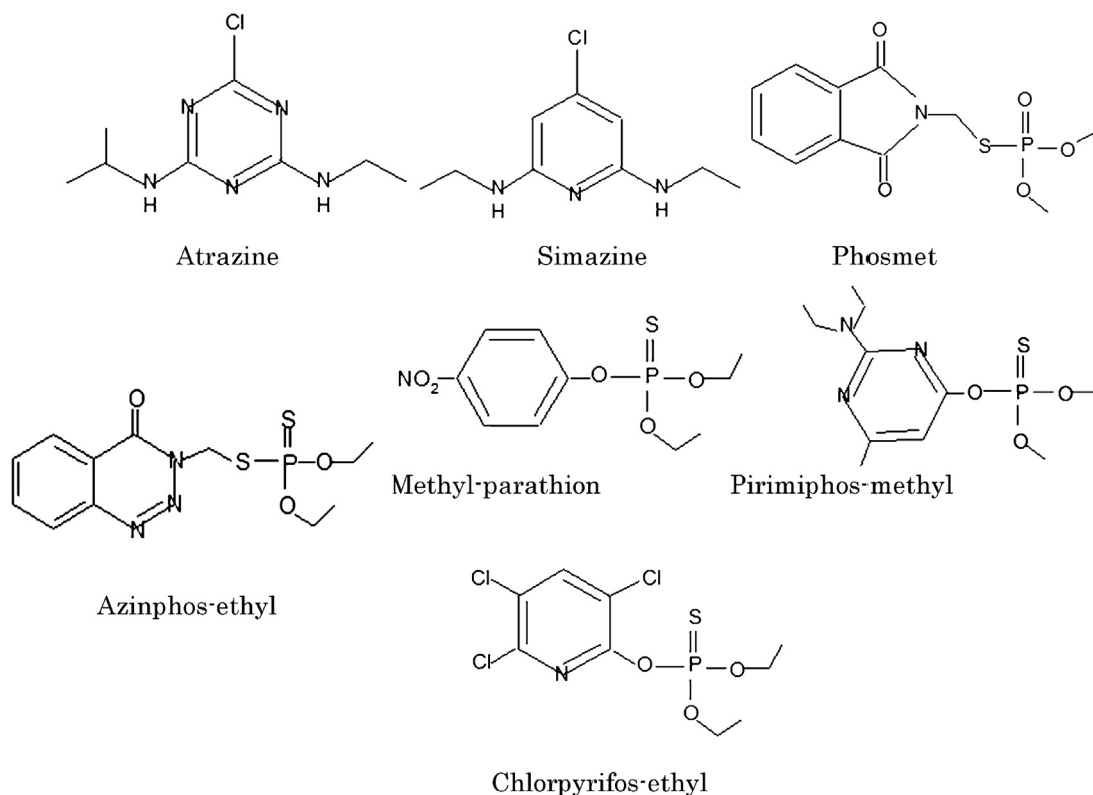


Fig. 1. Structures of the triazine and organophosphorus pesticides studied.

photochemical processes (i.e. UV radiation in presence of oxidants (H_2O_2)), catalytic particles such as Fe^{3+} or $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, ZnO , TiO_2 , CdS [8], or treatments emitting higher light intensity (e.g. pulsed light technology).

Pulsed light (PL) technology consists of discharges of high power electrical pulses in a rare gas (e.g. xenon or krypton) flashlamp to produce the intense light pulses. Even though the peak power of each pulse is high, the total pulse energy, compared to that obtained by continuous radiation, is relatively low because of its short duration [9]. The duration of each pulse generally ranges between 50 and 3000 μs . Contrary to the low or high pressure mercury lamps, where light is mainly emitted at wavelengths close to 254 nm and 365 nm respectively, the PL technology provides a broadband emission light (approximately 200–1000 nm) with a considerable amount of light in the short-wave UV spectrum. About 20% of the emitted light corresponds to the UV-C, 8% to the UV-B and 12% to the UV-A [10]. Furthermore, the UV irradiance of flashlamps is about three or four orders of magnitude higher than standard mercury lamps [11]. Apart from this, the PL technology overcomes the disadvantages of the presence of mercury in traditional UV processes which is of environmental concern.

PL technology has been used for the elimination of microbiological hazards in foods and food-related items [12] and its main use in water has been the inactivation of pathogens [13]. However, chemical pollutants that absorb UV light could also be considered due to the characteristics of the technology (broadband emission light with high UV content).

A recent work shows how atrazine may be photodegraded by PL technology [14]. According to the degradation efficacy, the short treatment time and the lack of chloroderivatives in this study, the authors proposed this new technology could be considered as an alternative for water treatment.

With the aim to assess this technology for water treatment and enlarge its range of application the PL technology was tested

to degrade several pesticides. Therefore, seven pesticides were selected: two triazidic compounds (atrazine and simazine) usually used as herbicides, and five organophosphorous compounds (phosmet, azinphos-ethyl, methyl-parathion, pirimiphos-methyl and chlorpyrifos-ethyl) applied as insecticides. These compounds are widely used and frequently detected in shallow ground water [15] causing environmental concern because of their low biodegradability and moderately or high toxicity.

The new proposed decontamination technology will be evaluated from its degradation effectiveness as well as from the generation of photoproducts.

2. Materials and methods

2.1. Chemicals

The triazine compounds atrazine, simazine and simazine deuterated, simazine- d_5 , as internal standard (IS) were purchased from Dr. Ehrenstorfer (GmbH, Augsburg, Germany). The organophosphate pesticides phosmet, azinphos-ethyl, methyl parathion and pirimiphos-methyl were supplied by Riedel de Haën (Seelze, Germany) and chlorpyrifos-ethyl was purchased by Chem Service (West Chester, PA, USA). All the standards (Fig. 1) had a purity of at least 99%.

Acetonitrile HPLC-grade from Merck (LiChrosolv, Darmstadt, Germany) was of analytical-reagent grade. The high purity water was taken from a Milli-Q plus water system from Millipore (Bardford, MA, USA).

Standard stock solutions of each pesticide and IS were prepared in acetonitrile (Panreac, Barcelona, Spain). Working solutions used in further analysis were prepared by diluting different amounts of the standard stock solutions with water. Both standard stock and working solutions were protected from light by means of dark coloured vials and stored in darkness at 4 °C.

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