

Photodegradation of the Triazole Fungicide Hexaconazole

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The increasing importance of environmental aspects in agriculture involve the production of chemicals that will assure the best crop productions. These products must be highly effective but not toxic to humans, easily decomposed and at low environmental impact. In environmental field partial degradation with parallel and subsequent microbiological degradation happens and might produce undesirable toxic substances (Mansour 1993; Mansour et al. 1993).

Photochemical methods for removing and estimating kinetic degradation of chemicals in solution are applied. In particular, UV light or sunlight was used in direct photodegradation of pesticides molecules and the effect on contamination is highly dependent on specific organic compounds or functional groups. The levels of pesticide residues in fruit and vegetables grown in greenhouses may be the consequence of reduced interaction between light and pesticide molecule (Santoro et al. 1999).

Hexaconazole [(*RS*)-2-(2,4-dichlorophenyl)- 1-(1*H*-1,2,4-triazol-1-yl)hexan-2-ol] which represents one example of modern and effective fungicide (Figure 1), was chosen among the active ingredients used in the treatment of sicilian vines to study photodegradation mechanisms, in consequence of high levels of residues found by researchers (Santoro et al. 1998). This active ingredient at broad spectrum of action against ascomycetes and basidiomycetes (Worthington 1991) is highly efficacious to control staining, and interferes with fungal sterol synthesis fundamentals for controlling plant fungal pathogens.

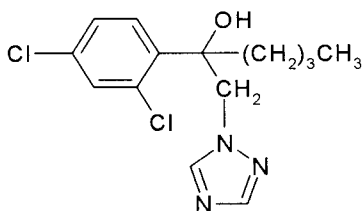


Figure 1. Structure of hexaconazole

The aim of this work was to know the contribution of photodegradation process to the environmental fate of the active ingredient. To obtain results close to field conditions, solvents with different polarity were used to examine the effect of the medium's polarity on photodegradation (Schwack et al. 1995) of the active ingredient. Moreover, the influence of active ingredient concentration on his photodegradation was investigated. The active ingredient was studied in solution as pure compound or in the form of commercial mixture or in the presence or absence of sensitizers (acetone and humic acids).

MATERIALS AND METHODS

Hexaconazole was purchased from Lab Service Analytica (purity >99%). The commercial product used was Anvil (ICI Agrochemicals, 2.9% active ingredient). The pesticide solution to be irradiated was prepared in distilled deionized water, n-hexane and acetonitrile. Solvents used for photolysis and chromatographic measurements were of HPLC grade (Merck, Germany).

The photoreactor was equipped with a high pressure mercury vapour lamp (Philips HPK 125 W), placed in a Pyrex jacket, into a vessel where the irradiated solution was continually shaken and maintained at 25°C by water cooling. At the pre-established times 10 ml of solution were taken for each sampling, filtered (0.2 µm, cellulose acetate), extracted with 10 ml of n-hexane, taken to dryness in a rotavapor (T≤40 °C) and then in a nitrogen current and recovered with 1 ml of n-hexane. The re-extraction with n-hexane for all samples allowed to compare the results obtained. For all experiments, tests in identical working conditions and on the same solutions, were performed in the dark.

For the tests we followed a methodology which is widely used by researchers concerned with photodegradation *in vitro* (Mansour 1996; Sanlaville et al. 1996)). Tests with different solvents and with active ingredient and commercial product were performed respectively at 5 and 10 mg/kg concentration. Solutions with the addition of acetone or humic acids were prepared at 1% and 1/1 (ratio pesticide/humic acid, w/w) concentration respectively (pesticide concentration 5 mg/k).

Analyses were done using a HPLC HP-1090 equipped with a UV-VIS diode array detector, at 230 nm, 20 µL sample injection loop, RP-7104-00 Baker Bond™ Octadecyl 5 µm column, flow rate 1 ml/min. Mobile phase was acetonitrile/water (4/1, v/v). Calibration curve of pesticide standard (0.01÷2 mg/kg) was prepared by dilution from a stock solution. Calibration curve was linear over the concentration range. Detection limit of the active ingredient was 0.01 mg/kg.

Kinetic data were elaborated with Microsoft excel 5.

RESULTS AND DISCUSSION

Tests performed in the dark did not show any degradation of the active ingredient. Photodegradation rate of hexaconazole in n-hexane was higher than in water, and further still in acetonitrile (Figure 2). So photodegradation rate increased with the increase of

solvent polarity, Tests were performed at 5 mg/kg concentration of the active ingredient.

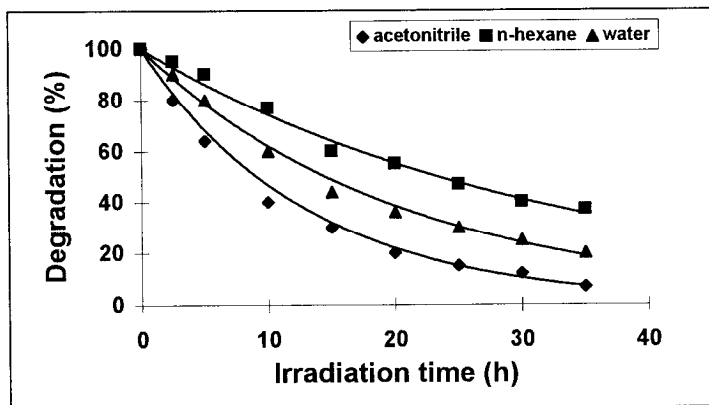


Figure 2. Influence of solvent on photodegradation kinetic

The increase of concentration of the irradiated solution led to a greater degradation rate (Figure 3) according to a first order degradation kinetic. $t_{0.5}$ values were 14.8, 23.1, and 9.12 for experiments in water, n-hexane and acetonitrile respectively. Commercial formula of hexaconazole had a lower degradation velocity than that of the active ingredient, probably due to the protection action of additives (Figure 4). Tests were performed at a concentration of 10 mg/kg (active ingredient).

The addition of irradiated solutions of acetone or humic acids led to an increase in the speed of hexaconazole photodegradation (Figure 5) according to literature data (Choudhry et al. 1979; Choudhry et al. 1985) related to other active ingredients. In this case it is possible to suppose the initiation of radical reactions by UV-light. Tests were performed at 5 mg/kg concentration of the active ingredient

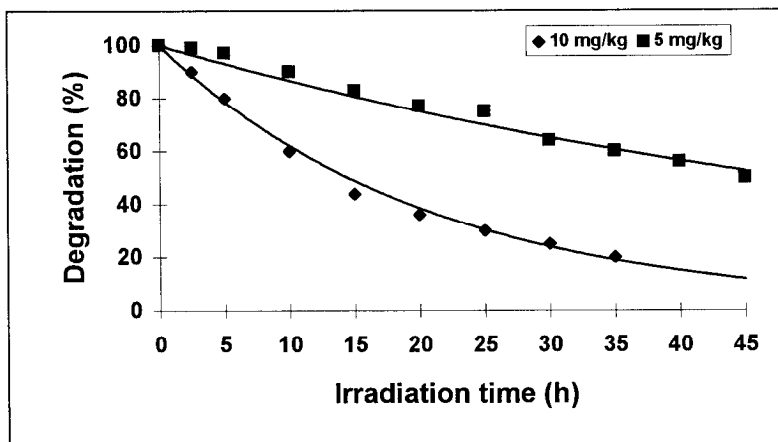


Figure 3. Influence of concentration on photodegradation kinetic

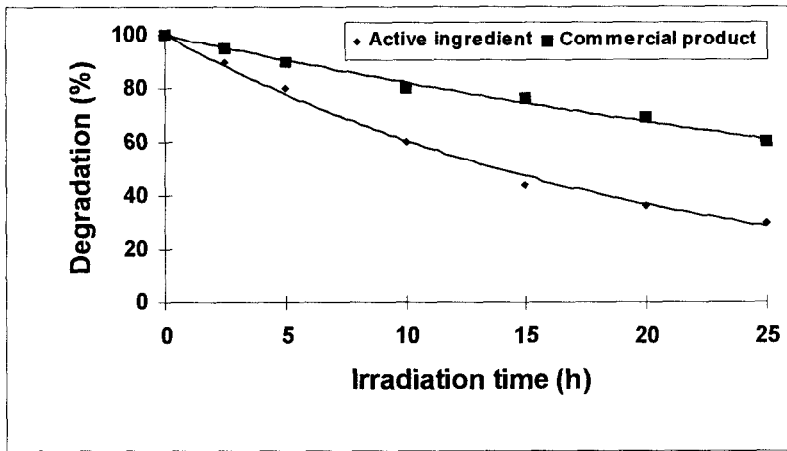


Figure 4. Influence of additives on photodegradation kinetic

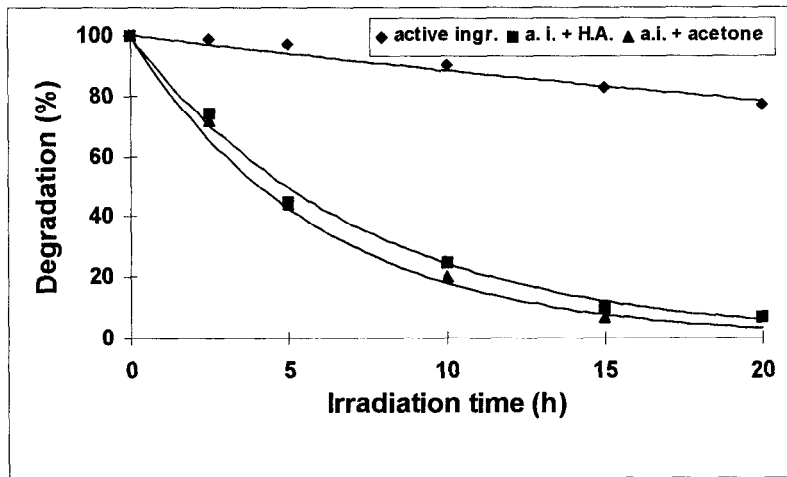


Figure 5. Photodegradation of hexaconazole in water with humic acids and acetone

In table 1 are reported kinetic parameters of hexaconazole in the photodegradation experiments carried out.

Table 1. Kinetic parameters of hexaconazole in photodegradation experiments

	water	n-hexane	acetonitrile	10 mg/kg	5 mg/kg	a.i.*	Comm. prod.	a.i.**	a.i. + H.A.	A. i. + acetone
$t_{0.5}$ (hr)	14.48	23.10	9.12	14.48	49.50	13.86	34.66	57.76	4.92	4.05
k (sec ⁻¹)	0.05	0.03	0.08	0.05	0.01	0.05	0.02	0.01	0.14	0.17
r^2	0.99	0.99	0.99	0.99	0.98	0.99	0.99	0.97	0.99	0.99

*10 mg/kg, ** 5 mg/kg

With reference to $t_{0.5}$ values it is possible to observe the faster degradation in correspondence of the solutions irradiated in presence of acetone or humic acids, that emphasises the importance of the interaction between pesticides and other organic molecules. Commercial product additives show an opposite action with a

$t_{0.5}$ value 2.5 times higher than active ingredient. An important role is acted by the concentration of irradiated solutions and the polarity of the solvent used for the experiments. So this parameter increase passing from solutions more concentrated to solutions more diluted and still using solvents more polar instead of solvents less polar.

From the results of the photodegradation tests it is possible to highlight the following:

- the important role of UV-light in degradation of the active ingredient applied in field crop; on the contrary in greenhouses the degradation is very low probably for the reduced interaction between the pesticide molecule and UV-light;
- the activator function performed by acetone and the humic acids with regard to the photodegradation process of hexaconazole;
- the increase in degradation rate of the active ingredient in relation to tests with higher concentration;
- variable photodegradation kinetics of the active ingredient in the different organic solvents used, in the sense that hexaconazole degraded faster in the more polar solvents;
- an influence of the commercial formula on the degradation rate because the pure active ingredient degraded more rapidly than the commercial product.

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