



Chloridazon Photodegradation Monitoring in Aqueous Solution

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Abstract The aim of this work is to study the photodegradation of the pesticide chloridazon. The kinetic study under excitation at 254 nm shows that this degradation follows a pseudo-first kinetic order with a correlation coefficient $R = 0.99864$ and a rate constant of $7.9 \times 10^{-3} \text{ min}^{-1}$. Oxygen has an inhibitory effect on chloridazon photodegradation, but our results don't show pH or presence of inorganic ions effects. The quantum yield of chloridazon degradation is about 9.1×10^{-5} and depends on the initial concentration of chloridazon. This aspect reflects a multimolecular reactivity of chloridazon. Most of the photoproducts are result of condensation process.

Keywords pesticide, photodegradation, chloridazon, quantum yield, photoproducts

Introduction

Pesticides are chemicals used to preserve crops. First, they appeared beneficial to agriculture but their side effects like human toxicity, biodiversity damage, environmental pollution and resistance of the targets were quickly found (surface or groundwater, soil, air) [1-5]. Photochemical transformation is one of the main pathways of pesticide degradation. It has benefit of increasing interest over the last thirty years. Photodegradation process study provide a better knowledge of pesticides transformations in the environment, their degradation rate and their metabolites [6-10].

Our study focus on photodegradation of Chloridazon (5-amino-4-chloro-2-phenylpyridazin-3(2*H*)-one), which belongs to the pyridazinone pesticide class. Chloridazon is a selective systemic herbicide which inhibits photosynthesis and is used for pre-plant, preemergence, and early post-emergence use, for the control of annual broad-leaved weeds, on sugar beets and red table beets [11,12].

In 1995, Capri studies established high persistence and low mobility of chloridazon in clay loam soil in northern Italy [13]. Russo et al. (1993) found no traces of this herbicide in ground water samples collected in the same area [14]. In 2003, Carabias-Martinez et al. found no trace of the herbicide either in surface waters or in groundwater samples from northern Spain and concluded that chloridazon is non persistent in aqueous environment [15]. However, other studies show high mobility in several soil types and easy leaching to surface or groundwater [16-18]. The half-life of chloridazon in soil varies considerably from 8 to 104 days depending on soil type, moisture content and temperature [19-21].

Few studies on the degradation of chloridazon in the UV-visible and sunlight have been reported in the literature [22, 23].



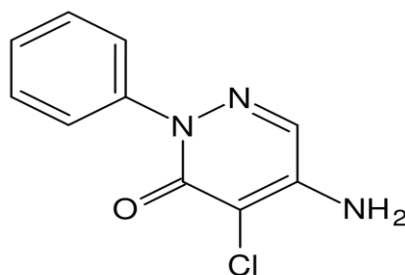


Figure 1: Chloridazon formula

Our main goal is to study the photodegradation kinetics and mechanism of this herbicide. In the present work we study the impact of different physico-chemical parameters on the kinetic aspect of chloridazon's photodegradation and identify the photoproducts.

Materials and Methods

1. Reagents and solutions

Chloridazon 99.5%, was obtained from SIGMA-ALDRICH and was used as received. Methanol and acetonitrile for HPLC (High Performance Liquid Chromatography) analysis, were purchased from SIGMA-ALDRICH.

All the solutions were prepared with deionized ultrapure water purified by a Milli-Q device (Millipore) and its purity was controlled by its resistivity ($\geq 18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$). pH measurements were carried out with a JENWAY 3310 pH-meter ± 0.01 pH unit.

The deoxygenation of the solutions was accomplished by bubbling argon or nitrogen for 30 minutes at room temperature. The suroxygenation was accomplished by bubbling pure oxygen. For prolonged irradiations, the bubbling was maintained during the irradiation.

2. Irradiations system

For the determination of the quantum yields, monochromatic irradiation was carried out using light from a xenon lamp (1000 W) filtered with a grating monochromator set at 300 nm. The beam was parallel and the reactor was a quartz cell of 1 cm path length. The light intensity I_0 was measured by radiometry.

Irradiations at 254 nm and 310 nm were carried out in an elliptical stainless steel cylinder equipped with six high-pressure mercury lamps (black lamp, Mazda MAW 125 W). The reactor is a water-jacketed Pyrex tube containing a maximum of 50 mL of the sample. SUNTEST is an irradiation system that simulates solar radiation. The device is equipped with a xenon lamp and a filter that permits the transmission wavelength above 290 nm. The power was fixed to provide about $550 \text{ W}\cdot\text{m}^{-2}$, and sample temperature was controlled by a water flow ($T=20^\circ\text{C}$).

3. Analysis

UV-Visible spectra were recorded with a Cary 3 double beam spectrophotometer. The degradation of Chloridazon and formation of the products were followed using HPLC with:

- A HPLC Hewlet Packard (HP series 1050) equipped with a UV-visible detector and two pumps
- A HPLC (Waters) equipped with a diode-array detector (Waters 990), two pumps (Waters 515), and an autosampler (Waters 717).
- An Alliance 2695 photodiode array detector (DAD) chromatograph (Waters SA, St-Quentin en Yvelines, France).
- A Waters/Micromass LC/QTOF tandem mass spectrometer (Micromass, Manchester, UK), with an orthogonal geometry Z-spray ion source, was used for LC/ESI-MS and LC/ESIMS 2 experiments. Eluate was subjected to electrospray ionization (ESI) in the positive ion mode and resulted in the formation of protonated molecules of the sample components. Scanning was performed in the range between m/z 60 and 600.

Reversed-phase column were used: Nucleodur C8 column ($150\text{mm} \times 4.6 \text{ mm}; 10.5 \mu\text{m}$) Kinetex MS C18 column ($2.6 \mu\text{m}, 100 \text{ mm} \times 2.1 \text{ mm}$; Phenomenex).



The elution was accomplished using an isocratic program with water (0.1% formic acid) and acetonitrile (or méthanol) at 60% and 40%, respectively.

The flow was fixed at $1 \text{ mL}\cdot\text{min}^{-1}$ and $0.2 \text{ mL}\cdot\text{min}^{-1}$. Twenty microliters ($20 \mu\text{L}$) of samples were injected at least three times for each irradiation time.

Results and Discussion

Chloridazon (CDZ) presents at $\text{pH}=5.5$ in aqueous solution an absorption spectrum (Figure 2) with two maximums at 282 nm and 225 nm. The absorption molar coefficients were estimated to 7540 and $23960 \text{ mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ respectively.

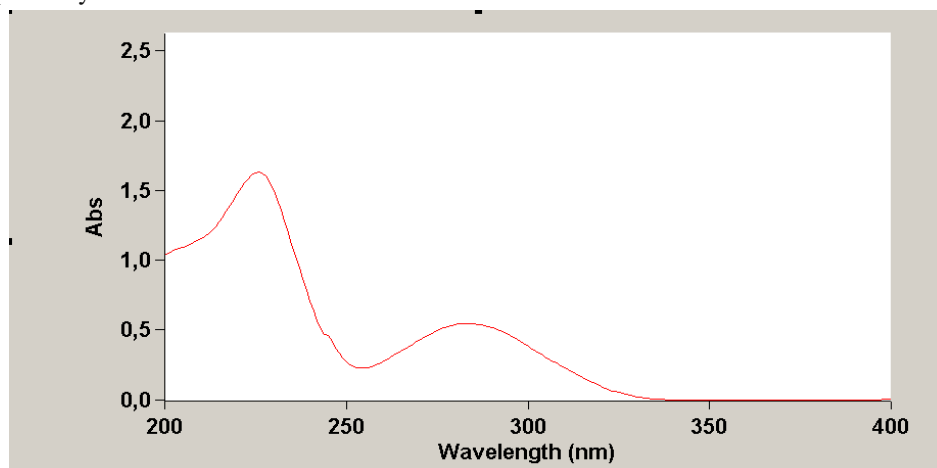


Figure 2: Absorption spectrum of Chloridazon ($5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at $\text{pH} = 5.5$

No significant change in absorption spectrum and absorption molar coefficients is observed in the pH range: 2-9. In alkaline solution, we notice a significant degradation of CDZ, probably due to hydrolysis. In our studies, all solutions are stored at $\text{pH} = 5.5$ and protected from light. Under these conditions, chloridazon is perfectly stable. In order to explore excitation in short wavelength band effect, irradiations were performed in aqueous solutions at 254 nm. The long wavelength band is explored in polychromatic light ($\lambda > 300 \text{ nm}$) and a suntest is used to reproduce environmental conditions.

1. Determination of kinetic parameters

The evolution of irradiated chloridazon chromatogram is presented in Figure 3. The decrease of Chloridazon at the retention time of 9.5 minutes and appearance of several degradation products was observed.

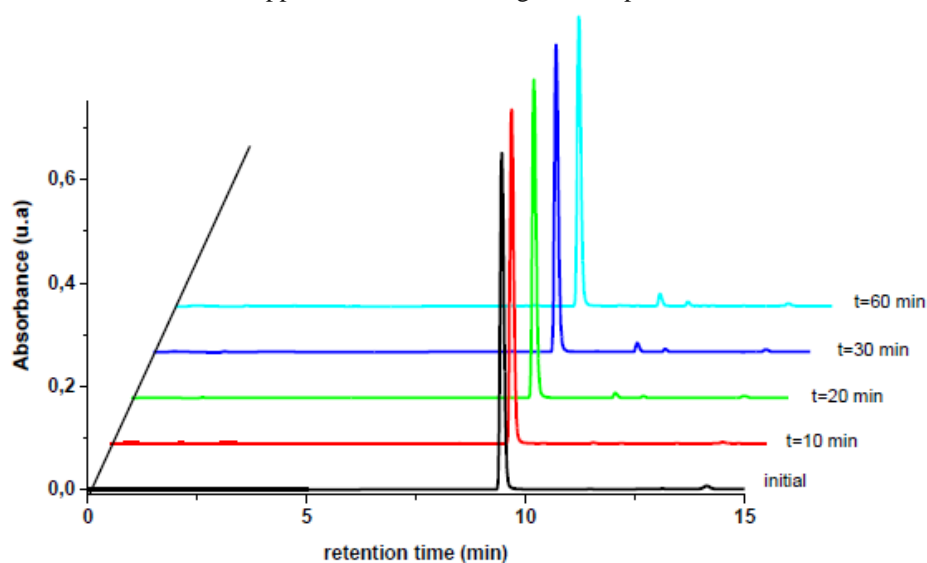


Figure 3: Evolution of the Chloridazon chromatogram ($5.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at $\text{pH} = 5.5$



The figure 4 shows that excitation at 254 nm of chloridazon in aerated solution ($C = 5 \times 10^{-5} \text{ mol.L}^{-1}$ and $\text{pH} = 5.5$) leads to an efficient degradation. A conversion of 80% is reached after 80 minutes of irradiation. The adjustment of the experimental points gives the kinetic parameters corresponding to the degradation of Chloridazon ($5.0 \times 10^{-5} \text{ mol.L}^{-1}$) in this solution. We can conclude that the disappearance of chloridazon under excitation at 254 nm follows pseudo-first order kinetic with a correlation coefficient $R = 0.99864$ and a rate constant of $7.9 \times 10^{-3} \text{ min}^{-1}$.

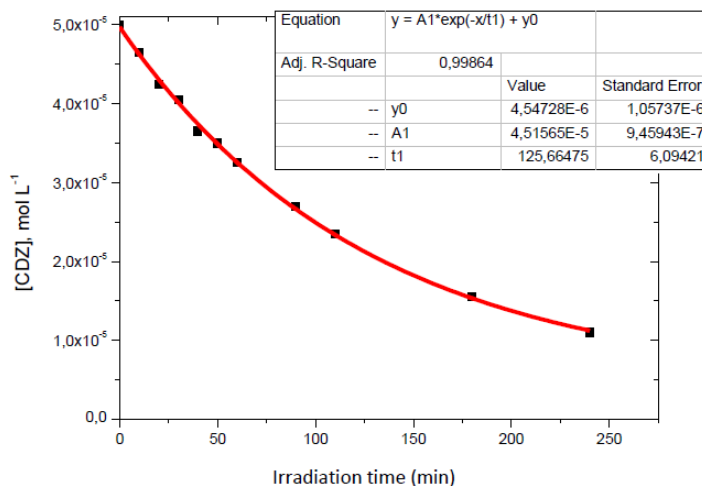


Figure 4: Evolution of Chloridazon concentration ($5.0 \times 10^{-5} \text{ mol.L}^{-1}$) at $\text{pH} = 5.5$.

2. Influence of oxygen concentration

The molecular oxygen most often plays an important role in the photochemical degradation of organic pollutants. We studied this during our work, the effect of oxygen presence by analyzing the results under three different conditions: aerated solution, deoxygenated solution and suroxygenated solution. Under these experimental conditions, the concentrations of dioxygen are respectively: $2.6 \times 10^{-4} \text{ mol.L}^{-1}$; $< 10^{-5} \text{ mol.L}^{-1}$ and $1.3 \times 10^{-3} \text{ mol.L}^{-1}$. As shown in Figure 5 disappearance of chloridazon increases when the oxygen concentration decreases. A factor of about 8 is observed when the experiments were undertaken in deoxygenated and aerated solutions. In each case, the degradation follows a pseudo first order kinetics. Chloridazon degradation is inhibited by oxygen. We can suppose that by adding more O_2 to the solution, more reactive species are being formed that instead of promoting degradation, act as "trap" of the reactive species that are responsible for the degradation in aerated solution.

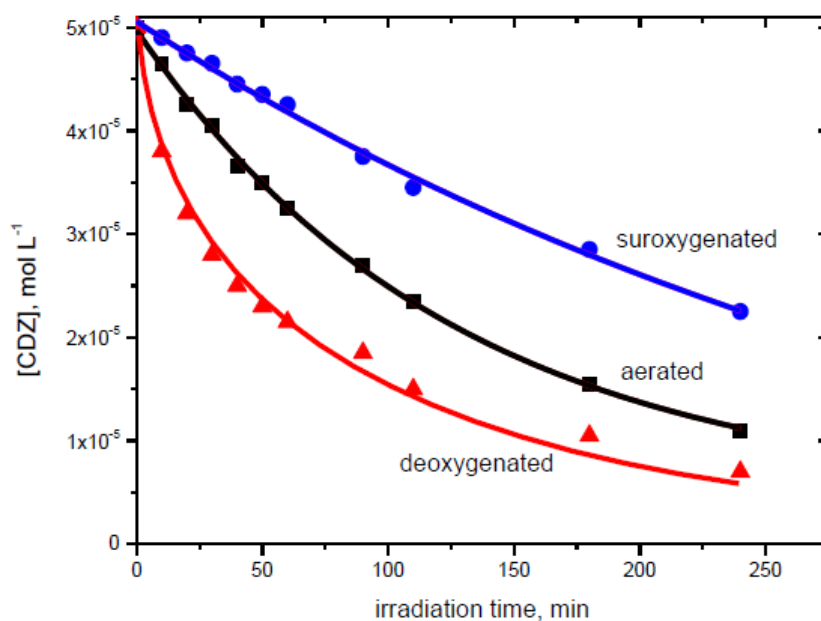


Figure 5: Evolution of Chloridazon concentration at different oxygen concentrations



The rate constants, determined by exponential adjustments, are listed in Table 1.

Table 1: Effect of oxygen on the photodegradation rate constants of chloridazon

Conditions	k (min ⁻¹)	oxygen concentrations (mol.L ⁻¹)
sueroxygenated	2,7x10 ⁻³	1,3x10 ⁻³
aerated	7,9x10 ⁻³	2,6x10 ⁻⁴
deoxygenated	2,1x10 ⁻²	<10 ⁻⁵

3. Influence of pH

A series of reactions were performed at different pH values to evaluate the pH effect on chloridazon photodegradation. In our experimental conditions, the solutions are stable from pH 2 to 9 and appear to have the same absorbance at the excitation wavelengths. Table II shows the values of the rate constants for chloridazon solutions (C= 5.0x10⁻⁵ mol.L⁻¹) under irradiation at 254 nm in aerated aqueous solution and at different pH. Apart from the high value obtained for pH = 9.1 (which may be due to hydrolysis of Chloridazon in alkaline solution) the rate constants can be considered as constant. We conclude that the photochemical behavior of Chloridazon is therefore independent of the pH of the solution in the range from pH 2 to 9.

Table 2: Effect of pH on the rate constant of chloridazon photodegradation

pH	2.1	2.9	3.4	4.2	5.0	5.5	6.7	7.9	8.5	9.1
k x10 ³ , min ⁻¹	6.8	7.3	6.9	7.0	7.3	7.9	7.2	7.6	7.5	9.5

4. Influence of inorganic ions

We were interested in the effect of several inorganic ions (chloride ions, sulfate ions, magnesium ions at concentration of about 1.0x10⁻³ mol.L⁻¹) potentially present in natural waters. The ions selected do not absorb in the field of excitation studied in order to be not disturbed by the photochemistry of these ions. No significant effect on the apparent first order rate constants is found after irradiation of an aerated aqueous solution of chloridazon at the concentration of 5.0x10⁻⁵ mol.L⁻¹ at 254 nm in the presence of these ions.

5. Influence of chloridazon initial concentration

This effect was studied within the concentration range 2.0x10⁻⁴ mol.L⁻¹ to 1.0x10⁻⁶ mol.L⁻¹.

The results reported in Table 3, clearly show that the photochemical reaction is more effective when the chloridazon concentration is high. This reflects the involvement of multimolecular processes in the photochemistry of chloridazon.

Table 3: Variation of the degradation rate of chloridazon as a function of the initial concentration

Concentration mol.L ⁻¹	Absorbance at 254 nm	Initial speed mol L ⁻¹ min ⁻¹
2,0x10 ⁻⁴	1,0	2,7x10 ⁻⁸
1,0x10 ⁻⁴	0,5	2,8x10 ⁻⁸
1,0x10 ⁻⁵	0,05	2,4x10 ⁻⁹
1,0x10 ⁻⁶	0,005	2,6x10 ⁻¹⁰

6. Phototransformation quantum yield of chloridazon

We evaluated the quantum yield of chloridazon degradation at about 9.1x10⁻⁵, relatively low value but not negligible. The influence of various experimental parameters (oxygen concentration, presence of inorganic ions, pH) on the quantum yield was studied (table 4).

The results confirm the inhibitory role of oxygen. In the deoxygenated solution, the quantum yield is evaluated at approximately 7.2 × 10⁻⁴, approximately 13 times higher than in the sueroxygenated solution (5.6× 10⁻⁵). We did not find any effect of pH or presence of the inorganic ions on the quantum yield in accordance with the results above.

Table 4: Effect of Oxygen concentration, pH and presence of the inorganic ions on the quantum yield of chloridazon photodegradation (C=5.0x10⁻⁵ mol.L⁻¹)

λ _{excitation} , nm	[O ₂], mol L ⁻¹	Initial pH	Inorganicions, mol L ⁻¹	Φ * 10 ⁵
254	1,3x10 ⁻³ (Sueroxygenated)	5,4	≈ 0	5,6
254	2,6x10 ⁻⁴ (Aerated)	5,5	≈ 0	9,1
254	< 10 ⁻⁵ (Desoxygenated)	5,3	≈ 0	72
254	2,6x10 ⁻⁴	3	≈ 0	10,1



254	$2,6 \times 10^{-4}$	6,5	≈ 0	9,5
254	$2,6 \times 10^{-4}$	8,2	≈ 0	11,3
254	$2,6 \times 10^{-4}$	3	$[\text{Cl}^-] = 1,0 \times 10^{-3}$	11,1
254	$2,6 \times 10^{-4}$	3	$[\text{SO}_4^{2-}] = 1,0 \times 10^{-3}$	8,9
254	$2,6 \times 10^{-4}$	3	$[\text{Mg}^{2+}] = 1,0 \times 10^{-3}$	9,0

7. Photoproduct Analysis

The HPLC analyses of an irradiated solution of chloridazon ($C = 5.0 \times 10^{-5}$ mol.L ; pH = 5.5) at 254 nm for 30 minutes gave the chromatogram (figure 6) where the chloridazon has the retention time $t_{\text{ret}} = 9.5$ minutes ($\lambda_{\text{detection}} = 282$ nm).

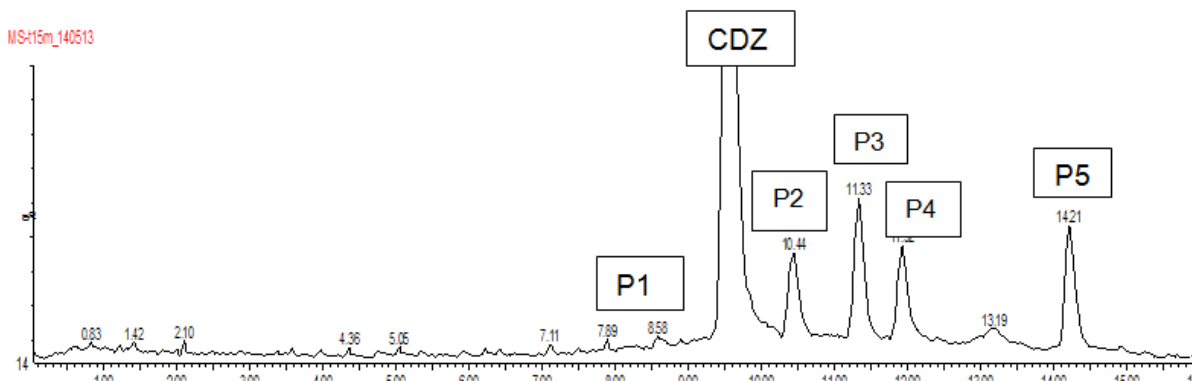


Figure 6: Chromatogram HPLC of an irradiated chloridazon solution for 30min

This chromatogram shows the formation of a product P1 with a lower retention time than chloridazon ($t_{\text{ret}} = 8.5$ minutes) and at least four products (P2, P3, P4, P5) with higher retention times (10.4min; 11.3min; 11.8min; 14.1min). All products appeared from the early stages of the irradiation and accumulate in the solution (Figure 7).

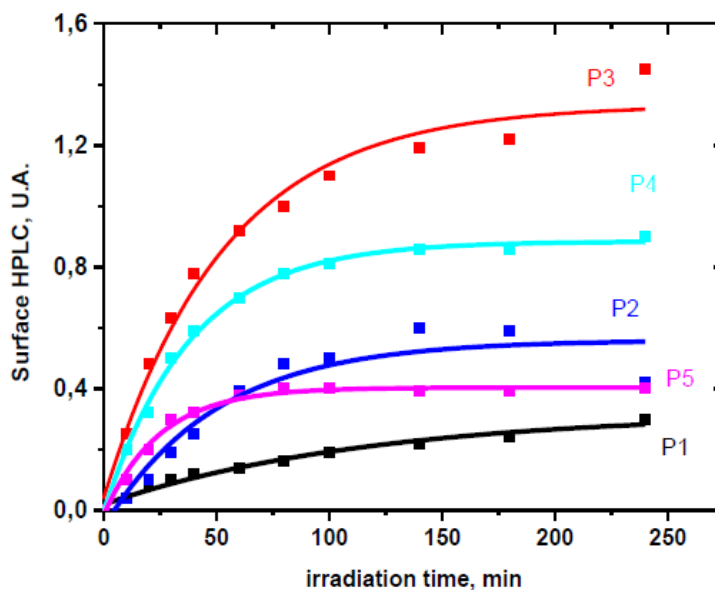


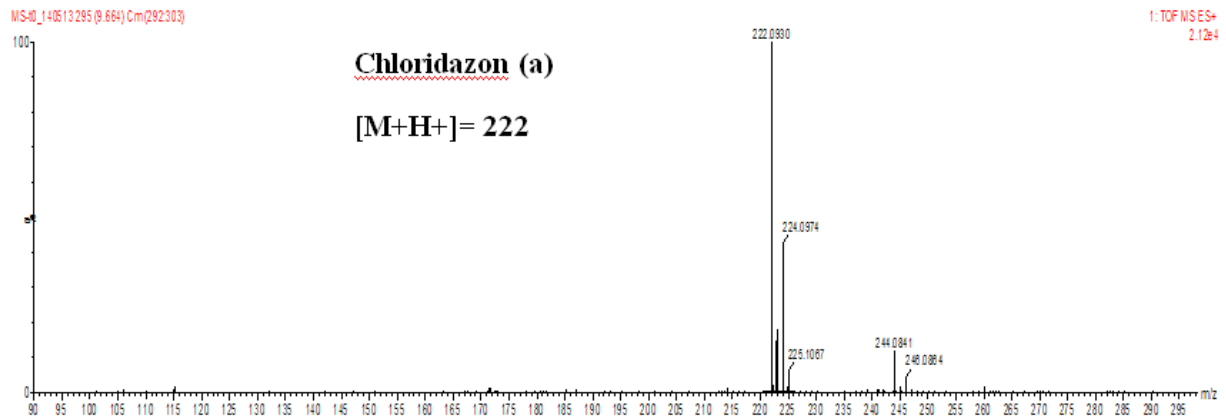
Figure 7: Evolution of the photoproducts P1, P2, P3, P4, P5 as a function of the irradiation time

We studied the influence of the initial concentration of chloridazon on the evolution of the quantity of these photoproducts. The concentration 1.0×10^{-4} mol.L⁻¹ was used as the reference. Irradiation at 254 nm of an aerated aqueous solution (pH = 5.5) of chloridazon at concentrations 1.0×10^{-5} mol.L⁻¹, 1.0×10^{-4} mol.L⁻¹, 2.0×10^{-4} mol.L⁻¹ led to chloridazon effective disappearance but also to formation of various photoproducts previously mentioned. The amount of these photoproducts depends on chloridazon's initial concentration. More the concentration of the initial compound is high, more the quantity of photoproducts is important. This remark is in favor of a reactivity involving multimolecular processes.

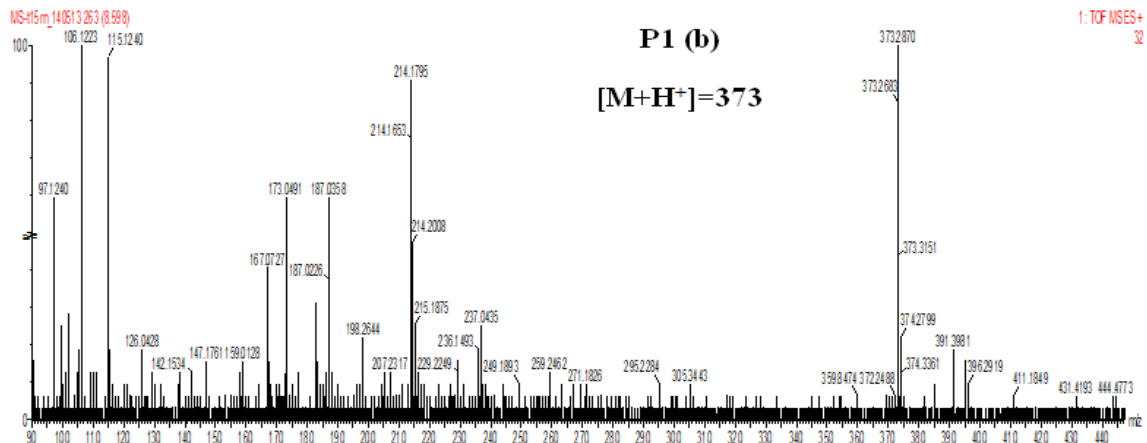


8. Photoproducts identification by LC/MS

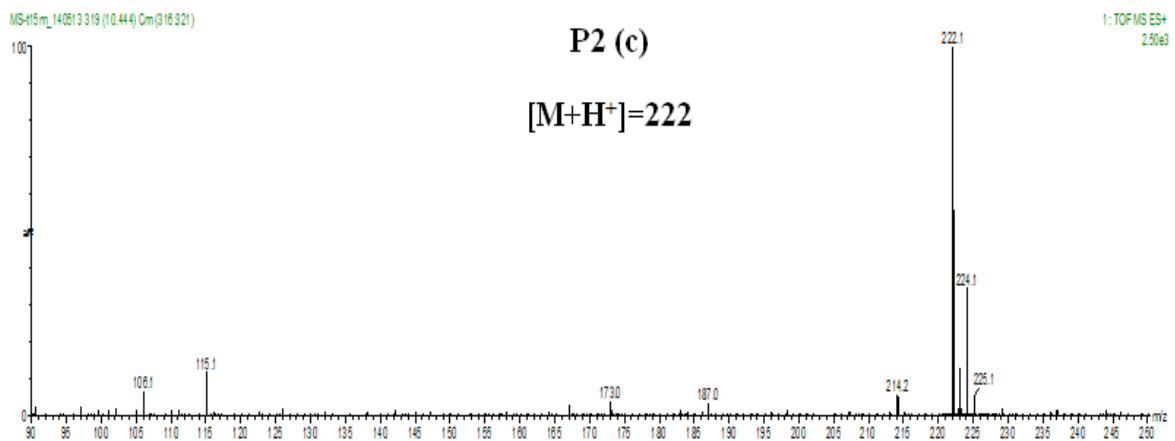
The ESI+ mode mass spectra of chloridazon and photoproducts formed after irradiation at 254 nm of chloridazon ($5.0 \times 10^{-5} \text{ mol L}^{-1}$; pH = 5.5) in aerated solution are given on figure 8.



$$[\text{M}+\text{H}^+]_{35} = 222, [\text{M}+\text{H}^+]_{37} = 224, [\text{M}+\text{Na}^+]_{35} = 244, [\text{M}+\text{Na}^+]_{37} = 246$$

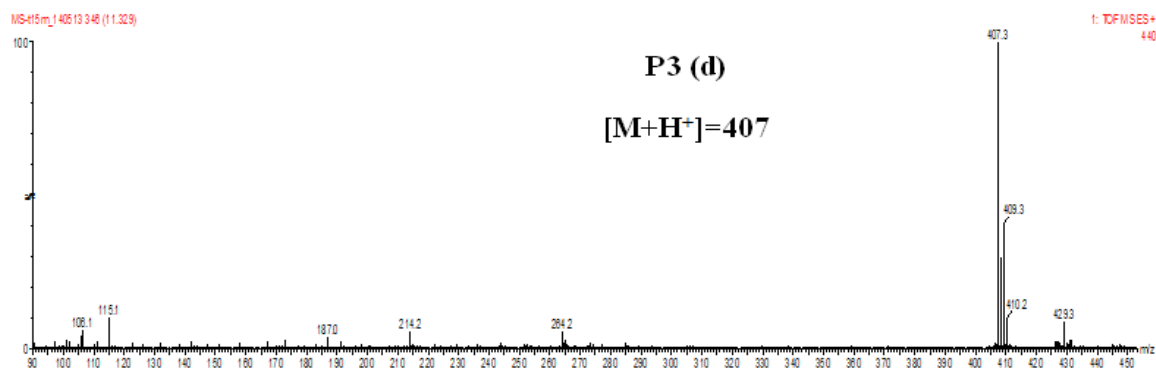


$$\text{P1: } [\text{M}+\text{H}^+] = 373, [\text{M}+\text{Na}^+] = 395$$

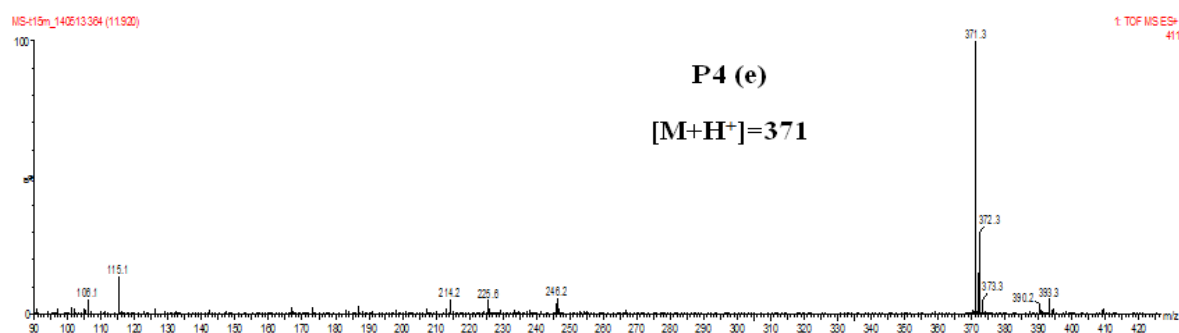


$$\text{P2: } [\text{M}+\text{H}^+]_{35} = 222, [\text{M}+\text{H}^+]_{37} = 224, [\text{M}+\text{Na}^+]_{35} = 244, [\text{M}+\text{Na}^+]_{37} = 246$$

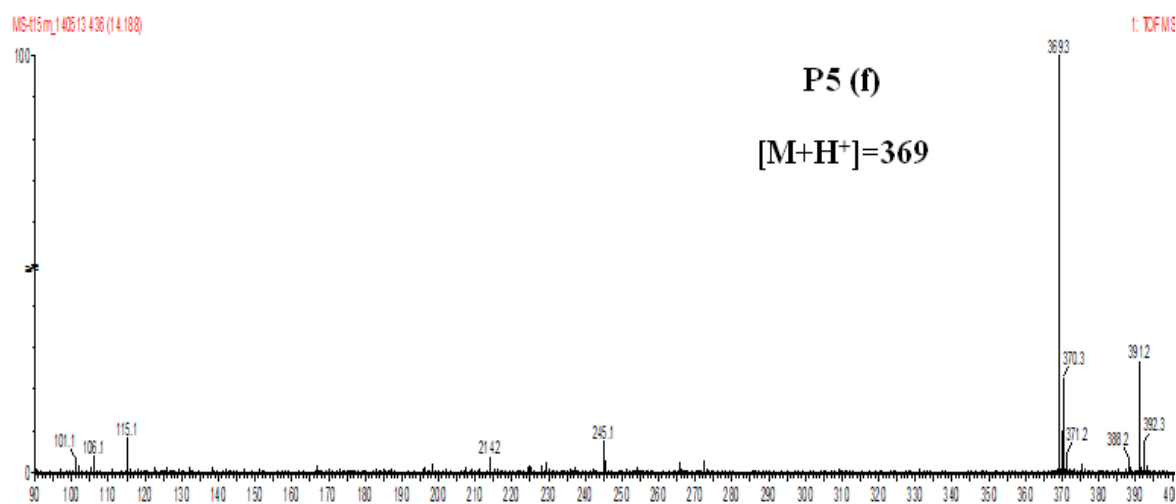




P3: [M+H⁺]₃₅Cl = 407, [M+H⁺]₃₇Cl = 409, [M+Na⁺]₃₅Cl = 429, [M+Na⁺]₃₇Cl = 431



P4: [M+H⁺]= 371, [M+Na⁺]= 393



P5: [M+H⁺]= 369, [M+Na⁺]= 391

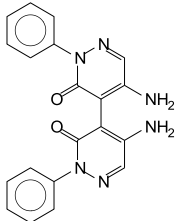
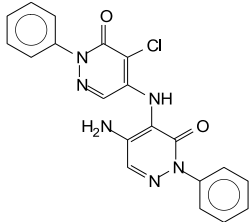
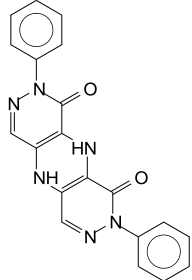
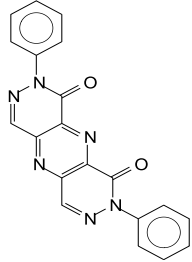
Figure 8: LC/MS mass spectra of chloridazon (a) and the photoproducts P1 (b), P2 (c), P3 (d), P4 (e), P5 (f)



The analysis of these spectra using the exact mass enables us to determine the formula and the structures of the different products (Table 5).

Except for the product P2, all the other products have high masses (approximately double of Chloridazon mass). They are probably condensation products of Chloridazon.

Table 5: Exact masses, calculated masses and proposed chemical structures of the photoproducts

Photoproduct	Retention time, minutes	ExactMass	Calculated Mass	Formula	ProposedChemical Structure
P1	8,6	373,1420	373,1413	C ₂₀ H ₁₆ N ₆ O ₂	
P2	10,4	222,0427	222,0434	C ₁₀ H ₈ N ₃ OCl	
P3	11,3	407,1017	407,1023	C ₂₀ H ₁₄ N ₆ O ₂ Cl	
P4	11,9	371,1247	371,1256	C ₂₀ H ₁₅ N ₆ O ₂	
P5	14,2	369,1090	369,1100	C ₂₀ H ₁₂ N ₆ O ₂	

Conclusion

Photochemical degradation can be one of the main pathways for the elimination of pesticides in the environment. We have studied the photodegradation of chloridazon. The kinetic study of chloridazon degradation under excitation at 254 nm shows that it follows pseudo-first order kinetics. The rate of degradation increases when oxygen concentration decreases, demonstrating the inhibiting role of oxygen. We did not find significant effects of pH or presence of inorganic ions. Irradiation at 254 nm of an aerated aqueous solution of chloridazon at a



concentration of 5.0×10^{-5} mol.L⁻¹ (pH = 5.5) allowed us to evaluate the quantum yield at about 9.1×10^{-5} . The higher the concentration is, the more important the quantum yield is. This aspect reflects a multimolecular reactivity of chloridazon.

Many photoproducts were detected. Except for the product P2 which is an isomer of chloridazon the other products formed, as the analyses by Mass Spectrometry attest it, correspond to condensation processes.

Acknowledgements

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References

- [1]. Loague, K., Llyod, D., Nguyen, A., Davis, S. N. and Abrams, R. H. (1998). "A case study simulation of DBCP groundwater contamination in Fresno County, California I. Leaching through the unsaturated subsurface." *Journal of Contaminant Hydrology* 29: 109–136.
- [2]. Sudo, M., Kunimatsu, T. and Okubo, T. (2002). "Concentration and loading of pesticide residues in Lake Biwa basin (Japan)" *Water Research* 36: 315–329
- [3]. Toé, A. M., Kinané, M. L., Koné, S. and Sanfo-Boyrm, E. (2004). "Le non respect des bonnes pratiques agricoles dans l'utilisation de l'endosulfan comme insecticides en culture cotonnière au Burkina Faso: quelques conséquences pour la santé humaine et l'environnement. ." *Revue Africaine De Santé et de Production Animales* 2(3-4): 275-278.
- [4]. Añasco, N., Uno, S., Koyama, J., Matsuoka, T. and Kuwahara, N. (2010). "Assessment of pesticide residues in freshwater areas affected by rice paddy effluents in Southern Japan" *Environmental Monitoring and Assessment* 160(1-4): 371-383
- [5]. Ouattara, B., Savadogo, O. W., Traore, O., Koulibali, B., Sedogo, M. P. and Traore, A. S. (2010). "Effet des pesticides sur l'activité microbienne d'un sol ferrugineux tropical du Burkina Faso." *Cameroon Journal of Experimental Biology* 6(1).
- [6]. Archer, T. E., Nazer, I. K. and Crosby, D. G. (1972). "Photodecomposition of endosulfan and related products in thin films by ultraviolet light irradiation." *Journal of Agricultural and Food Chemistry* 20(5): 954–956.
- [7]. Leitis, E. and Crosby, D. G. (1974). "Photodecomposition of trifluralin." *Journal of Agricultural and Food Chemistry* 22(5): 842–848.
- [8]. Rosen, J. D. (1972). "Photochemistry of several pesticides." *Environmental Toxicology of Pesticides*: 435-447.
- [9]. Meallier, P. (1999). "Phototransformation of pesticides in aqueous solution." in *Environmental PhotoChemistry, The Handbook of Environmental Chemistry*. P. Boule, Springer. 2: 241-261.
- [10]. Floesser-Mueller, H. and Swack, W. (2001). "Photochemistry of organophosphorus insecticides." *Reviews of Environmental Contamination and Toxicology*. 172: 129-228.
- [11]. EPA, Registration Eligibility Decision (RED) Document for Pyrazon, US Environmental Protection Agency, 2005.
- [12]. Qasem, J.R., 2006. Chemical weed control in seedbed sown onion (*Allium cepa* L.). *Crop Protection* 25, 618–622.
- [13]. Capri, E., Ghebbioni, C. and Trevisan, M. (1995). "Metamitron and chloridazon dissipation in a silty clay loam soil." *Journal of Agricultural and Food Chemistry* 43: 247–253.
- [14]. Russo, E., Fava, A., Achilli, F., Sassi, E., 1993. "Groundwater contamination by pesticides: extensive field studies". In: del Re, A.A.M., Capri, E., Evans, S., Natali, P., Trevisan, M. (Eds.), Proceedings of the IX Symposium in Pesticide Chemistry: Mobility and Degradation of Xenobiotics, 11–13 October 1993, Edizioni G. Biagini, Lucca, Italy, pp. 707–718.
- [15]. Carabias-Martinez, R., Rodriguez-Gonzalo, E., Fernandez-Laespada, M. E., Calvo-Seronero, L. and Roman, F. J. S.-S. (2003). "Evolution over time of the agricultural pollution of waters in an area of Salamanca and Zamora (Spain)." *Water Research* 37: 928–938.



- [16]. Pérez, M. F., Sanchez, M. V., Cespedes, F. F., Garcia, S. P. and Fernandez, I. D. (2010). "Prevention of chloridazon and metribuzin pollution using lignin-based formulations." *Environmental Pollution* 158(5): 1412–1419.
- [17]. Tomlin, C., (2002). *The e-Pesticide Manual*. Version 2.2. British Crop Production Council, Hampshire, UK, 12th edition.
- [18]. Cespedes, F.F., Villafranca Sanchez, M., Perez Garcia, S., Fernandez Perez, M., 2007. "Modifying sorbents in controlled release formulations to prevent herbicides pollution". *Chemosphere*, vol. 69, 785–794.
- [19]. Pestemer, W. and Malkomes, H. P. (1983). " Effect of various pesticides of sugarbeet spray program on biological-activities and chloridazon degradation in soil. I. Field experiments." *Weed Research* 23: 283–291.
- [20]. Rouchaud, J., O. N. and Hermann, O. (1997). "Influence of application rate and manure amendment on chloridazon dissipation in the soil " *Weed Research* 37: 121–127.
- [21]. Tomlin, C., (1994). *The Pesticide Manual*, 10th ed. The British Crop Protection Council and the Royal Society of Chemistry, Surrey, Cambridge. 179–180.
- [22]. Muszkat, L., Feigelson, L., Bir, L. and Muszkat, K. A. (2002). "Photocatalytic degradation of pesticides and bio-molecules in water." *Pest Management Science* 58(11): 1143–1148.
- [23]. Fouad, D. M. and Mohamed, M. B. (2011). "Photodegradation of chloridazon using Coreshell Magnetic Nanocomposites." *Journal of Nanotechnology*. Vol. 2011.

