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Disposal of pesticides into the environment by photo degradation: Case of Atrazine

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ABSTRACT

Atrazine is an active substance which belongs to the chemical family of triazine representing an effects of an herbicide, Atrazine is one of the herbicides used in the world according to the United States environmental protection agency(EPA), while it was banned in the European Union, Atrazine is used in a large number of countries including Morocco, it uses for the elimination of undesirable in many cultures annual or perennial plants. Its physicochemical characteristics influence the risk of transfer of this active substance into the water as a water pollutant, this research has enabled us to record different channels of elimination of Atrazine by photochemical degradation of Atrazine in absence and in the presence of Humic acids in the soil. This study synthesizes some of the work that we have carried out on the behavior of herbicide Atrazine and, with the aim of understanding and predicting the fate of the plant protection product. For the photodegradation of Atrazine in the absence of Humic acids at different pH values, wavelengths and oxygen concentrations, results showed that:

- *The pH affects the photochemical behavior of Atrazine in solution.*
- *The ionic form of the carboxylic acid function photo degradation faster than the molecular form and in the absence of oxygen.*
- *The Concentration of Atrazine has an effect on the kinetics of photochemical degradation, which is explained by a bimolecular process with formation of photoproducts.*
- *A Keto-enol equilibrium was noticed after the calculation of the quantum yields at different wavelengths of radiation. So that in the presence of the Humic acids, It is clear from these results that these Humic acids that were tested have played a dual role: inhibitory and generator of active species. To below 340 nm wavelengths, it certifies a competitive absorption of light radiation between Atrazine and Humic acids which play a role of screen*

Keywords: Atrazine, Elimination, Photodegradation, pesticides, Montmorillonite.

INTRODUCTION

Pesticides are substances that have active ingredients that Act on various physiological functions and more often result in the death of the living organism which could absorb it[1, 2].

These active ingredients are sought to fight the enemies of plants and pests, animal and human, but their ways to use it can present a number of toxicological risks and Ecotoxicological with respect to the composition of our ecosystem as reflected by pollution whose consequences can be detrimental to its quality[3].

The Moroccan market is based on the importation of pesticides for agricultural use there by category insecticides that are at the top and then fungicides, herbicides. Pesticides include several chemical families including Triazine contained in herbicides in majority, and its herbicide in a substance active Atrazine used for corn, which has been widely used in the past and forbidden recently at the rate of its negative impact on the environment and is a chronicle of the surface water and groundwater pollutant of the past two decades[36-37].It has a hydrolysis half-life of 30 days and relatively high water solubility (32 mg·L -1), which aids in its infiltration into ground water [38]. Atrazine concentrations of 20 µg·L -1 have been commonly detected in surface water runoff, while concentrations as high as 700 µg·L -1 have been reported [39-40].

Atrazine and its metabolites will be present in still waters for several years.
- Atrazine toxicity;
- Adsorption of atrazine on montmorillonite in the presence of Humic acids and copper;
- Photochemical degradation of Atrazine in absence and in the presence of Humic acids in the soil.

MATERIALS AND METHODS

2.1 Presentation of the study area.

2.1.1 Geographic framework

The Gharb-Chrarda-BeniHssen (CWM) area is located north west of the country. And limited to the North by the region of Tanger-Tétouan - Al Hoceima, on the Southeast by the regions of Fes-Meknes, on the South by the region of Rabat-Salé-Kenitra and on the West by the Atlantic Ocean.

2.1.2 Agriculture in the study area.

Its useful agricultural surface is 576.442 ha, representing 63.9%.

Table 1 : Main crops grown in the area of the Gharb-Chrarda-BeniHssen

Cultures	**Irrigated**			**Bour**			**Total**	
	Area **(ha)**	performance **(T/ha)**	production **(T)**	Area **(ha)**	performance **(T/ha)**	production **(T)**	Area **(ha)**	Performance **(T)**
Cereals which	**39 530**	**3,5**	**140 384**	**295 400**	**2,1**	**607 774**	**334 930**	**748 158**
Grains fall	26 130	3,0	77 274	295 400	2,1	607 774	321 530	685 048
Rice	4 300	6,9	29 670				4 300	29 670
But grain	9 100	3,7	33 440				9 100	33 440
Legumes	**6 240**	**2,0**	**12 456**	**30 854**	**1 2**	**37 205**	**37 094**	**49 661**
Fodder:	**31 580**	**53**	**1 678 200**	**9 216**		**174 767**	**40 796**	**1 852 967**
Cultures Indust. Whose	**50 631**		**1 321 321**	**25 762**		**44 879**	**76 393**	**1 366 200**
Beet	14 000	43,6	610 000	400	40	16 000	14 400	626 000
Cane	12 000	64,4	614 000				12 000	614 000
Peanut	13 000	2,3	26 000				13 000	26 000
Arboriculture which	**22 409**		**398 168**	**46 817**		**51 062**	**69 226**	**449 230**
Citrus	16 230	23	339 600	0			16 230	339 600
Olivier	1 460	2	2 920	45 260	1,1	48 180	46 720	51 100
-Futures which	**38 806**		**1 187 027**				**38 806**	**1 187 027**
Primeursdon’t	**2 981**	**32**	**96 962**				**2 981**	**96 962**
Strawberries	2 109	**40**	84 360				2 109	84 360
Gardening season whose	**30 950**	**28,7**	**889 686**				**30 950**	**889 686**
Artichoke	2 650	16	42 400				2 650	42 400
Gardening agro Indust. whose	**4 875**	**41,1**	**200 379**				**4 875**	**200 379**
Industrial tomato	4 200	46	193 200				4 200	193 200
Tropical crops	**1 466**		**58 120**				**1 466**	**58 120**
TOTAL GENERAL	**190 662**		**4 795 676**	**408 049**		**915 688**	**598 711**	**711 364**

2.2 Toxicity of Atrazine

When Atrazine was first released for agricultural use, it was thought that since photosynthesis is limited to plants, animals would be immune to any effects of Atrazine. It was soon suspected that Atrazine might have non-target action in animals including genotoxic [41], clastogenic [42] and biochemical effects [43]

Atrazine has a low acute toxicity to mammals. Due to its low solubility, this toxicity does not occur by dermal absorption. It causes no irritation of the skin or eyes. Atrazine may have adverse effects on the health of people exposed to higher concentrations than recommended. Exposure to high concentrations of Atrazine in drinking water can cause nausea and dizziness. Studies in humans have been somewhat highlighted an association between Atrazine and increased risk of cancer of the ovaries or lymphoma. However, the information gathered does not allow concluding that Atrazine is the cause. According to studies done on rats, Atrazine is possibly carcinogenic to humans [10-14]

- Animal studies also show that Atrazine can induce hormonal imbalances by exerting a negative impact on the pituitary gland.
- Indicative table 2 gives some values of LD50 (lethal dose killing half of a population in a given time) of Atrazine for different types of animals.

Table 2 : Atrazine toxicity in terms of LD50 Oral (O) and by way of dermal absorption (DA) for some animals

Pet	Rats/O	Rats/DA	Mouse/O	Rabbits/O	Rabbits /DA	Hamsters/O
LD_{50} (mg/kg)	3090	>3000	1750	750	7500	1000

2.3 Elimination of Atrazine.

2.3.1 Photodegradation of Atrazine in the presence of Humic acids from soils

2.3.1.1 Physicochemical characterization

Table 3 brings together the results of elemental analysis and functional groups of Humic acids known as AH (Sol) extracted from a Moroccan agricultural soil in the region of Chaouia.

Table3 : Elemental analysis and functional groups of AH.

Acidity meq/g						
AH	%C	%H	%N	Total	COOH	PhOH
AH(Sol)	62,9	3	1,9	12,42	9	3,42

2.3.1.2 Spectral characteristics of Atrazine in the presence of Humic acids

Spectra UV of Atrazine in the presence of AH at different concentrations are shown in figure 1. Only atrazine is characterized by a banded'absorption 222 nm (ε = 12769 L.mol - 1.cm - 1) and a shoulder at 270 nm (ε = 8196 L.mol - 1.cm - 1). Beyond 319 nm, atrazine absorbs more light.

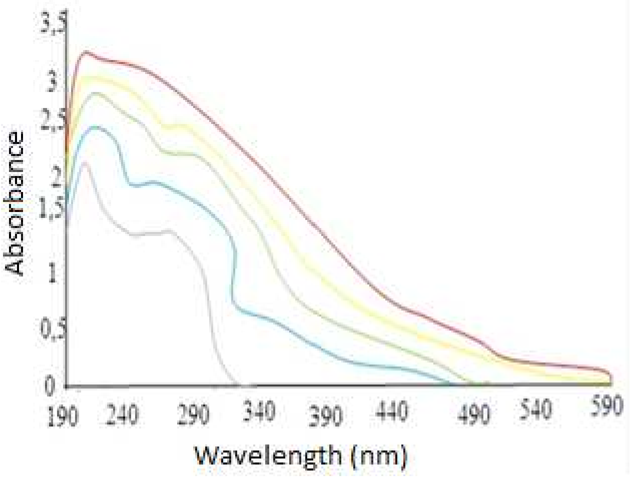

Figure 1 : UV spectrum of Atrazine in the presence of Humic acids to various reports

By increasing the concentration of Humic acids, there is an increase in absorbance and especially to the long wavelengths.

2.3.1.3 Photodegradationof Atrazine in the presence of Humic acid

For this study, a solution of Atrazine (50 ppm) in the presence of Humic acids has been prepared at different concentrations. Solutions have been adjusted with a phosphate buffer. They have been irradiated in a Pyrex reactor. To better understand the photochemical behavior of Humic acids, two wavelengths were chosen λ< 340 nm and λ> 290 nm.

- **Photolysis of Atrazine in the presence of Humic acid to 290 <λ< 340 nm For Atrazine above 340 nm photons are absorbed only speak Humic acids.**

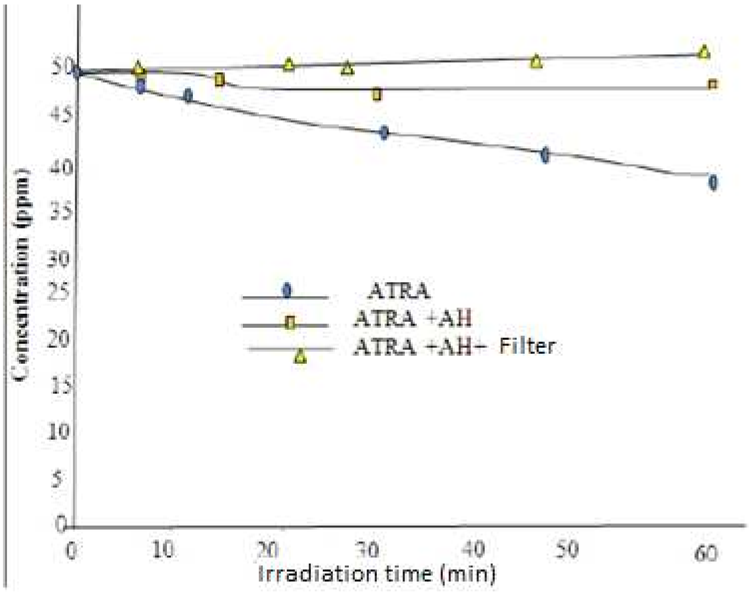

Figure 2 : Kinetics of photodegradation of the ATRA ATRA + AH + filter, ATRA + AH (50 ppm)

Figure 2 shows the kinetics of photodegradation of Atrazine only in the presence of Humic acids and with a filter cutting 340 nm <λ. Rate constants were calculated and the time of half-life of the photodegradation of Atrazine under different conditions, the results are shown in table 4.

Table 4 : Rate constants of single ATRA, ATRA + AH, ATRA + AH + filter

	Atrazine	Atrazine+AH	Atrazine+AH+filtre
K -1(min)	0,0046	0,0028	0,0018
T1/2 (min)	150	247	385

It notes that the presence of Humic acids slows the kinetics of the photodegradation of Atrazine t1/2 (ATRA) 1 50 min = << t1/2 (ATRA + AH) = 247 min. in addition, the presence of a filter cutting λ> 340 nm still allows to observe degradation while direct photolysis is impossible under these conditions. So, it seems that the Humic acid generates active species responsible for this deterioration.

- **Photolysis of Atrazine to different concentrations of Humic acids to irradiation λ> 290 nm**
-

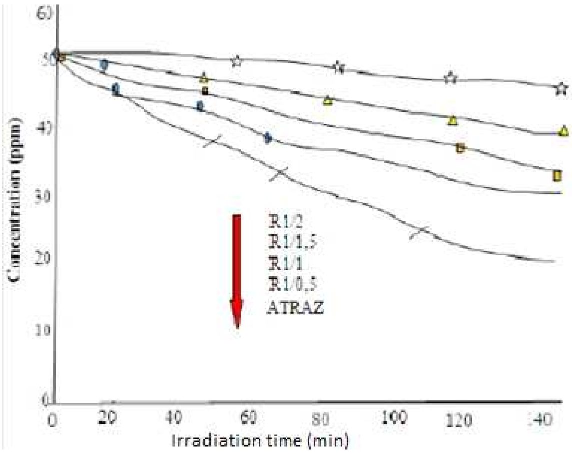

Figure 3 : Kinetics of photodegradation of atrazine in the presence of humic acids

Atrazine in the presence of Humic acids with different concentrations has been irradiated workplace ventilated with HPK lamp in a Pyrex reactor. In figure 3, we represented the kinetics of disappearance of Atrazine + AH. They have performed at a concentration of 50 ppm and followed by HPLC. This disappearance is very fast as the solution is less concentrated in AH. The Atrazine rate constants were calculated in the presence of Humic acids with different concentrations. The results are given in table 5.

Table 5 : Rate constant and half-life of atrazine in the presence of humic acids

	Atrazine	Report 1/0,5	Report 1/1	Report 1/1,5	Report 1/2
K -1(min)	0,0104	0,008	0,0053	0,0042	0,0018
T (min)	69	86	130	165	385

Direct photodegradation of Atrazine is a relatively rapid phenomenon (half-life of 69 min time). On the other hand, in the presence of Humic acids, obtained photodegradation is a process much more slow (time of half-life 130 min for a 1/1 ratio). Photodegradation of Atrazine speed depends on the concentration of Humic acids. II emerges from these results that Humic acids that were tested have played a dual role: inhibitory and generator of active species.

To below 340 nm wavelengths, it certifies a competitive absorption of light radiation between Atrazine and Humic acids which play a role of screen. At the same time as AH absorb photons, they generate active species able to degrade Atrazine.

2.3.2 Photochemical Degradation of Atrazine in absence of Humic acids

2.3.2.1 Evolution of pH-dependent absorption spectrum

Buffered solutions of Atrazine in a concentration of 50 ppm and at different pH values have been prepared. The used tampon is a phosphate buffer and solutions are adjusted to pH using NaOH and H_3PO_4. UV - Visible spectra of Atrazine at different pH values are given in Figure 4.

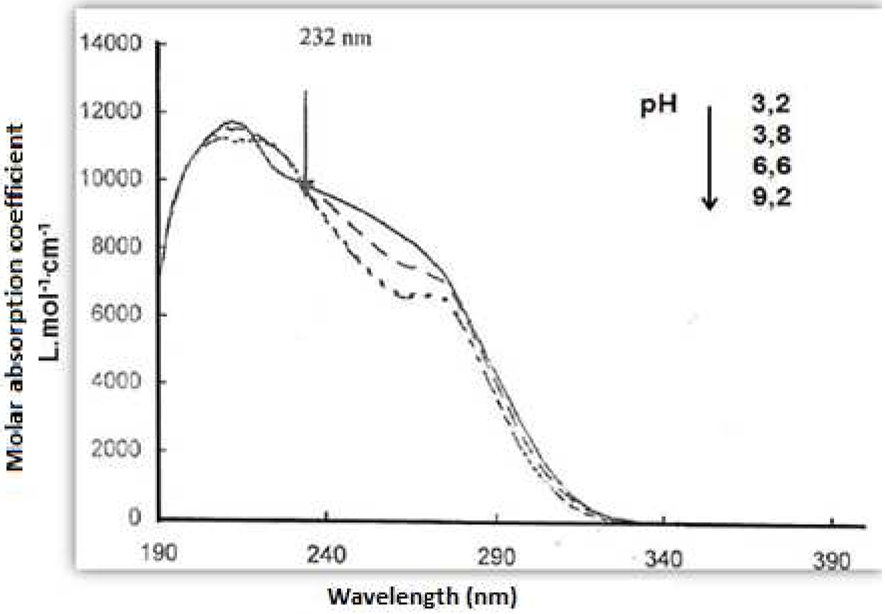

Figure 4: Absorption spectra of Atrazine at different pH values

An isosbestic point was observed in the pH range studied at 232 nm. Atrazine is characterized by the presence of two acid-base equilibrium. We will try to determine the pKa value of these balances.

2.3.2.2 Determination of pka

The molar absorption coefficient variation, depending on the pH, has enabled us to show that there are two points of inflection. This indicates that there are two pKa in the pH range studied, the pKa of Atrazine have been determined according to the evolution of the absorption spectrum as function of pH (Fig.5). We have charted the evolution of 220 nm molar absorption coefficient as function of pH buffered solutions (pH = 1.5 to pH = 4.5) at a concentration of 50 ppm. The method of differential and a mathematical adjustment were also used to determine pKa values [19].
The mathematical adjustment method:

$$AH \underset{}{\overset{Ka}{\rightleftarrows}} A^- + H^+$$

$$Ka = \frac{[A^-]\,[H^+]}{[AH]}$$

$$C = [A^-] + [AH]$$

αi = Mole fraction

$$\alpha_{AH} = \frac{[AH]}{C} = \frac{[H^+]}{K_a + [H^+]}$$

$$\alpha_{A^-} = \frac{[A^-]}{C} = \frac{K_a}{K_a + [H^+]}$$

Absorbance at a wavelength given as function of pH can be obtained using the Beer Lambert law in a mixture:

$$A_{solution} = (\varepsilon_A - [A] + \varepsilon_{AH}\,[AH])\;l$$

With: A total solution = absorbance of the solution at a given wavelength εA and εAH = coefficient of molar absorption of anionic form and the molecular form at a given wavelength. l: optical drive cm.

$$A_{solution} = lc\,\frac{\varepsilon A\text{-}Ka + 10^{-pH}\ \varepsilon AH}{10^{-pH} + Ka}$$

It gets pKa1 = 2.1 and pKa2 = 3.9.

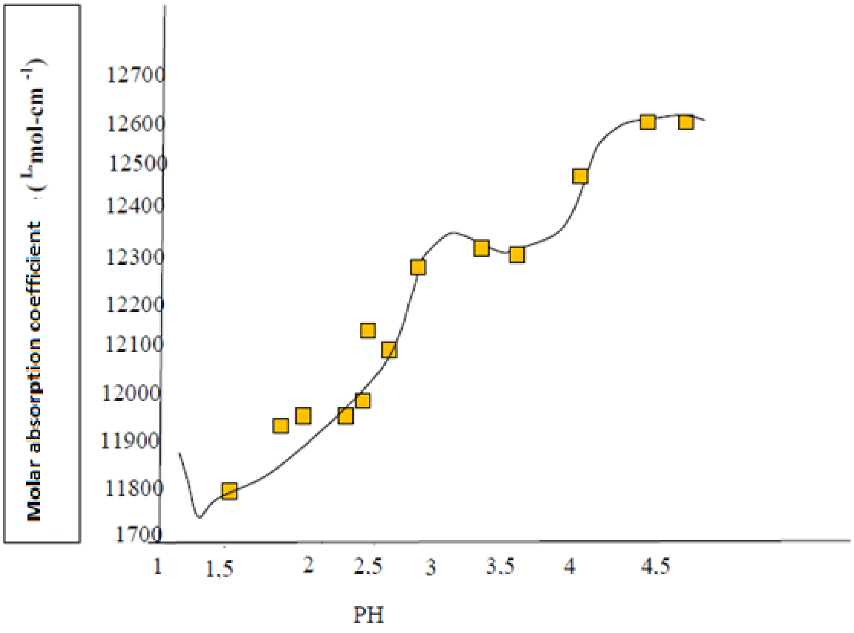

Figure 5: Evolution of the absorption of Atrazine at 220 nm (C = 50 ppm) with pH

2.3.2.2 Direct photodegradation of Atrazine

Following his absorption in the presence of the solar spectrum spectrum, it turned out that Atrazine is likely from photodégrade into the environment under a radiation of wavelengths above 290 nm. Two systems of irradiation have been used to study the kinetics of disappearance of Atrazine: Simulator of solar radiation (SUNTEST) equipped with a xenon lamp and the Pyrex where the source of irradiation is a HPK 125 W lamp.

- **Kineticstudy**

To compare the photochemical behavior of Atrazine in the irradiation systems, we irradiated solution of pesticide (C = 50 ppm) in distilled water and followed the evolution of the concentration of Atrazine by HPLC (see operating conditions, experimental technical chapter) without another chemical influence. The pH of the solution is equal to 3.5. To avoid any influence of the transformation on the calculation of the kinetic products, photodegradation of Atrazine rate should be less than 15%. It was able to verify that the disappearance of Atrazine is done according to order kinetics l.

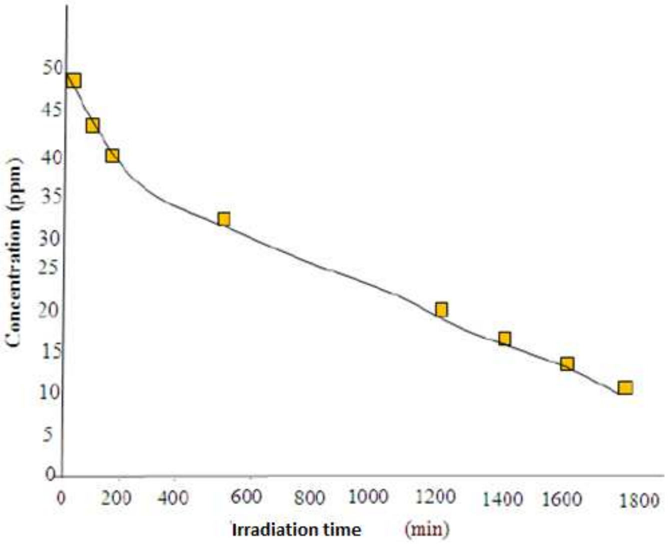

Figure 6: Photodegradation of Atrazine under irradiation of the lamp HPK

To compare the kinetics in the two reactors, we calculated their rate constant and their time of half-life from the experimental data. The values obtained in the two reactors are summarized in table 6

Table 6 : Rate constant and half-life of atrazine time calculated in the reactor

	K -1 (min)	**t ½ (min)**
Suntest	,0012	77
HPK	,0079	7

The rate of disappearance of Atrazine is faster with HPK lamp in the suntest of because of the difference in power of lamps.

RESULTS AN DISCUSSION

The results of the different routes of elimination of Atrazine by adsorption of Atrazine on Montmorillonite in the presence of Humic acids and copper, and photochemical degradation of Atrazine in absence and in the presence of Humic acids in the soil, are:

The Humic effects of Cu and Cu-acids on the adsorption of herbicide Atrazine by Montmorillonite have been studied and the results showed that:

- The photochemical degradation of Atrazine in absence of Humic acids has been studied. The study on the basis of the oxygen concentration was undertaken to clarify and explain the assumptions that this first draft allowed to sketch, including the influence of the excited triplet on the kinetics of the molecule.

All of the results found in monochromatic irradiation (254 nm) allowed us to conclude that:

- The concentration of Atrazine has an effect on the kinetics of photochemical degradation, which is explained by a bimolecular process.
- A Keto-enol equilibrium was noticed after the calculation of the quantum yields at different wavelengths of

radiation.[4]

CONCLUSION

Atrazine is used for the elimination of unwanted plants and that although it is forbidden the Morocco always use, the major risk of this herbicide is the contamination of water because of its physico-chemical characteristics.

This study on the elimination of this material active by photochemical degradation with or without the presence of Humic acids in the soil has allowed us to conclude that:

- The pH affects the photochemical behavior of Atrazine in solution.
- The ionic form of the carboxylic acid function photodegradation faster than the molecular form and in the absence of oxygen.

All of the results found in monochromatic irradiation (254 nm) allowed us to conclude that: the concentration of Atrazine has an effect on the kinetics of photochemical degradation, which is explained by a bimolecular process. Keto-enol equilibrium has been noticed after the calculation of the quantum yields at different wavelengths of radiation[4-35].

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