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Disposal of pesticides into the environment by adsorption: 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 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. 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. In the presence of humic acids, and copper clay (montmorillonite), the main results showed that:

- The pH has major role in the adsorption of Atrazine in the case of montmorillonite and Cu-HA-M. However, no effect of pH was observed for the complex Cu - M
- The kinetics of adsorption of Atrazine was faster on both Cu - M complexes and Cu-HA-M for montmorillonite;
- Atrazine feels a growing affinity for holders of the order of M < Cu-HA-M < Cu - M.

Keywords: Atrazine, Elimination, adsorption, pesticides, montmorillonite.

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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.

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 Eco toxicological with respect to the composition of our ecosystem as reflected by pollution whose consequences can be detrimental to its quality.

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. 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.

MATERIAL AND METHODS

Presentation of the study area:

Geographic framework:

The Gharb-Chrarda-Beni Hssen (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.

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-Beni Hssen

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	26 000

							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**
Primeurs dont	**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**	**5 711 364**

Toxicity of Atrazine

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.

- 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

Elimination of Atrazine:

Adsorption of atrazine on montmorillonite in the presence of humic acids and copper:

Absorbent and preparation of Cu-montmorillonite and M-AH-Cu complexes:

The clay used in this study is montmorillonite (K10 with a fraction < 2 um). Humic acids are complex compounds from the soil. They play an important role in the interaction with pesticides.

The process used for the synthesis of Cu-montmorillonite (Cu - M) complex has been described by Cox et al. 1998. Fifteen grams of montmorillonite were agitated in 200 mL of 0.1 M $CuCl_2$, 24 hours. The mixture is then kept at 4 ° C for 16 h to facilitate decantation. The resulting solid is washed three times with distilled water to remove clay not complexed and chloride and is eventually placed in a steam bath at 80 ° C overnight for the evaporation of the water. The Cu - M complex obtained was retained to avoid contamination.

The M-AH-Cu complex has been prepared according to the method described by Schnitzer (2000). Five grams of montmorillonite K10 have been agitated in 200 mL of a solution of CuCl2 0.1 M for 24 hours at room temperature.

The mixture was maintained at 4 ° C for 16 h to facilitate decantation. Got solid was stirred for 24 h in a humic acid solution of (0.5 g/L) previously solubilized in 0.01 M NaOH. The resulting solid is then washed five times with distilled water and kept in a water bath at 80 ° C overnight in order to remove water by evaporation.

Adsorption of atrazine:

All tests were conducted using 25 mL centrifuge tubes. Tubes were closed with plugs in PTFE specially designed covered with aluminum foil to avoid losses by adsorption on the plugs. Non-clay samples showed no decrease in the concentration of atrazine solution under the experimental conditions.

As a result, degradation, volatilization and adsorption on the vials are negligible. The supernatant was separated by centrifugation, followed by filtration using glass fibre filters.

Adsorption isotherms were determined at room temperature and at a pH of 5 (±0. 2). Twenty milligrams of montmorillonite samples have been added to 20 mL of solutions of atrazine concentrations: 17.3; 34.6, 51.8; 69.1; 85.4 and 103.7 mol/L 0,01 N CaCl2. Mixtures have agitated for 24 h prior to their analysis, and the experiment was conducted in three replicates.

Studies of interaction at different pH values were made by using the same procedure. The pH of the samples was adjusted with H2SO4 or KOH for the pH levels of 4, 5.6 and 7 (± 02).

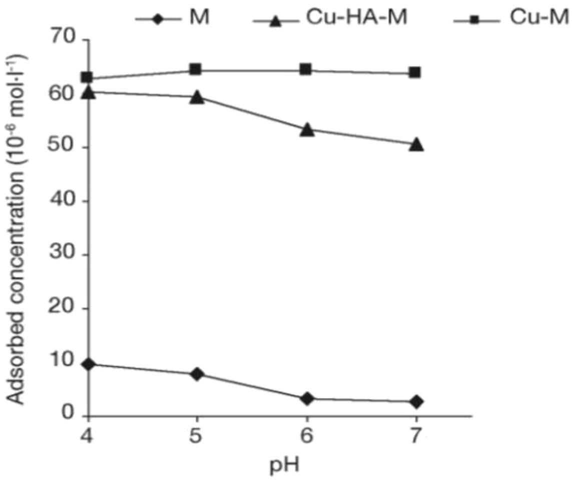


Figure 1: Effect of PH on the adsorption of Atrazine on (M), montmorillonite-Cu (Cu-M) and montmorillonite-Cu- humic acide (Cu-HA -M).

Analysis

The HPLC analysis was performed using a Perkin-Elmer 200 equipped with a diode detector 235 ° C (Wellesley, MA, USA). A LiChrospher l00RP-18(250x4 mm ID, 5 pm) has been used for studies of adsorption of atrazine and flow of isocratic elution (60% H2O acidified to pH = 2 with H3PO4 and 40% CH3CN) was 1.0 mL/min. The injection volume was 50 L and data have been collected and quantified at 255 nm.

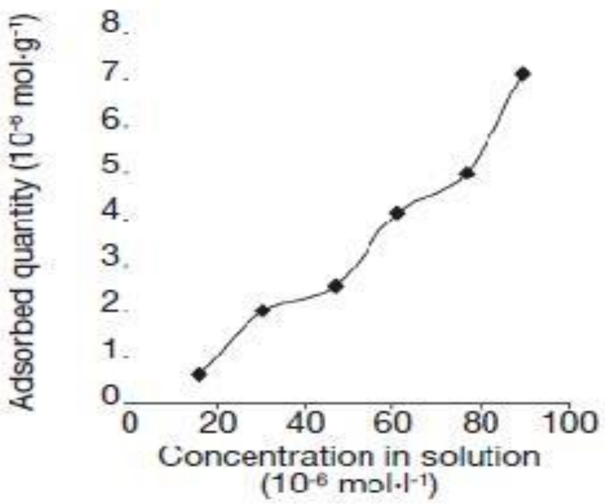


Figure 2: Adsorption isotherm of Atrazine on montmorillonite

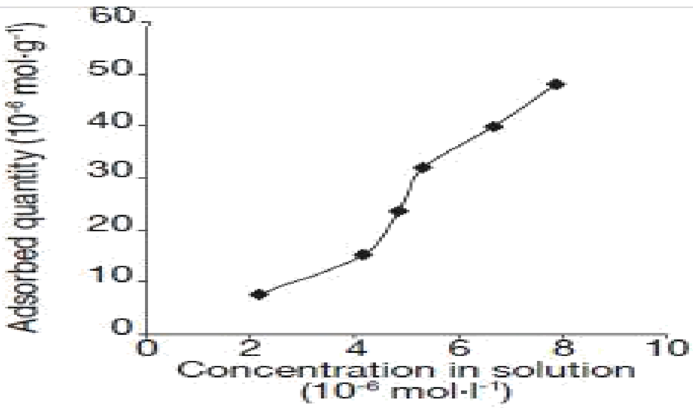
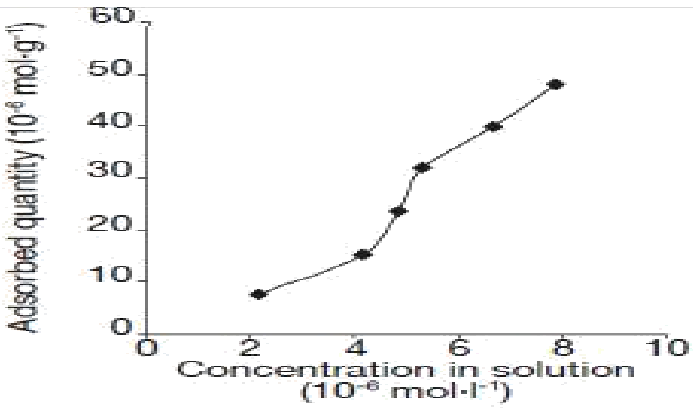


Figure 2: Adsorption isotherm of Atrazine on montmorillonite -Cu



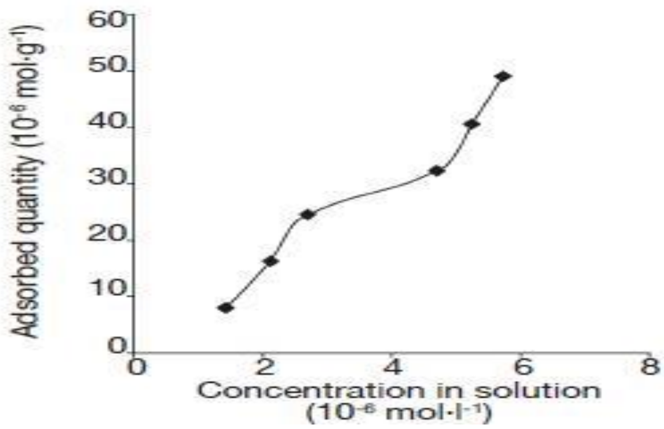


Figure 3: Adsorption isotherm of Atrazine on montmorillonite M-AH-Cu

RESULTS AND 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, 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 pH appears to affect the adsorption of atrazine in the montmorillonite and Cu-HA-M. However, no effect of pH was observed for Cu - M complex probably due to complexation of atrazine with copper at pH higher;
- The kinetics of atrazine is faster during adsorption on both Cu - M and Cu-HA-M complexes for montmorillonite;
- The Freundlich equation gives the best fit to the data on the investigated concentration range, with a growing affinity for holders of the order of M< Cu-HA-M < Cu - M;
- Adsorption of atrazine on the Cu - M complex can be attributed to the intercalation of atrazine in space leaf inter clay and adsorption on copper montmorillonite-related.

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 adsorption on montmorillonite in the presence of humic acids and copper, has allowed us to conclude that the humic effects of Cu and Cu-acids on the adsorption of herbicide atrazine by the montmorillonite showed that pH seems to affect the adsorption of atrazine in the montmorillonite and Cu-HA-M.

However, no effect of pH were observed for Cu - M complex probably due to a complexation of atrazine with copper at higher PHS, the kinetics of atrazine is faster during the adsorption on two M - Cu and Cu-HA-M complexes for the montmorillonite, the Freundlich equation gives the best fit to the data on the range of studied concentration, with a growing affinity for holders of the order of M <Cu-HA-M <Cu - M.

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