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Adsorption and Photochemical Behaviour of the Herbicide Monuron on Clay Surfaces

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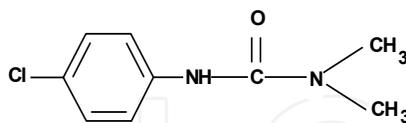
1. Introduction

The intensive use of pesticides on large areas of agricultural soil has given rise to concern about their fate in the environment. For many years, their presence as well as their environmental impact has attracted much attention due to the wide use of such compounds in agriculture and household applications (Beck et al., 1993; Serrano et al., 2005; Mansour, 1993). Less than 1% of total applied pesticides reach the target pests, the vast majority being dispersed in the different environmental compartments (water, air and soil) but mainly in aquatic environment via agricultural runoff or leaching (Pimentel, 1995). The application of herbicides on agricultural soils is a well-established and effective practice to control weed growth. They represent about 50% of the demand for agricultural chemicals; their prolonged use involves the risk of their retention in crops and soils. Soil is an ultimate reservoir for these products, whether applied directly or received indirectly from spray drift and residues of treated sites (Barbash & Resek, 1996). These products can be the subject of various transformations and they can react with different fractions of soil minerals or organic.

Mineral soil colloids play an important role in adsorption of polar organic compounds, mainly due to the high surface areas associated to their small particle size and, in the case of Smectites, because they have internal (expandable) surfaces accessible to water and polar organic molecules such as pesticides (Lagaly, 1994; Cox et al., 1995; Lee & Kim, 2002). These clay minerals possess layered structures and the presence of interlayer space thus gives a sterically constrained reaction environment for pesticide molecules when intercalated (Caine et al., 1999). Iron is one of the most abundant transition metals in soil and is considered to play a large role in photoinduced redox reactions generating active oxygen species such as $\cdot\text{OH}$ (Sherman, 1989). The clay surface is also covered with humic substances that represent 60%–70% of soil organic matter, probably via formation of clay-metal-organic complexes. These complexes are characterized by the presence of stable radical species detected by ESR (Senesi & Schnitzer, 1977).

Regarding the presence of these substances in soil, they may either contribute to the degradation of the pesticide through the formation of reactive species (Albanis et al., 2002) or be involved as inhibitors by a screen effect phenomenon (Hebert & Miller, 1990).

The present work reports the results of monuron (3-(4-chlorophenyl)-1,1-dimethylurea) adsorption onto some selected clays followed by its degradation induced by light solar excitation.



Monuron

Monuron is an herbicide from the group of phenylurea derivatives widely used as an inhibitor of photosynthesis and it is used mainly for the total weed control of non-crop areas. This chemical is characterized by long life times in the environment; its persistence is rather high about 10 months (Khan, 1980) which means that there is a potential risk of waters contamination. Not much information can be found on monuron adsorption and photoreactivity at the surfaces clays and soils.

The aims of the work are first to assess the influence of different components of soils clay of Moroccan region and commercial clays, montmorillonite and kaolin, in adsorption of a monuron herbicide and second to study the photodegradation process of monuron at the surface of some montmorillonite clays.

2. Part I: Adsorption studies of monuron on surface clays

2.1 Introduction

The sorption of pesticides by soil colloidal particles is of great interest in the transport of these compounds in runoff, surface and ground waters, because this particulate matter can act as a carrier of organic contaminants from point sources (Hermosin et al., 1993), and that is also affected by the solid/solution ratio (Cox et al., 1996). Batch sorption experiments were carried out under various conditions to determine the influence of solution chemistry (herbicide concentration, pH and solid-liquid ratio).

2.2 Materials and methods

2.2.1 Adsorptive molecule

Monuron was purchased from Aldrich standards with a purity of 99%. It is a crystalline solid with a vapor pressure of 0.067mPa (25°C) and water solubility 230mg/l (Zhou et al., 2001) Monuron concentrations were determined by high performance liquid chromatography HPLC Water equipped with two pumps type 510, UV- VIS detector with standard diode arrays 996 and a sampler type 717. The unit is controlled by Millennium software. The column used was C₈ phase reverse grafted by silica of granulometry 5µm, length 250m and internal diameter of 4.5 mm. The mobile phase was Methanol and water 60/40 at flow rate of 1mL/min. Under these experimental conditions, the retention time of monuron was 6.5 min.

The herbicide solutions were prepared with ultra pure water (Millipore MilliQ) of resistivity 18.2 MΩcm⁻¹ and the pH has been measured using a pH-meter JENWAY 3310 equipped with a combined electrode of Orion type.

2.2.2 Mineral sorbents

Clays extracted from soils: The clays were extracted from the first 20cm of tow Moroccan soils from Settat and Berrechid. The soil samples were air dried and sieved to pass 2 mm mesh. Physicochemical properties are given in table1.

Origin of soil	pH	CEC(10 ⁻² meq/g)	OM ⁰ %	Clay %	Sand %	Limon ⁰ %	Silt ⁰ %
Settat	7.8	27.17	3.7	30.4	26.3	35.5	15.4
Berrechid	7.95	23.10	2.15	19.5	37.4	21.8	19.5

O.M: Organic Matter

CEC: Cation Exchange Capacity

Table 1. Selected physical and chemical characteristics of soil

The clay fraction of the soils (< 2µm particle size fraction) was obtained by sedimentation using method developed by Tessier and Collaborators (Robert & Tessier, 1974; Robert, 1975). In the followings, the clays extracted from Settat and Berrechid are named CESS and CEBS respectively.

Pure clays: Adsorption experiments with pure clays are also carried out for monuron, the minerals used as model adsorbents were potassic montmorillonite: K-M and kaolin: Ka. Both were purchased from Fluka chemistry AG and they were used as received.

Major elements were analyzed by X-ray fluorescence using AXIOS-P analytical equipment. The chemical composition of all studied clays fraction is summarized in table 2.

Clay	K-M	Ka	CEBS	CESS
% SiO ₂	71,42	45,41	32,743	41,445
% Al ₂ O ₃	14,362	35,066	13,139	16,22
% Fe ₂ O ₃	2,992	0,652	3,95	4,612
% MnO	0,016	0,012	0,069	0,078
% MgO	1,412	0,211	1,513	2,133
% CaO	0,207	0,052	16,937	10,558
% Na ₂ O	0,372	0,13	0,228	0,326
% K ₂ O	1,722	1,453	2,257	3,032
% TiO ₂	0,518	0,054	0,426	0,644
% P ₂ O ₅	0,049	0,108	0,334	0,782

Table 2. Chemical composition of the studied clays

2.2.3 Adsorption studies

Adsorption of monuron on clays was carried out by the batch equilibration technique (Sukul & Spitteller, 2000) using various mass adsorbent-solution volume ratio and at the desired herbicide concentration, the suspensions were shaken in centrifuge tubes at a known time and then centrifuged at 3500rpm for roughly 10min. The resulting was then filtered through 0.45µm cellulose membranes and the filtrate was analyzed by HPLC Water under the condition mentioned in paragraph 2.1.

Difference between Ce and Ci were assumed to be due to adsorption. Adsorption isotherms were obtained by plotting the amount of herbicide adsorbed ($C_s = \text{mmolkg}^{-1} \text{ clay}$, C_e (mM)).

2.3 Results and discussion

2.3.1 Characterization of studied clays

The Cation Exchange Capacity CEC and Surface Specific Area SSA are important characteristics of clays. CEC represents the overall quantity of charges available on the exchanger material. It is related to the surface density of charges through the SSA. For the

sorbents having no organic matter, SSA is anticipated to become a sorbent characteristic most likely to reflect sorption capacity.

Table 3 gathers the CEC and SSA values for different minerals used. These results indicate that montmorillonite represent the major fraction of soil clays and have been confirmed by some other characterization method.

Mineral	Ka	K-M	CESS	CEBS
CEC (meq/100g)	5,72	60,72	52,47	47,25
SSA (m ² .g ⁻¹)	5	166	60	21

Table 3. Cation Exchange Capacity and Surface Specific Area for clay minerals

The Infra Red spectra were obtained with Perkin Elmer 2000 spectrophotometer. The clay pastilles were prepared with KBr (0.1%). Infra Red spectrums of clays are illustrated in Figure 1.

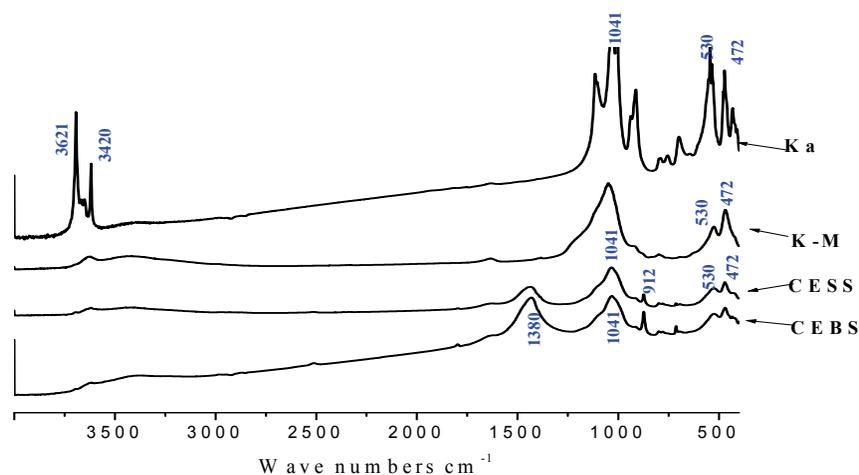


Fig. 1. IR spectrum of kaolin (Ka), K-montmorillonite (K-M), Clay extracted from Settata and Berrechid soil (CESS) and (CEBS).

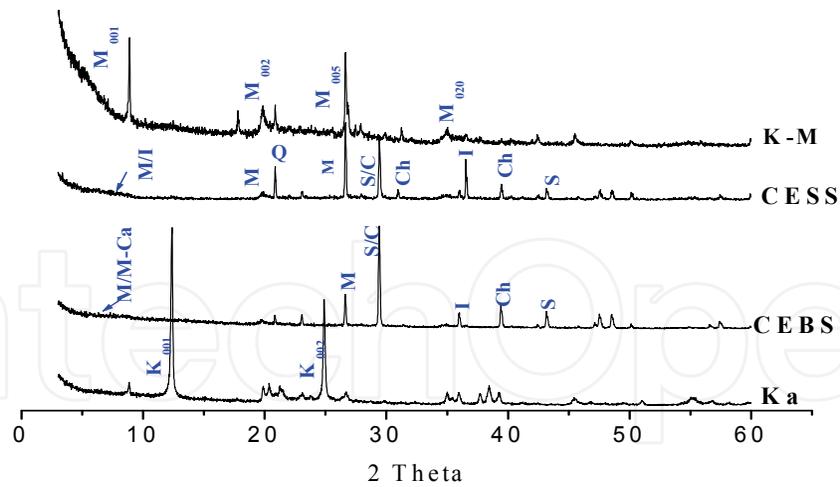
The kaolin spectrum reveal an intense band at 3621 cm⁻¹ corresponding to stretching vibration of OH groups coordinated to Al-Al pairs and another band located at 3420cm⁻¹ corresponding to the H₂O-stretching vibrations (Russell & Fraser, 1994). However, CESS and CEBS spectra present a broad band located at 1382cm⁻¹ that can be attributed to the presence of carbonate solid phases (Gueu et al., 2007). Such results are also confirmed by XRD analysed.

Moreover, all the spectra show a large band around 1041cm⁻¹ equivalent to Si-O-stretching (Madejova & Komadel, 2001). The double band observed at 530 and 472cm⁻¹ was related to Al-O-Si and Si-O-Si deformations (Madejova et al., 2002).

XRD measurements were performed using a Philips X-Ray diffractometer employing nickel filtered CuK α radiation. The X-Ray powder diffraction pattern of clays is given in Fig.2.

The principal equidistance of the most intense lines as well as the hkl plans relative to these rays are presented in table 4.

The comparison of experimental d_{hkl} and those taken from JCPDS chart show that CESS and CEBS are composed of several mineralogical phase; montmorillonite, saponite, chlorite, illite, quartz and calcite (table III and figure 2). These soils clays have similar mineralogical phases with different percentages. saponite and calcite represent the major phase of CEBS. However, CESS is rich of illite and montmorillonite.



M: Montmorillonite, Q: Quartz, I: Illite, Ch: Chlorite, S: Saponite, C: Calcite and Ka: Kaolin

Fig. 2. XRD pattern of clays studies

K-M		Ka		CEBS and CESS		
d _{hkl}	hkl	d _{hkl}	Hkl	d _{hkl}	hkl	Mineralogical phase
9,94	001	7,15	001	10,1	001	Montmorillonite
4,48	002	3,58	002	4,48	002	
3,35	005	2,39	003	4,26	*	Quartz
2,56	020	1,79	004	3,04	005	Saponite + Calcite
2,13	004	1,49	060	2,13	134	Saponite
*****	*****	*****	*****	2,89	005	Chlorite
*****	*****	*****	*****	2,28	133	
*****	*****	*****	*****	2,46	004	Illite

Table 4. Basal distances obtained for clays

2.3.2 Adsorption kinetics

In order to determine the optimum contact time for monuron adsorption onto clays, equilibrium concentrations were measured at definite times. As can be seen from Figure 3.

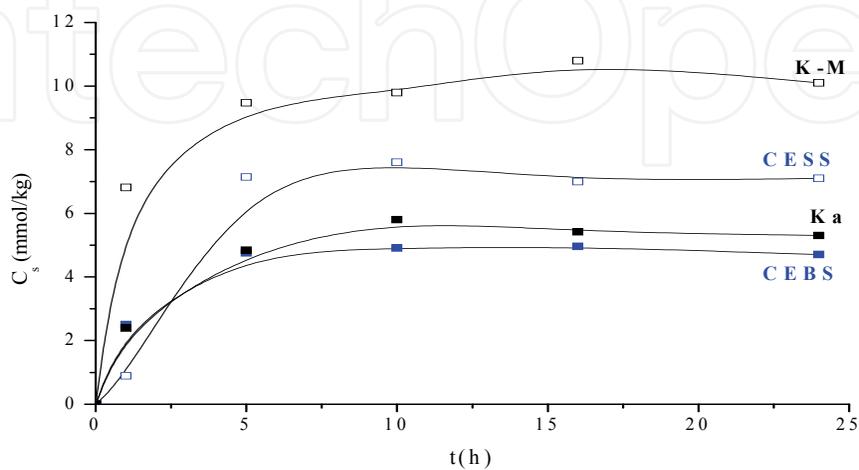


Fig. 3. Effect of contact time on adsorption

From figure 3, when the equilibrium time was increased, the amount of adsorption was also increased. Under our experimental conditions, the equilibrium was reached within 6h for K-montmorillonite (K-M), within 10h for kaolin (Ka), clay extracted from Settat soil (CESS), and clay extracted from Berrechid soil (CEBS).

Adsorption kinetics is usually controlled by different mechanisms. The most limiting ones are the diffusion mechanisms. The initial curved portion is attributed to a rapid external diffusion or boundary layer diffusion and surface adsorption, while the linear portion represents a gradual adsorption stage due to intraparticle diffusion. This starts to decrease due to the low concentration in solution as well as fewer available adsorption sites (Guibal et al., 2003).

2.3.3 Adsorption isotherms

Figure 4 and 5 show monuron adsorption isotherms in commercial clays and soils clays. Most of the curves do not reach the plateau of saturation when the solid/liquid ratio was 5mg/ml. Only 11.97 mmol of monuron was adsorbed in one Kg of K-montmorillonite. This is equivalent to 9.4%. The amounts of monuron adsorption in CESS, CEBS and kaolin, were 6.8, 5.4 and 5.8mmol/Kg respectively with corresponding percent adsorptions; 5.1, 4.01 and 4.3.

In order to optimize the design of an adsorption system, it is important to establish the most appropriate correlation for the equilibrium curves. In this respect, the equilibrium experimental data for adsorbed monuron on clays were studied using Freundlich equation.

The Freundlich equation (Freundlich, 1906) is an empirical equation employed to describe heterogeneous systems; characterized by the heterogeneity factor n_f , describes reversible adsorption, and is not restricted to the formation of the monolayer,

$$C_s = K_f C_e^{n_f}$$

Where K_f is the adsorption capacity evaluated at 1mM C_e and n_f is the intensity factor, expressing the slope of the adsorption isotherm.

A linear form of the Freundlich expression can be obtained by taking logarithms of the equation:

$$\log C_s = \log K_f + n_f \cdot \log C_e$$

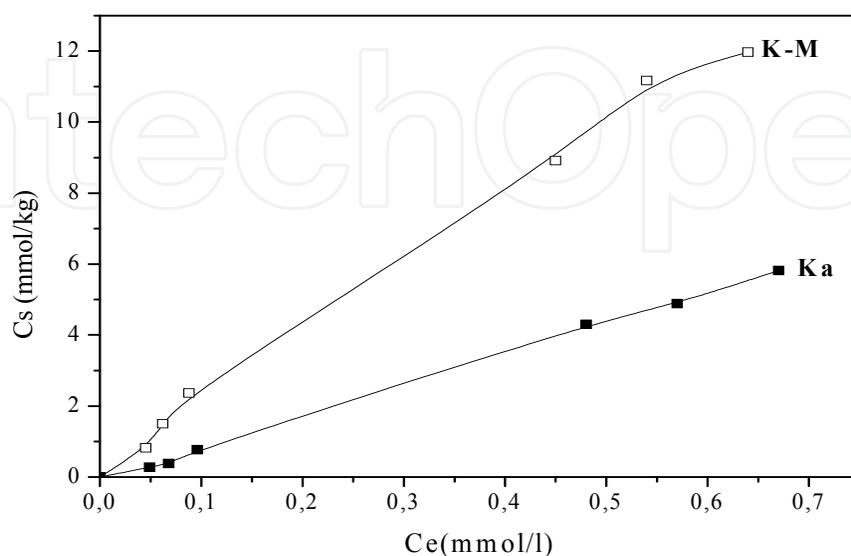


Fig. 4. Monuron adsorption isotherms on K-montmorillonite and kaolin

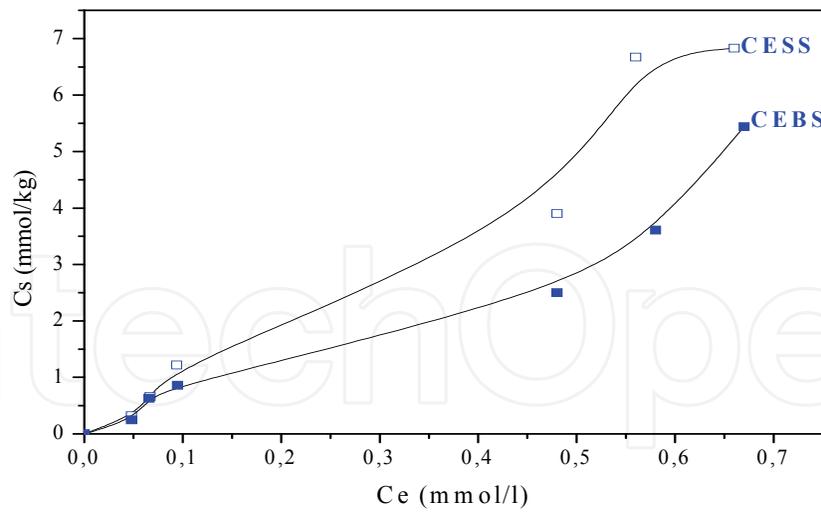


Fig. 5. Monuron adsorption isotherms on clays extracted from soils CESS and CEBS

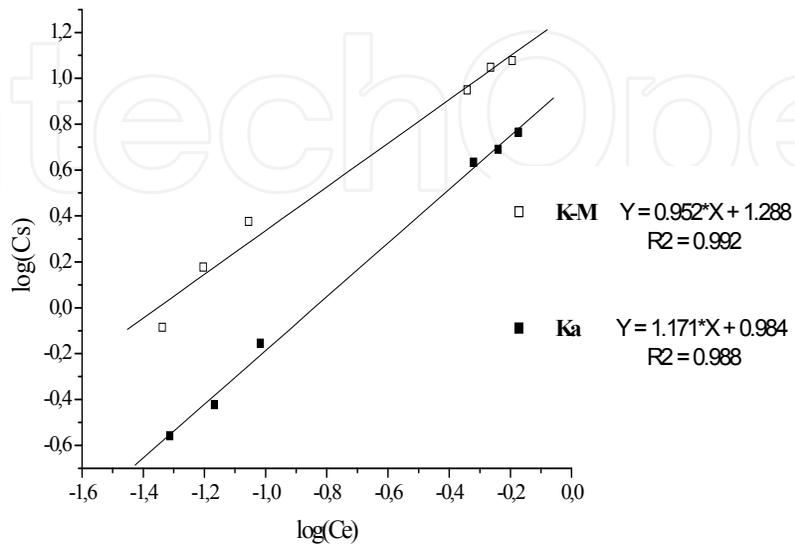
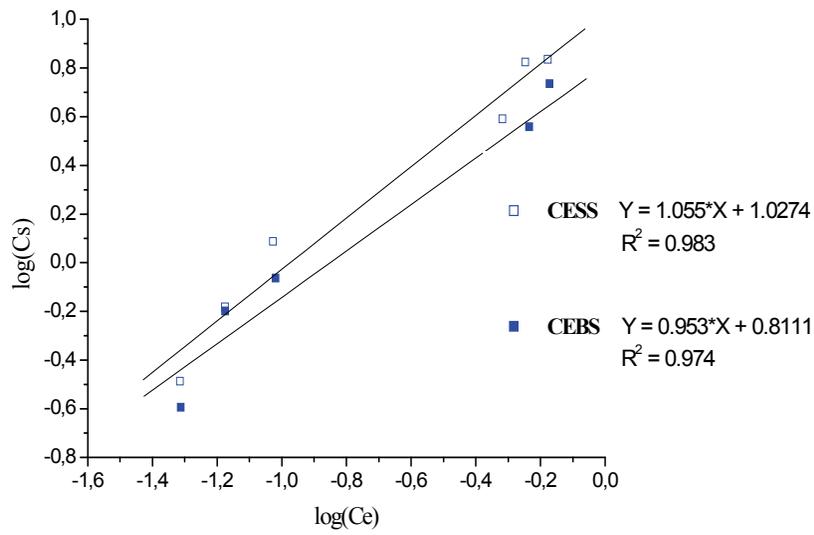


Fig. 6. Freundlich isotherms adsorption on K-M, Ka, CEBS and CESS

Therefore, the plots of $\log C_s$ vs $\log C_e$ for the adsorption of monuron onto clays were employed to generate the intercept value of K_f and the slope of n_f .

Figure 6 illustrate Freundlich isotherms for studied clays.

The adsorption isotherms of monuron followed the Freundlich equation with a high regression factor ($R^2 > 0.98$). Table 5 contains the adsorption coefficients values K_f and n_f extrapolated from Fig.6

Clay	K_f	n_f	R^2
K-M	19,4	0,952	0,992
Ka	9,64	1,171	0,983
CESS	10,6	1,055	0,974
CEBS	6,47	0,953	0,988

Table 5. Freundlich sorption coefficients K_f and n_f of monuron adsorption onto clays

The adsorption capacity of monuron was in the following order:

$$K-M > CESS > CEBS > Ka$$

K_f values indicated that adsorption capacity of CESS is better than that of CEBS. This difference can be attributed to CEC and specific surface area; these parameters are the most key factors influencing adsorption on clays. High CEC of CESS suggests that this clay has strong ability for cation exchange. By consequent this clay has an important adsorption capacity when compared to the CEBS

The value of n_f is smaller than 1 for K-M and CEBS clays, it's reflecting favourable adsorption then the sorption capacity increases and new adsorption sites occur. For Ka and CESS clays the value of n_f is larger than 1, the adsorption bond becomes weak and unfavourable adsorption takes place, as a result of the decrease in adsorption capacity (Jiang et al., 2002; Tsai et al., 2003).

In order to determine the adsorption type, the Dubinin-Radushkevich equation can be expressed as follows (Dubinin, 1960):

$$\ln C_s = \ln X_m - k\varepsilon^2,$$

Where ε (Polanyi Potential) can be written as:

$$\varepsilon = RT \ln(1 + 1/C_e),$$

C_s is the amount of pesticide adsorbed per unit weight of adsorbent (mol/g), X_m is the adsorption capacity (mol/g), C_e is the equilibrium concentration of pesticide in solution (mol/L), k is the constant related to adsorption energy (mol²/kJ²), R is the gas constant (kJ/mol K), T is temperature (K).

Radushkevich and Dubinin (Radushkevich, 1949; Dubinin, 1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant, k , is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution (Hasany & Choudhary, 1996).

A plot of $\ln C_s$ vs ε^2 should be linear. The values of X_m and k were calculated from intercept and slope of this plot. The results are summarized in Table 6.

Clay	$X_m \times 10^4$ (mol/g)	$k \times 10^2$	R^2	E(kJ/mol)
K-M	2.4	0.93	0.989	7.33
Ka	2.2	1.14	0.996	6.62
CESS	1.8	1.04	0.972	6.93
CEBS	0.85	0.91	0.952	7.41

Table 6. The sorption parameters of Dubinin-Radushkevich equation for monuron on clays

The values of k increased from 0.91×10^{-2} to 1.14×10^{-2} in clays. The mean free energy change of adsorption (E) can be considered as the free energy change during the transfer of one mole of molecule from infinity in solution to the surface of the solid particles. Its value can be evaluated from the following equation:

$$E = - (2k)^{-0.5}$$

It should be noted that magnitude of E is useful for the estimation the adsorption type. If this value is found within 8-16kJ/mol, adsorption type can be explained by ion exchange (Singh & Pant, 2004; Mahramanlioglu et al., 2002). The values of E estimated in the present study are 6.62, 6.93, 7.33 and 7.41 kJ/mol. for kaolin, clay extracted from Settat soil, K-montmorillonite and clay extracted from Berrechid soil respectively. The adsorption type under our experimental conditions can be considered as a physical adsorption (Paul & Long, 1957). However, the forces involved are intermolecular forces (Van Der Waals forces), and which do not involve a significant change in the electronic orbital patterns of the involved species. The adsorbed molecule is not affixed to a specific site at the surface but is free to undergo translational movement within the interface. It is predominant at low temperature, and is characterized by a relatively low energy of adsorption.

2.3.4 Initial pH effect

The amount of herbicide adsorbed on each adsorbent as a function of pH was also investigated (Figure7).

It is apparent that adsorption is independent on the pH of the solution. The pKa of monuron is too weak, it is about -0.082 (Ozcan et al., 2004), and does not have ionisable functions.

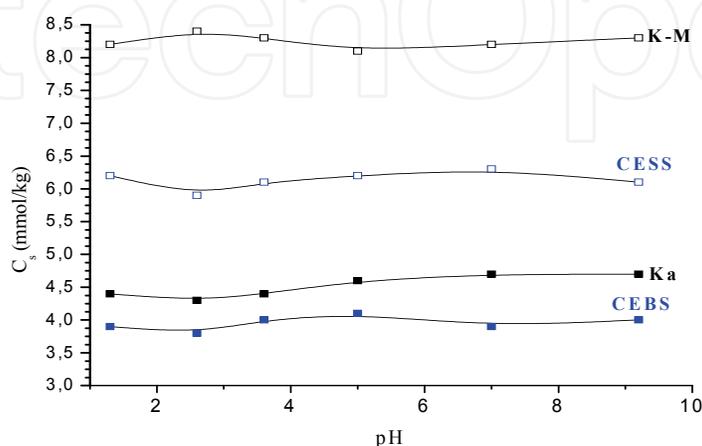


Fig. 7. pH effect on monuron adsorption by clays

Therefore the pH does not influence its sorption to the clays. However it's probable that pH affects the surface charge of clays; in the acidic medium, the H^+ ion can competitively exclude the adsorption of pollutant by exchanging with cation on the surface or in the interlayer region of the clay. When the pH value of the solution was increased, the surface of the adsorbent becomes negatively charged. According to the reported results (Yu et al., 2001), no significant attraction is observed between herbicide molecules and negatively surface.

2.3.5 Effect of the ratio solid/liquid

In order to select the best conditions of monuron adsorption in clays support, the influence of adsorbent/solution ratio on the capacity of adsorption were carried out at solid/liquid ratio ranging from 1 to 12 mg/ml. figure 8 presents the obtained results.

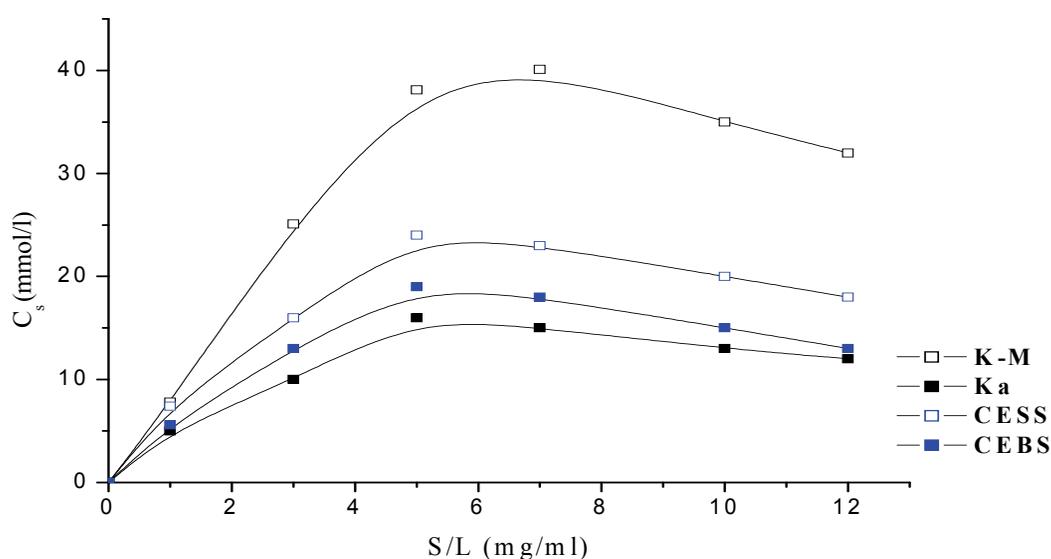


Fig. 8. Solid liquid ratio effect on monuron adsorption by clays

As clearly shown, the results indicate that the dispersion of the clays particles in suspension is modified according to the ratio S/L used. Clays have a better capacity of monuron adsorption in the range of 5-7mg/ml, the increase of ratio solid/liquid more than 7mg/ml allows the reduction of the rate of adsorption. Contact surface increases and the solute reaching the sorption sites of the different components when adsorbent/solution ratio increases. At a given mass, an aggregation phenomenon of the clay particles between them will be present that would decrease the total adsorbent surface and the rate of monuron adsorption (Mountacer et al. 2008).

2.3.6 Conclusion

Interaction between mineral sorbents and monuron herbicide is influenced by the dispersion conditions used in the preparation of the mixture. The favourable adsorption was realized at the following optimal conditions: contact time was 10 hours and sorbent/solution ratio was in the range of 5-7 mg/ml but pH does not have any effect on monuron adsorption onto clays studied.

The present work confirms that the mineralogical characteristics of clays play an important role in the retention of pollutants. A correlation between the maximum adsorption, CEC and

SSA of all sorbents was found. The adsorption capacity of monuron was in the following order: K-M > CESS > CEBS > Ka

3. Part II: Photodegradation process of monuron adsorbed on surface clays

3.1 Introduction

Photodegradation by solar light excitation is a process that pesticide may undergo once dispersed in the environment. The study of these abiotic transformations makes an appreciable contribution in determining the final fate of these xenobiotics. However, the phototransformation of herbicide adsorbed by clays in absence of water is an important question. Kinetic photodegradation of monuron was studied in various clay matrices: K-montmorillonite, Fe(III) exchanged montmorillonite (Fe(III)-montmorillonite) and montmorillonite complexed with humic acid (HA-montmorillonite) complexes. The nature of intermediate products during the photodegradation was investigated in order to compare the efficiency of different clays supports and to elucidate the mechanism of organic substrate photodegradation.

3.2 Materials and methods

3.2.1 Clay samples

The mineral used as a model adsorbent was K-montmorillonite (K-M), purchased from Fluka chemistry AG. Fe(III)-montmorillonite (Fe-M) and HA-montmorillonite (HA-M) were prepared by adsorption using the method developed by Cox and Koskinen (Cox & Koskinen, 1998). Clay minerals were analyzed by X-ray Fluorescence using AXIOS-P analytical equipment. The chemical composition of clay fractions is summarized in Table 7.

Composition (%)	Clay		
	K-M	Fe-M	HA-M
SiO ₂	71,42	66,861	70,354
Al ₂ O ₃	14,362	15,024	14,276
Fe ₂ O ₃	2,992	5,342	2,999
MnO	0,016	0,019	0,017
MgO	1,412	1,609	1,426
CaO	0,207	0,102	0,2
Na ₂ O	0,372	0,322	0,434
K ₂ O	1,722	1,557	1,696
TiO ₂	0,518	0,496	0,503
P ₂ O ₅	0,049	0,052	0,047

Table 7. Chemical composition of clay fractions obtained by X-Ray fluorescence

Adsorption of monuron on clay samples was carried out by the batch equilibration technique, using 100 mg clay and 30 ml of pesticide solution at 0.5 mmol L⁻¹. The suspensions were shaken in centrifuge tubes for 10 hours and then centrifuged at 3500 rpm for 10 min. The solid was recovered and transferred to desiccator for vacuum drying during 24 h.

3.2.2 Irradiation experiments

30 mg of pesticide-clay was irradiated in Suntest set up at different times, the pesticide was extracted from each irradiated sample by 1 ml of methanol, agitated for 10 min and filtered

through 0.45 μm cellulose membranes. The procedure was repeated for all clay complexes prepared.

3.2.3 Analytical procedure

The photodegradation of monuron and the formation of the photoproducts were followed by high performance liquid chromatography. LC/MS analyses were carried out with Q-TOF-Micro/water 2699 from CRMP centre at the Blaise Pascal University. It is equipped with an electrospray ionization source (ESI) and a Waters photodiode array detector. Each single experiment permitted the simultaneous recording of both UV chromatogram at a preselected wavelength and an ESI-MS full scan. Data acquisition and processing were performed by MassLynx NT 3.5 system. Chromatography was run using a Nucleosil column 100-5 C18 ec (250 \times 9.4 \times 5 mm). Samples (5–10 μL) were injected either directly or after evaporation of the solvent for better detection

3.3 Results and discussion

3.3.1 Absorption spectrum of the studied pesticide

The absorption spectrum of monuron is given in Fig 9. It shows a maximum at 245 nm with a molar absorption coefficient of $17800 \text{ mol}^{-1}\text{L cm}^{-1}$ and a small shoulder at 280 nm. The comparison with the solar light emission (represented here by the emission spectrum from the suntest lamp) clearly shows a very weak not negligible overlap. Such overlap permits a direct excitation of monuron from the sunlight.

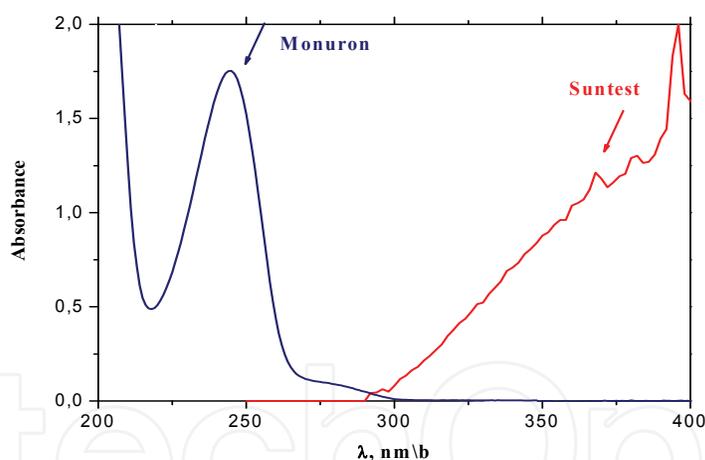


Fig. 9. The absorption spectrum of monuron in aqueous solution and the emission spectrum of suntest (xenon lamp)

3.3.2 Characteristics of clay fractions

The method used for determining CEC, which involves the complete exchange of the naturally-occurring cations by ammonium, is a standard method for CEC determination. Table 8 shows the values of CEC for the different studied minerals clay.

Mineral fraction	K-M	Fe-M	HA-M
CEC (meq/100g)	60.72	53.64	70.52

Table 8. Cation exchange capacity of clay minerals

The values consigned in Table 8 shows that the CEC of montmorillonite enriched by iron is low compared with that of K-montmorillonite. This result is due to the difficulty in moving the ferric cations by the ammonium cations. Moreover, the presence of the humic acid complexed with montmorillonite increases its capacity of cation exchange. This result is well correlated with those of many authors who showed that the CEC of the organic matters is higher than that of minerals clay (Baize, 1988).

The examination of IR spectra of clay fractions reveals the principal absorption bands; a slight band at 3631 cm^{-1} which is due to the stretching vibration of structural OH groups coordinated to Al-Al pairs. Adsorbed water gives a broad band at 3420 cm^{-1} corresponding to the H_2O -stretching vibrations (Russell & Fraser, 1994). The broad band around 1041 cm^{-1} corresponds to Si-O-stretching (Madejova & Komadel, 2001). The 530 and 472 cm^{-1} is related to the Al-O-Si and Si-O-Si deformations (Madejova et al., 2002). Results obtained are shown in Fig. 10.

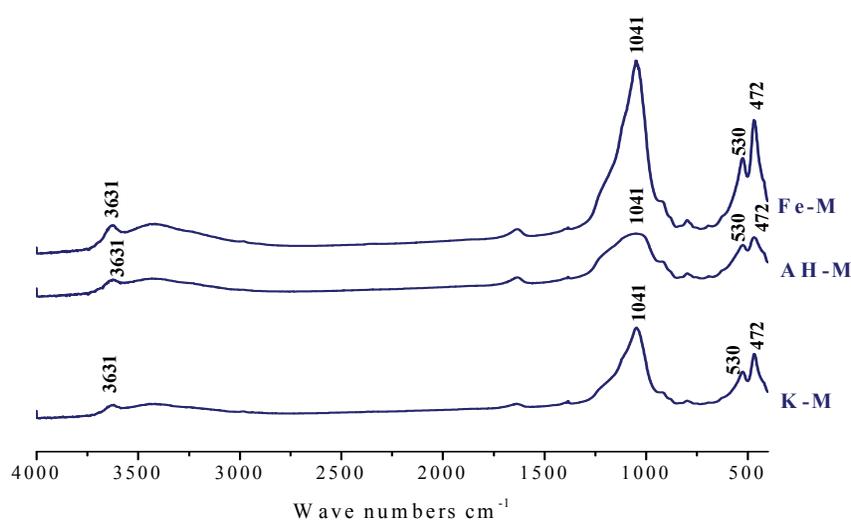


Fig. 10. IR spectra of K-M, Fe-M and HA-M.

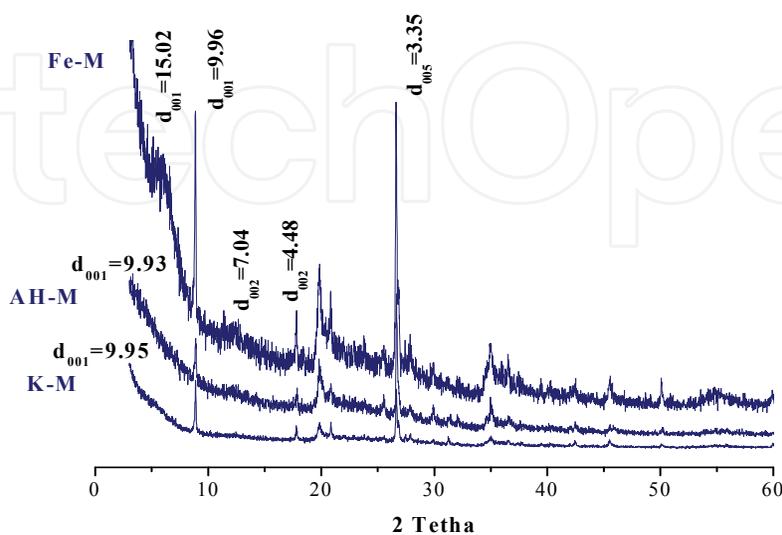


Fig. 11. XRD pattern of K-M, Fe-M and HA-M.

The spectra show also a widening of the band centred at 1041 cm^{-1} in AH-M and a stressing of the latter for Fe-M. Additionally, the band located at 472 cm^{-1} became more marked in the case of the complex Fe-M. This result confirms the exchange of potassium by iron, while this band weakened in the case of AH-M because of the interaction of humic acids in clay layer (Tajeddine et al., 2010).

The XRD measurements were performed using a Philips X-ray diffractometer employing nickel filtered CuK α radiation. The X-ray diffraction pattern of clay fractions is given in Fig.11. The equidistance appears to vary regularly according to the rate of hydration and the nature of exchanged cation. With the introduction of iron in montmorillonite, the reticular distance corresponding to plane 001 was evolved from 9.45 to 15.04. This indicates that the specific surface area was also increased. The presence of the equidistance 9.4 characteristic of K-M in the spectrum of Fe-M indicates that the substitution of K $^{+}$ by Fe $^{3+}$ was not complete.

3.3.3 Photodegradation experiments of monuron adsorbed on surface clays

3.3.3-a Kinetics of monuron disappearance in presence of humic acid (HA)

The kinetics of monuron disappearance on K-montmorillonite and HA-montmorillonite are shown in Fig. 12.

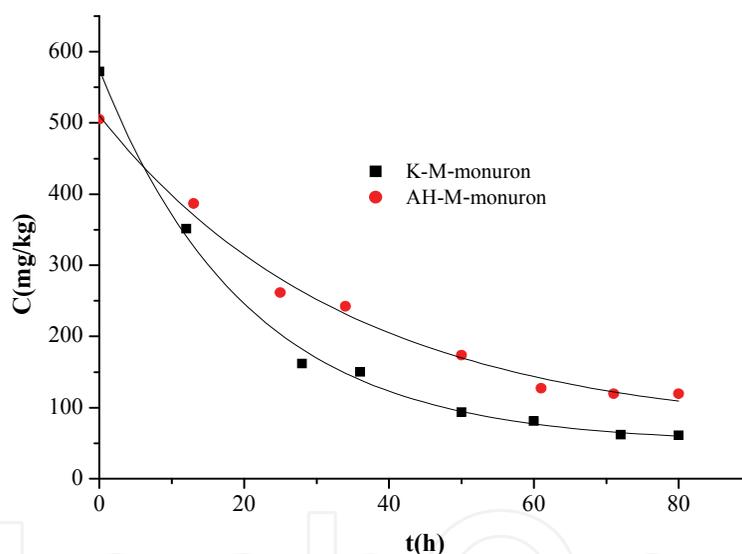


Fig. 12. Kinetics of disappearance of monuron irradiated on K-M and HA-M.

As clearly shown in Fig. 12, the photodegradation rate of monuron is slower for montmorillonite complexed with humic acid than that for K-montmorillonite alone. This is primarily due to the fact that light attenuation was more obvious by montmorillonite complexed with humic acid than K-montmorillonite. The absorption of the incidental light by the pesticide is quasi-total in the experiment of K-M. Kinetics and half lives of these experiences are given in Table 9.

The results show that the disappearance rate of monuron decreased from 18.4 to $9.09\text{ mg kg}^{-1}\text{ h}^{-1}$ by the complexation of humic acid to K-montmorillonite. It indicates that the presence of humic acid, complexed with K-montmorillonite, protects pesticide from photodegradation, due to the screen effect or light attenuation effect.

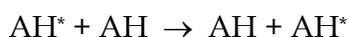
The phototransformation of monuron sensitized by the humic substances into aqueous medium was studied by Richard and Bengana (Richard et al., 1997). They showed that no

		$k(\text{mg kg}^{-1}\text{h}^{-1})$	$k_{\text{app}}(\text{h}^{-1})$	$t_{1/2}$
monuron	K-M	18.4	0.032	21h 35min
	HA-M	9.09	0.018	38h 54min

Table 9. Rate constants and half-life times of OPP and monuron irradiated onto K-M and HA-M

consumption of monuron was observed when it was irradiated alone at 365 nm with black light lamps. By contrast, monuron was degraded when it was irradiated in the presence of Fulvic acid or Humic Acid. It was observed that without oxygen no reaction takes place and that the rates of transformation are lower in oxygen-saturated than in air-saturated solutions. It was suggested that reactive excited triplet states of humic substances abstract an electron or a hydrogen atom (Canonica et al., 1995). The hydrogen atom is then transferred onto oxygen which is reduced into hydroperoxyl radical or superoxide anion; oxygen is thus needed for the chromophores to be regenerated. At high concentrations, oxygen quenches efficiently the triplets and inhibits the consumption of substrates. It is concluded that in this case a hydrogen atom transfer between oxidant excited states of humic acid and monuron occurs.

Under the current conditions, inhibitive processes, such as for example the auto-inhibition can also contribute in the reduction of the total process effectiveness (Vulliet et al., 2001).



3.3.3-b Kinetics of monuron disappearance

The photodegradation kinetics of monuron adsorbed by Fe(III)-montmorillonite complexes are presented in Fig. 13.

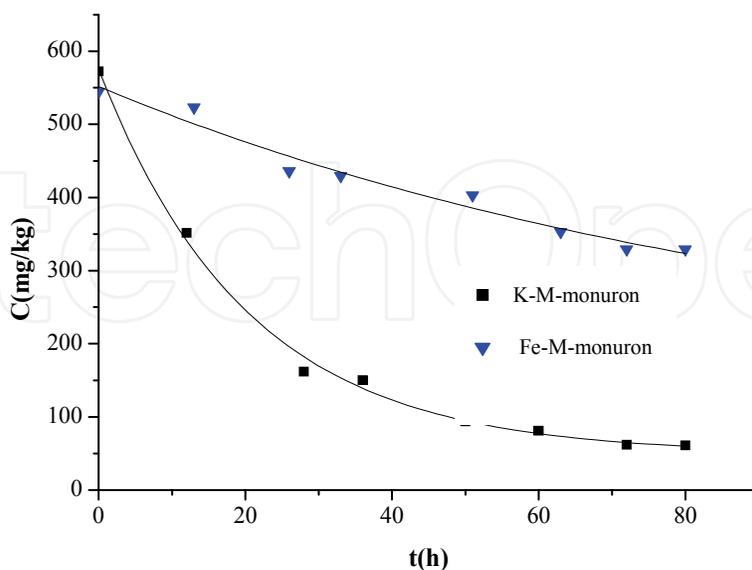


Fig. 13. Kinetics of disappearance of monuron irradiated on K-M and Fe-M

The presence of iron related to montmorillonite has a negative effect on the degradation rate of monuron. Table 10 illustrates the kinetics and the half lives of these experiences.

As shown in Table 10 the half-life times of monuron photodegradation were 43 and 78 hours for K-montmorillonite and Fe(III)-montmorillonite, respectively. The slow degradation can be explained by the absorption of light by Fe^{3+} , these ions cause a competition with the pesticide molecule.

		$k(\text{mg/kg.h})$	$k_{\text{app}}(\text{h}^{-1})$	$t_{1/2}$
monuron	K-M	18.4	0.032	21h, 35min
	Fe-M	9.09	0.018	38h, 54min

Table 10. Rate constants and half-life time of monuron irradiated onto K-M and Fe-M

In aqueous medium Mest'ankova and collaborators have noted that the direct photolysis of Monuron was negligible: no photodegradation of monuron occurred in the absence of Fe(III) (Mest'ankova et al., 2004). The kinetics of monuron degradation are strongly dependent on Fe(III) concentration. The disappearance of monuron became faster when the concentration of Fe(III) increased from 1.0×10^{-4} to $1.0 \times 10^{-3} \text{ mol.l}^{-1}$. This effect can be correlated with the increase of the monomeric species present in Fe(III) solution. However at highest Fe(III) concentrations, 1.0×10^{-2} and $5.0 \times 10^{-2} \text{ mol.l}^{-1}$, a decrease of the rate of monuron disappearance was observed when compared to the kinetics of the reaction with Fe(III) concentration equal to $1.0 \times 10^{-3} \text{ mol.l}^{-1}$. These results illustrate the importance of the speciation of iron in aqueous solution. Indeed, the nature of the iron present in the environment is a parameter which can catalyse or induce pesticides photodegradation. Also, it should be noted that the method of introduction of iron into clay depends on the photochemical behaviour of pesticides; when it is added with clays, the pollutants photodegradation is accelerated. These results have been found in the studies carried out by Menager (Menager et al., 2009). However in our study iron was introduced between the layers of montmorillonite (Tajeddine et al., 2010).

3.3.4 Identification of photoproducts

The photoproducts formed in the irradiation of monuron adsorbed onto K-montmorillonite after 35 min irradiation were investigated by LC/MS analysis. Fig.14.

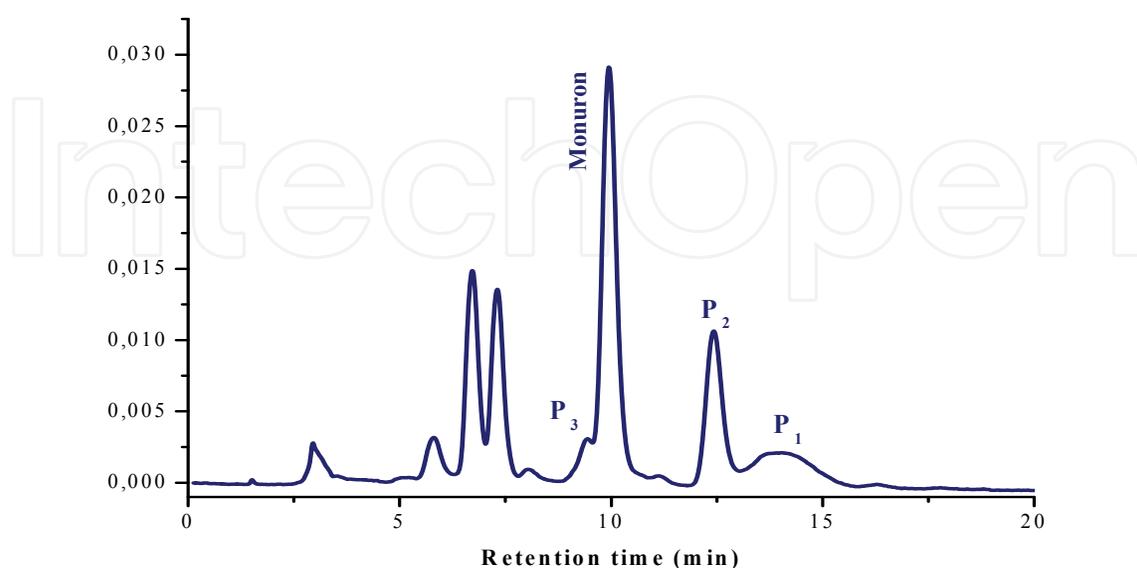


Fig. 14. Chromatogram of the methanol extract of the monuron irradiated on montmorillonite during 35 hours

Three photoproducts were identified by the molecular ion and mass fragment ions. The structures of the main photoproducts are presented in table 11. In addition to these compounds, some other products were detected but it was not possible to determine their structure due to their low concentration.

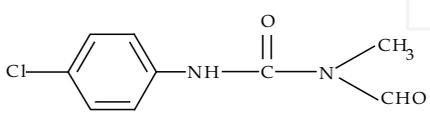
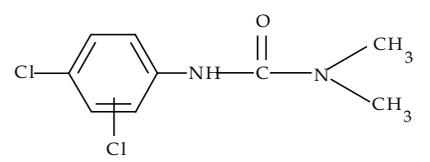
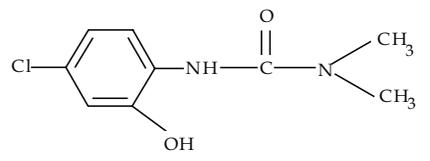
Photoproduct	Structure	Molecular weight (m/z)	Retention time (min)
P₁ N-(4-chloro-4-chlorophenyl)- N',N'- dimethylurea		232	14
P₂ N-(4-chlorophenyl)-N'- formyl, N-dimethylurea		212	12.5
P₃ N-(4-hydroxy-4-chlorophenyl)- N',N'- dimethylurea		214	9.4

Table 11. Photoproducts obtained by irradiation of monuron adsorbed onto K montmorillonite

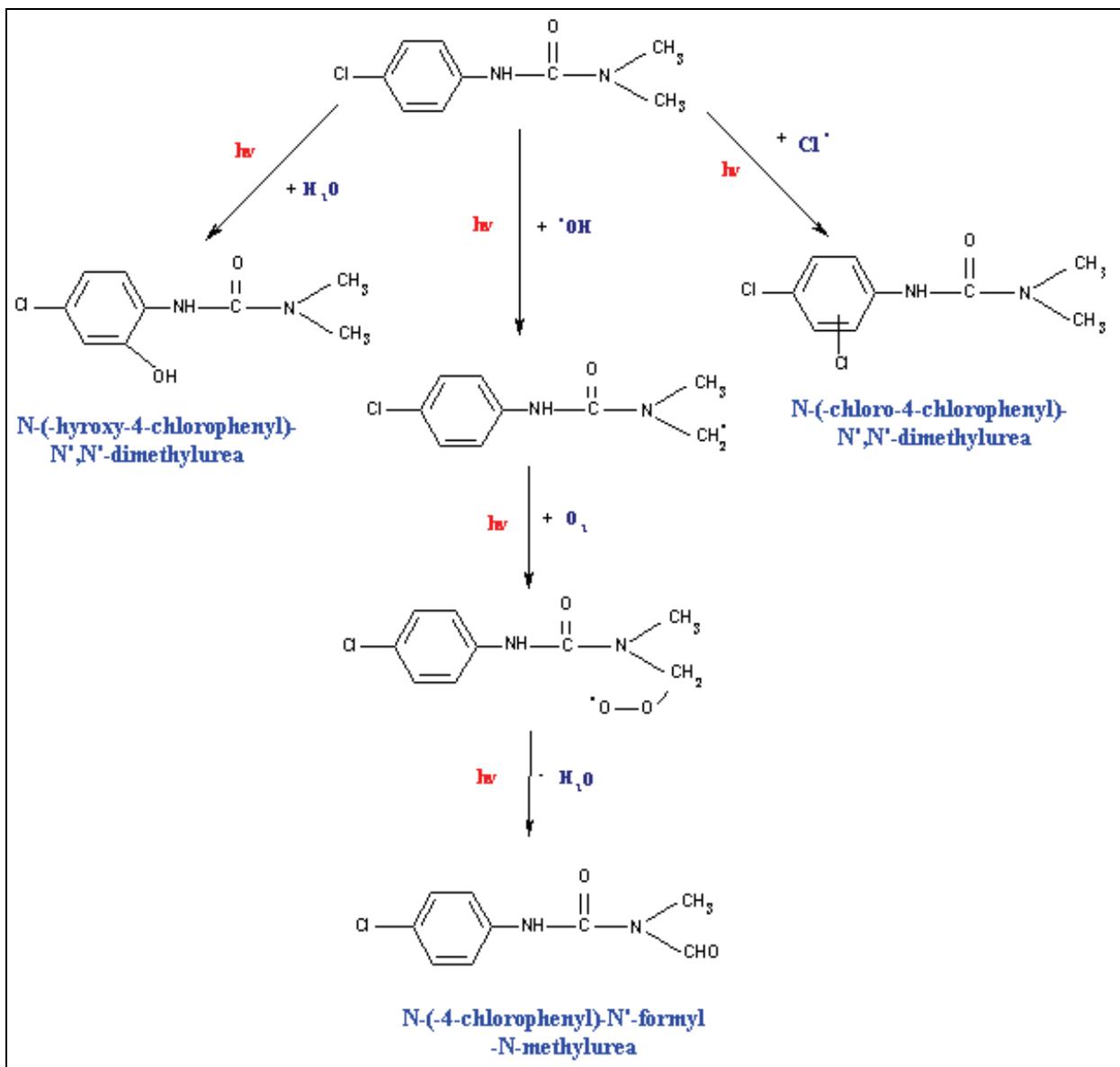
3.3.5 Photodegradation mechanism

Based on the intermediate products listed in table 11, the possible degradation pathway for monuron irradiated onto K-montmorillonite is proposed in schema 1.

Upon light excitation, the first step was initiated by the substitution of a hydrogen atom by a chlorine atom. This reaction occurs at the aromatic group. The formation of the two other products may attributed to the attack of the hydroxyl radicals, formed through the excitation of iron (III) species, to either the aromatic moiety or the methyl group of the amine moiety. In the latter case, the formation of the final product can be explained by oxidation of the methyl group to aldehyde function-N (CH₃)₂. This mechanism has been demonstrated in the most studied of phenylurea herbicides transformation (Macounova et al., 2003). It has been characterized as a majority path in the mechanism of photodegradation of aqueous monuron (Mest'ankova et al., 2004).

Some minor products may be formed from the photoproduct 2. The addition of OH on the aromatic cycle reacts rapidly with oxygen to form intermediates radical. These react with the

radicals formed after the opening of the aromatic ring (Pramuro & Vicenti, 1993). The disappearance of the aromatic structure might be due to the formation of a carbene by removal of HCl as was proved in the case of linuron irradiated onto the sand and clay (Richard & Bengana, 1996) and the case of 4 chlorophenol-irradiated in water (Oudjehani & Boule, 1995).



Schema 1. Phototransformation mechanism of monuron irradiated onto montmorillonite

4. Conclusion

The photo-transformation of monuron adsorbed on montmorillonite and irradiated under simulated sunlight is not sensitized by the humic acids and iron. On one hand, humic acid decreased the rate of monuron disappearance is slower owing to a screen effect phenomenon. On the other hand, the presence of iron cannot act an efficient photo inducer of monuron herbicide elimination from dry phase. However, in humid systems, Fe^{3+} appeared to be a good photocatalyst for the removal of monuron from water (Hana 2004).

From the analytical point of view, the Principal photoproducts identified by HPLC/MS/MS initially formed by irradiation of monuron adsorbed onto K-montmorillonite were; a product of oxidation of a methyl group (N-(4-chlorophenyl)-N'-formyl, N-dimethylurea), a product of hydroxylation on the level of the aromatic nucleus (N-(4-hydroxy-4-chlorophenyl)-N',N-dimethylurea) and the 3rd product obtained by a photo-substitution of a hydrogen atom of the aromatic nucleus by a chlorine atom (N-(4-chloro-4-chlorophenyl)-N',N-dimethylurea).

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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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