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Effect of humic substances extracted from Agricultural Moroccan soil on photolysis of Imazaquin herbicide

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ABSTRACT

The photodegradation of imazaquin (50 mg/L) was investigated under simulated sunlight experiments. This photodegradation was evaluated at pH=7 in the presence of humic acids (HA) isolated from Moroccan soil known for their interaction with organic and mineral components. The study was realized at different imazaquin/HA ratios (1/0.1; 1/0.5; 1/1). Irradiation was carried out with polychromatic light using cylindrical reactor equipped with HPK 125W lamp. The concentration of remaining herbicide was followed using a high pressure liquid chromatograph (HPLC) equipped with UV detector at 230 nm. The role of HA on the photodegradation of imazaquin was evaluated by the quantum yield determination. Kinetic parameters of photoreaction show a first order dependence of concentration of imazaquin versus time. The presence of HA induced a decrease of the photodegradation of the pesticide with respect to pure water solution. A short of protection and screen effect of humic substances on the pesticide molecule was observed.

Keywords: Imazaquin, photodegradation, humic substances, aqueous solution.

INTRODUCTION

Use light for the chemical treatment of water is a practical of last century. In all cases, the absorption spectra of pollutants to be degraded limit the direct action of light.

Humic substances representing the principal fraction of organic matter receive increased attention because their reactivity as sunlight absorbers[1]. Depending on their origin, humic substances have a remarkable ability to absorb light and transfer this energy to other substrates and in some cases strongly affect photolysis of xenobiotics[2,3]. In water and in soils humic substances have been found to act as photosensitizers when irradiated at wavelength longer than 290 nm and they have also been reported to produce oxygen species upon irradiation, and be able to photo induce the transformation of pesticides [4,5]. They could behave as quenchers or as light scatters [6].

Imazaquin(Figure. 1) is a herbicide used for pre- or post-emergence control of the broadleaf weeds and grasses in soybeans tillage applied to plant foliage. It is vulnerable to foliar wash off and herbicide washed off from foliage could promote surface water run off due to shorter contact time with soil for sorption [7].

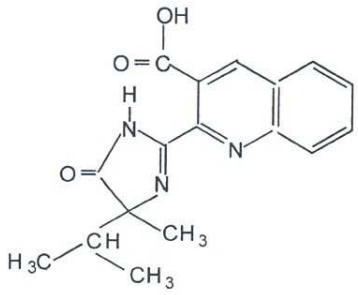

Figure.1: The chemical structure of Imazaquin

In Morocco, it is recommended for weed control in cereal crops [8].

Photodegradation or phototransforation of such molecule may be considered as a very important abiotic mechanism in its transformation in the environment. Several factors can influence the rate of photolysis including the dissolved absorbing compounds and/or sediments such as organic matter and clays.

MATERIALS AND METHODS

Chemicals

Imazaquin was purchased from Laboratory of Dr Ehrenstorfer, Germany, at purity greater than 99%. Ultra-pure water was used. HPLC reagents were from Riedel de Haen. Concentration of 50 mg/L, of Imazaquin was used. Experiments were carried out at pH=7 (pH of environmental interest), buffered with a mixture of K_2HPO_4 3.9.10-4 mol/L and KH_2PO_4 $6.1.10^{-4}$mol/L (v/v).

Humic substances

They were extracted from agricultural soil of Rabat region. The extraction was carried out by standard procedure described elsewhere[8]. In brief, the original material was shaken overnight in 0.5 NaOH under N atmosphere. HA were precipitated from alkaline extracts at pH=I (6N HCI). The isolated HA were purified by double acid-base precipitation-dissolution procedure, treated with HCI-HF 0.5% (v/v) solution, dialyzed against distilled water until chloride free, and freeze-dried. The HA were analyzed for their elemental content using a Perkin-Elmer 40C microanalyser and for total, carboxylic and phenolic fraction by standard methods [9,10]. (Table I).

Analytical procedure

UV-Vis absorption spectra were recorded using Uvikon 930 spectrophotometer. The disappearance of Imazaquinat various irradiation times was determined by Millipore Waters model 510 HPLC system equipped with UV detector at 230 nm and Ci8ODS2 column (25X4.6 i.d). A mobile phase was made by 75% water and 25% acetonitrile adjusted to pH=2.7 by concentrated H_3PO_4 (0.8m1/L), retention time was 5.6 min[8].

Photoreactor.

Photodegradation processes were carried out using cylindrical reactor. The irradiation source was HPK 125 W lamp (T=20°C), which is 95% monochromatique at 365 nm. The lamp was placed inside the reactor as shown in figure.2

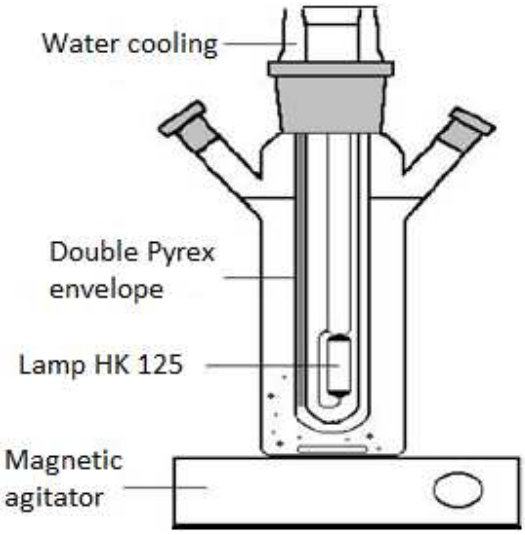

Figure.2 : Photoreactor

Procedure

50 ml of Imazaquin with HA at different weight ratios (1/0.1; 1/0.5; 1/1), were exposed for photodegradation at various illumination times (1, 2, 3, 5 & 8h). Quantum yield is the parameter which characterizes the photodegradation of organic molecule such as Imazaquin is defined as follows:

Φ=D/N [8].

Where D is the number of molecules degraded and N the number of photons absorbed by the solution. In the case of polychromatic light, the quantum yield was calculated at the wavelengths corresponding to the overlap of the absorption spectra of the molecule and the emission spectra of the lamp.

$$\phi_{pest,\Delta\lambda} = \frac{\Delta n_{pest}/\Delta t}{\sum_{\lambda_1}^{\lambda_2} p_{abs}\,\Delta\lambda} = \frac{\Delta n_{pest}/\Delta t}{\sum_{\lambda 1}^{\lambda 2} p_{0,\lambda}[1-10^{\mathrm{D^O}\lambda}]} \quad [II]$$

$\phi_{pest,\Delta\lambda}$: Quantum yield
$\Delta n_{pest}/\Delta t$: Rate of degradation of Imazaquin
$\sum_{\lambda_1}^{\lambda_2} p_{abs}\,\Delta\lambda$: Total photonic flux absorbed by the medium (Einstein/s)
$p_{0,\lambda}$: Incident flux at the wavelength λ
$\mathrm{D^O}\lambda$: Absorption of the medium at λ
$\Delta\lambda$: Wavelength range (5nm)
The quantum yield was determined by using Photon. This software takes into account photodegradation rate of pesticide and its absorption spectrum.

RESULTS AND DISCUSSION

Humic substances properties

The characteristics of HA (Table.1) are similar with that from two different Moroccan from Chaouia region (I and II) soils reported by Mekkaoui et al. [10]and close to those reported in the literature data [11].

Table 1: Elemental and functional characteristics of HA

				acidities in meq/g		
sample	%C	%H	%N	Total	COOH	PhOH
HA	62.9	3.0	1.9	9.0	3.4	5.6
HA (I)	41.7	2.51	2.47	6.04	3.93	0.77
HA (II)	47.6	1.52	2.14	7.84	4.6	0.74

Photodegradation

Generally, HA have no spectral bands characteristics in UV. The UV spectrum of HA shows a continuous absorption without recognizable peaks, increasing with the decreasing wavelength. The absorption spectra of solutions with different dissolved HA doses (weight ratio Imazaquin /HA: 1/0.1, 1/0.5, 1/1) present one maximum at 257 nm due to the Imazaquin molecule (Fig.3) with absorption coefficient of 5400 L.CmI.mol

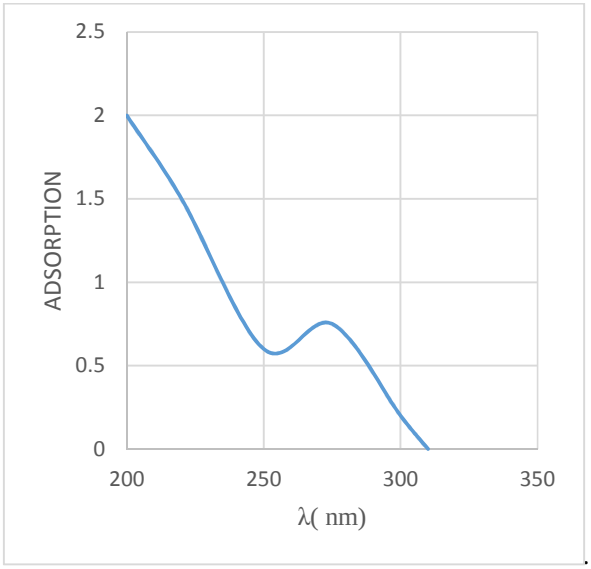

Figure 3: Absorption spectrum of Imazaquin (1mg/L)

The Photodegradation of Imazaquin follows a first-order kinetic in the presence of HA at different ratios studied (Fig.4). The quantum yield values calculated from equation III and the kinetic parameters are reported, respectively, in tables 2 and 3.

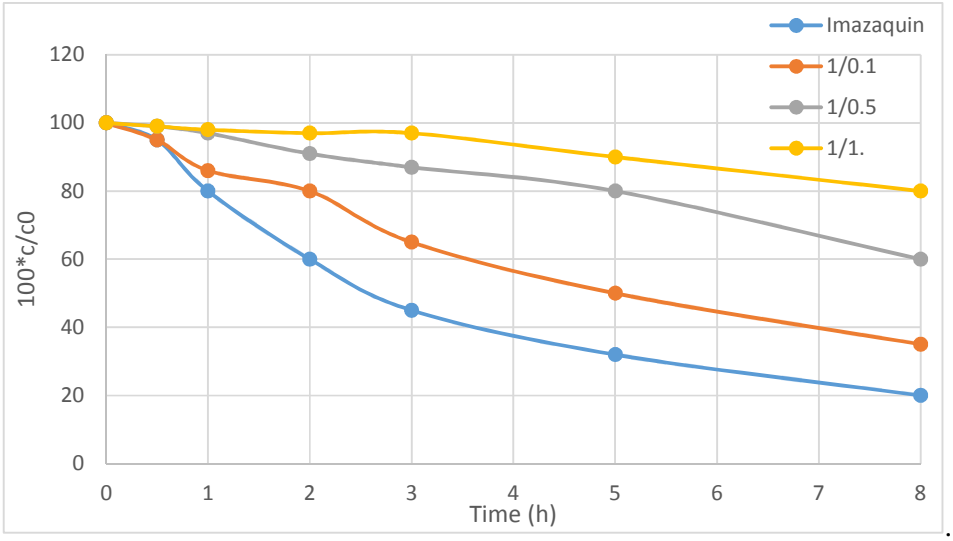

Figure 4: Photodegradation of Imazaquin in the presence of different rates of HA

Table.2: Photodegradation quantum yield values

Imazaquin/HA(weight ratio)	1:0	1:0.1	1:0.5	1: 1
Φ(molecules/photon)	10^{-2}	3.10^{-4}	5.10^{-5}	3.10^{-5}

Table 3: Parameters determined according to the first order kinetic

Imazaquin/HA (weight ratio)	1: 0	l: 0.1	1: 0.5	1: 1
$T_{1/2}$ (h)	3	23	44	49
k(h^{-1})	0.2420	0.0304	0.0156	0.0 l 45

Before addition of HA a quantum yield value of 10^{-2} molecules/photon was obtained. After addition of HA this value decreased drastically and the efficiency of the incident radiation decreased due to the presence of humic molecules. The half-life of imazaquin in water at pH-=.7 is 3h and its degradation reaches 80% within 8h. In the presence of HA the photodegradation of the herbicide decreased with the increase of the concentration of the HA. If we note Φ_0 the quantum yield of photodegradation in the absence of HA and Φ quantum yield in the presence of HA, we observe the linear desactivation of imazaquin by HA (Fi g.5).

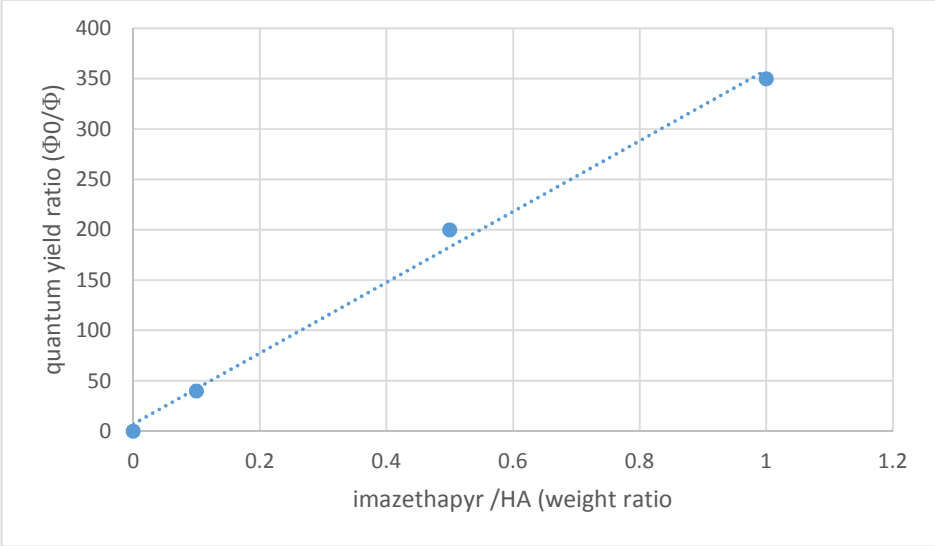

Figure 5: Desactivation of imazaquin by HA

In order to evaluate the role of the HA, we have computed new calculation of the photodegradtion quantum yield of Imazaquin (Table.4) by removing the absorption of the HA. The quantum yield was calculated from equation [III]

$$\phi_{pest,\Delta\lambda} = \frac{\Delta n_{pest}/\Delta t}{\sum_{\lambda_1}^{\lambda_2} p_{abs,-\mathrm{Im}\,az\Delta\lambda}} \text{[III]}$$

And

$$\sum_{\lambda_1}^{\lambda_2} p_{abs,-\mathrm{Im}\,az\Delta\lambda} = \sum_{\lambda_\lambda}^{\lambda_2} \frac{DO_{inaz\lambda}}{DO_T} I_{0,\lambda}\Delta\lambda\,[\,1 - 10^{D}O_{T,\lambda}]$$

With:

$\sum_{\lambda_1}^{\lambda_2} p_{abs,-\mathrm{Im}\,az\Delta\lambda}$: Total photonic flux absorbed by imazethapyr (Einstein/s)

$DO_{inaz\lambda}$: Absorption of Imazaquin at λ

$DO_{T,\lambda}$: Adsorption of medium at λ (AH+ Imazaquin)

Table.4: Photodegradation quantum yield of Imazaquin

Imazaquin/HA(weight ratio)	1: 0	1: 0.1	1: 0.5	1: 1
Φ	10^{-2}	$1.2.10^{-3}$	$0.9.10^{-3}$	10^{-3}
∑ Pabs(imaz)	1.75 10^{-6}	$1.58.10^{-6}$	1.12 10^{-6}	$0.87.10^{-6}$

The comparison of the results indicates that: -The HA has a screening effect on the photodegradation of Imazaquin. -A lower quantum yield is observed when HA are present in the medium compared to pure solution, this decrease

does not seem to be dependent on the HA concentration and can be explained by either the désexcitation of the excited state of Imazaquin or the adsorption of the pesticide on the HA which stabilized the molecule. Both in the pure herbicide solution and with HA, chromatographic data can show the presence of signals attributable to transformation products which number and area are varying with irradiation time. To use a logical photon (1.04), we worked at 10% of photodegradation, for this reason no attention was paid to the nature and formation mechanism of these photoproducts.

CONCLUSION

The photochemical behavior of Imazaquin in the presence of HA isolated from agricultural soil was completely different from that in buffered solution. HA delay the photodegradation of Imazaquin by their protective and screening effect favoring herbicide activity of the Imazaquin.

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