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ORIGINAL ARTICLE

Effect of iron and humic acid on photodegradation of some pesticides adsorbed on clay surfaces

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Abstract Photochemistry studies can be helpful in assessing the environmental fate of chemicals. For this reason, the photodegradation kinetic studies of the two pesticides orthophenylphenol (OPP) and monuron, largely used in agriculture, were carried out in solid phase. The fungicide OPP and the herbicide monuron were irradiated on the clay fractions (montmorillonite and modified clays) using a suntest simulator. The phototransformation of the parent compound was followed by HPLC technique. The photodegradation process appears to follow the first order reaction. Kinetic parameters were determined and the experimental results show that the photodegradation of these substrates was enhanced in presence of K-montmorillonite, in comparison with Fe(III) exchanged montmorillonite and montmorillonite complexed with humic acid complexes. This study has shown that the iron and humic acid adsorbed on clay surfaces did not increase the degradation rate.

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1. Introduction

Pesticides have become one of the most frequently occurring pollutants in nature. Great concern has developed about pos-

sible effects of such substances on human health and on the environment (Mansour, 1993; Trom et al., 2001). Photodegradation 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, especially in aquatic environments. The soil and its components, which are transported by surface water in the runoff events, play an important role in the process of the organic chemicals in solution, whereas some of the soil components such as humic acids or iron produce an acceleration of the photolysis through a photosensitizing effect (Cox et al., 1996; Liu et al., 2001; Giant et al., 2005).

However, the phototransformation of pesticide adsorbed by the soil components especially clays in absence of water is

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an important question. The aim of the present work was to study the kinetics of photodegradation of two model organic compounds adsorbed on three types of clay; K-montmorillonite, Fe(III) exchanged montmorillonite (Fe(III)-montmorillonite) and montmorillonite complexed with humic acid (HA-montmorillonite) complexes. The two pesticides chosen; OPP and monuron are different in important aspects, namely in their adsorption properties by clays and their physico-chemical proprieties. OPP is commonly used as a fungi-static wax for coating vegetables, and as a disinfectant of storage materials (Appel, 2000), and monuron is an herbicide from the group of phenylurea derivatives (Zhou et al., 2001).

Photodegradation experiments were performed in a Suntest photoreactor, in order to simulate the emission spectrum of sunlight.

2. Experimental

2.1. Materials and methods

2.1.1. Reagents and Clay samples

Orthophenylphenol (CAS no. 90-43-7) and monuron (CAS no. 150-68-5) were obtained from Aldrich (Milwaukee, WI), with purity (>98%). They were used without any further purification. The chemical structures of these pesticides are given in Fig. 1.

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 (1998). Clay minerals composition were analyzed by X-ray fluorescence using AXIOS-P analytical equipment. The chemical composition of clay fractions is summarized in Table 1.

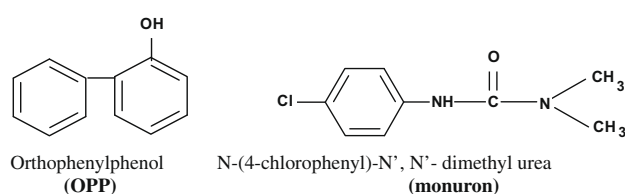


Figure 1 Chemical structure of OPP and monuron.

Table 1 Chemical composition of clay fractions obtained by X-ray fluorescence.

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

Adsorption of OPP and 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 a desiccator for vacuum drying during 24 h.

2.1.2. Irradiation experiments

30 mg of pesticide-clay was irradiated in Suntest 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.

2.2. Analytical procedure

OPP and monuron concentrations were determined by high performance liquid chromatography HPLC Water equipped with two pumps, type 510, UV-Visible detector with standard diode bar 996 and a sampler type 717. The unit is controlled by Millennium software. Chromatography was run using a reverse phase Nucleodur column (C₈-5 µm), length 250 m and intern diameter 4.5 mm. A programmable detector operating at a wavelength 245 nm was used. The mobile phase was methanol and water 65/35 at flow rate of 1 ml/min. The retention times of OPP and monuron were 8.4 and 6.5 min, respectively.

3. Results and discussion

3.1. Absorption spectra of pesticide studied

The absorption spectra of OPP and monuron are given in Fig. 2.

OPP presents two absorption bands centered on $\lambda_{\max} = 245$ nm and $\lambda_{\max} = 282$ nm with a molar absorption coefficient of 12600 mol⁻¹ L cm⁻¹ and 5160 mol⁻¹ L cm⁻¹, respectively. OPP is suitable for absorbing the solar radiation and to be degraded under the sunlight condition. Monuron presents a maximum at 245 nm with a molar absorption coefficient equal to 17800 mol⁻¹ L cm⁻¹ and a small shoulder at 280 nm. This molecule presents a very weak covering with the light of suntest and sunlight.

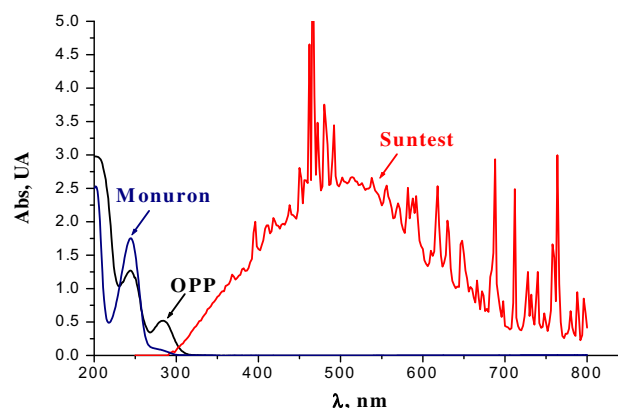


Figure 2 The absorption spectra of OPP and monuron in aqueous solution and the spectrum emission of suntest (xenon lamp).

Table 2 Cation exchange capacity of clay minerals.

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

3.2. Characteristics of clay fractions

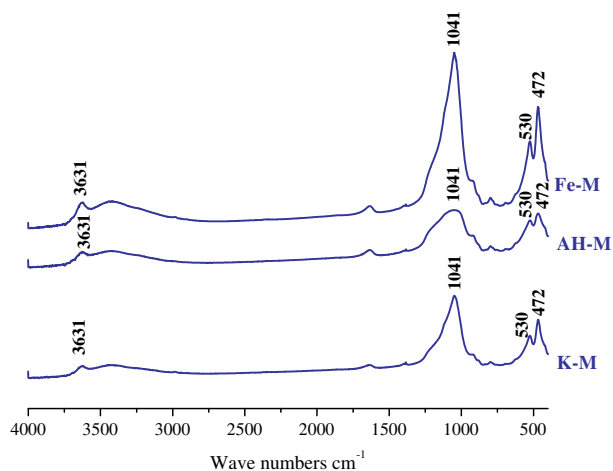
The cation exchange capacity (CEC) is an important characteristic of clays. It represents the overall quantity of charges available on the exchanger material. It is related to the surface density of charges through the specific surface area. The relative concentrations of the cations help determine the degree of adsorption. The method used for determining CEC, which involves the complete exchange of the naturally-occurring cations by ammonium, is the standard method for CEC determination.

Table 2 shows the values of CEC for the different clay minerals.

The values consigned in Table 2 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 clay minerals (Baize, 1988).

The IR spectra of clay fractions are obtained, starting from the pastilles of KBr (0.1%) using a spectrophotometer of the kind Perkin Elmer 2000. The examination of these spectra 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 and Fraser, 1994). The broad band around 1041 cm^{-1} corresponds to Si-O-stretching (Madjeva and 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. 3.

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

**Figure 3** IR spectra of K-M, Fe-M and HA-M.

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., 2008).

The XRD measurements were performed using a Philips X-ray diffractometer employing nickel filtered $\text{CuK}\alpha$ radiation. The X-ray diffraction pattern of clay fractions is given in Fig. 4. 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 corresponds to plane 001 was evolved from 9.45 to 15.04; which 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. Photodegradation experiments

3.3.1. Comparison of degradation kinetics for OPP and monuron
Fig. 5 shows the evolution of OPP and monuron adsorbed on clays with time under irradiation.

OPP is rapidly degraded in the presence of light, the OPP absorption of UV enters in the ranges of sunlight emission spectra, indicating that direct photolysis of the compound is

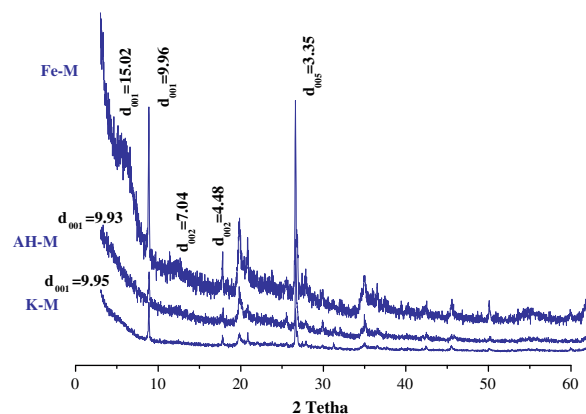
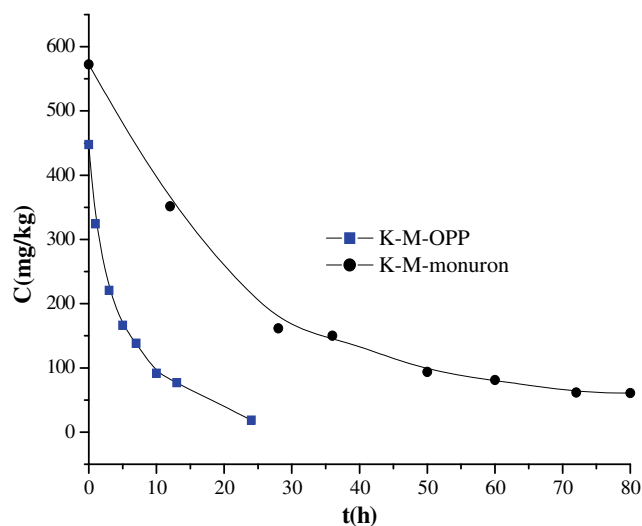
**Figure 4** XRD pattern of K-M, Fe-M and HA-M.**Figure 5** Kinetics of disappearance of the OPP and the monuron irradiated on K-M.

Table 3 Constants speed and half-life time of OPP and monuron irradiated onto K-M.

	k (mg kg ⁻¹ h ⁻¹)	k_{app} (h ⁻¹)	$t_{1/2}$
K-M - OPP	123.38	0.27	2 h 3 min
K-M - monuron	18.4	0.032	21 h 35 min

occurring. The disappearance of monuron was done on a scale of time much more important, half-life time was 21 hours. In aqueous medium Hill et al. (1955) showed that the disappearance of 83% of monuron in aqueous solution exposed to the sun during 48 days. Curves followed first order kinetics and half lives are given in Table 3. The different rates observed for the two pesticides suggest that the difference in chemical structure can give rise a different photochemical behaviour.

3.3.2. Kinetics of OPP and monuron disappearance in presence of humic acid (HA)

The kinetics of OPP and monuron disappearance on K-montmorillonite and HA-montmorillonite are shown in Fig. 6. As shown in Fig. 6, the photodegradation of pesticides is lower 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 two pesticides is quasi-total in the experiment of K-M. Kinetics and half lives of these experiences are given in Table 4.

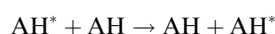
The results show that the speed of disappearance of pesticides was decreased from 123.38 to 77.05 mg kg⁻¹ h⁻¹ and from 18.4 to 9.09 mg kg⁻¹ h⁻¹ for OPP and monuron, respectively, by the complexation of humic acid to montmorillonite. So, the presence of humic acid, complexed with montmorillonite, protects pesticide from photodegradation, due to the screen or light attenuation effect of humic acid. This effect could be attributed also to the indirect photolysis due to absorption of light energy by humic acid.

The phototransformation of OPP and monuron sensitized by the humic substances into aqueous medium were studied by Richard and Bengana (1996). They were showed that the transformation of the pesticides photosensitized by humic acid is faster. This is explained by an effective reaction causing a transfer of hydrogen atom from humic acid to pesticides. Un-

Table 4 Constants speed and half-life times of OPP and monuron irradiated onto K-M and HA-M.

	k (mg kg ⁻¹ h ⁻¹)	k_{app} (h ⁻¹)	$t_{1/2}$
<i>OPP</i>			
K-M	123.38	0.27	2 h 3 min
HA-M	77.05	0.16	4 h 18 min
<i>Monuron</i>			
K-M	18.4	0.032	21 h 35 min
HA-M	9.09	0.018	38 h 54 min

der the current conditions, inhibitive processes, such as for example the auto-inhibition can also contribute in the reduction of the total process effectiveness (Scrano, 1997)



3.3.3. Kinetics of OPP and monuron disappearance

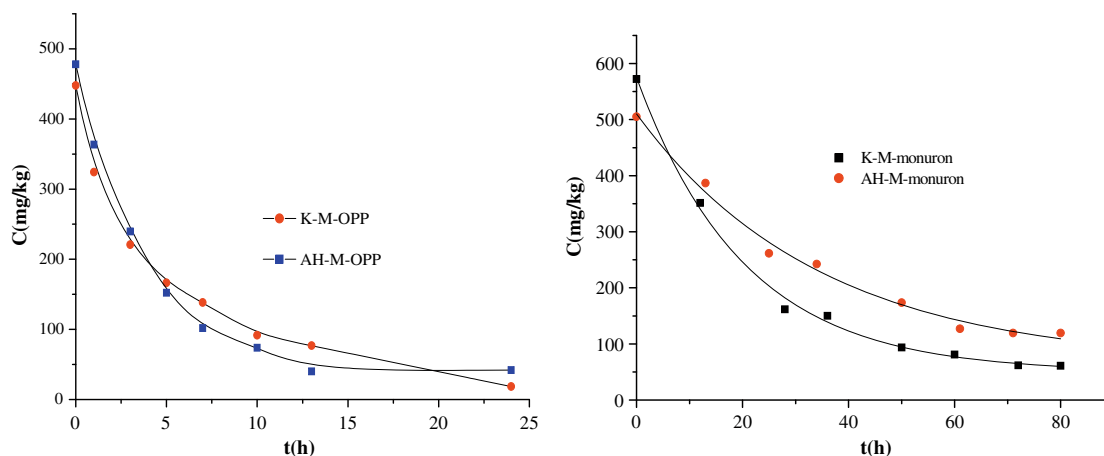
The photodegradation kinetics of OPP and monuron adsorbed by Fe(III)-montmorillonite complexes are presented in Fig. 7.

The presence of iron related to montmorillonite has a negative effect on the degradation speed of OPP and monuron. Table 4 illustrates the kinetics and the half lives of these experiences.

As shown in Table 5 the half-life times of OPP photodegradation were 2 h 3 min and 4 h 18 min for K-montmorillonite and Fe(III)-montmorillonite, respectively. For monuron, degradation is completed after 43 and 78 hours K-M and Fe-M, respectively. The slow degradation can be explained by the consumption of the rays luminous by Fe³⁺, these ions cause a competition with the pesticides molecules.

In aqueous medium Mestanko (2004) has observed that degradation speed of monuron photo induced by Fe III was accelerated and its strongly dependent on Fe(OH²⁺) concentration.

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 Ménager (2007). However in our study iron was introduced between the layers of montmorillonite

**Figure 6** Kinetics of disappearance of OPP and monuron irradiated on K-M and HA-M.

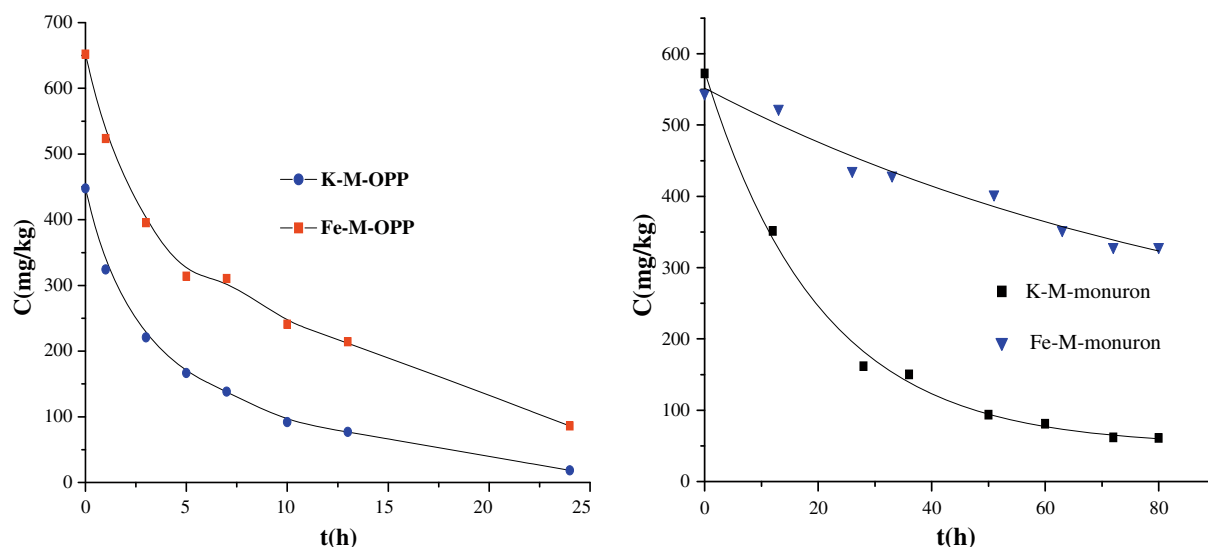


Figure 7 Kinetics of disappearance of OPP and monuron irradiated on K-M and Fe-M.

Table 5 Constants speed and half-life time of OPP and monuron irradiated onto K-M and Fe-M.

	k (mg/kg h)	k_{app} (h^{-1})	$t_{1/2}$
<i>OPP</i>			
K-M	123.38	0.27	2 h 3 min
Fe-M	77.05	0.16	4 h 18 min
<i>Monuron</i>			
K-M	18.4	0.032	21 h 35 min
Fe-M	9.09	0.018	38 h 54 min

through the adsorption process. This prevents the production of hydroxyl radical, which explains the results found.

4. Conclusion

The phototransformation of OPP and monuron adsorbed on clay under irradiation simulating sunlight gives the following conclusions:

- The speed of disappearance of pesticides depends on clay mineralogical phase, their capacities of adsorption, and on physicochemical proprieties of pesticides.
- The phototransformation process is relatively fast for OPP in comparison with monuron. The highest speed was noted for OPP irradiated on K-montmorillonite.
- Kinetics of OPP and monuron photodegradation was slowed down in presence of iron and humic acid complexed with montmorillonite. These substances do not play any photocatalyser part in dry phase.

Acknowledgement

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