Journal of Thermal Analysis, Vol. 50 (1997) 257-268

Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

ADSORPTION OF ALACHLOR BY MONTMORILLONITES

A. Nasser[1], *M. Gal*[1], *Z. Gerstl*[1], *U. Mingelgrin*[1] *and S. Yariv*[2]

[1]Institute of Soils and Water, The Volcani Center, ARO, P.O.Box 6, Bet Dagan, 50250
[2]The Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract

The adsorption of the tertiary aromatic amide alachlor by Na-montmorillonite and Al-polyhydroxy-montmorillonite was investigated by DTA, XRD, SEM and Thermo-FTIR Spectroscopy. This molecule is adsorbed into the interlayer space of the montmorillonite, replacing interlayer water. In this organo-clay complex the interlayer water forms hydrogen bonds with N or O atoms of the tertiary amide group. Samples which were aged during six months degraded by hydrolysis to give mainly secondary amide. This reaction was catalysed by Al-polyhydroxy-montmorillonite more than by Na-montmorillonite.

Keywords: adsorption, alachlor, degradation, montmorillonite

Introduction

Montmorillonite cross-linked with polyhydroxy cationic species of polyvalent metals, produces a three-dimensional network interlaced with channels and pores of different size, which may be considered as a precursor of pillared clay (PILC) [1, 2]. Different molecules of appropriate size present in the montmorillonite suspension during its saturation with polyhydroxy cationic species, can be adsorbed or become entrapped in the pores. Sorption of herbicides to organic and inorganic surfaces may decrease or increase their degradation rate, depending on the type of binding of the organic molecule to the surface [3, 4].

Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide], is a preemergence herbicide which has become popular for weed control in corn and soybeans. Very little information is found in the literature on the adsorption mechanism of alachlor by soil components. Alachlor sorption by soils was investigated and found to be the highest in surface soil (0–15 cm) and decreased with depth.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

It was positively correlated to soil organic carbon content [5]. A similar conclusion was obtained from radioactive studies [6].

Recently Almandros studied the effect of modified humic acids on the sorption of alachlor and other herbicides by soil components [7]. He showed a correlation between adsorption and the aromatic/aliphatic ratio in the humic acids and with the particle size of the substrate. To the best of our knowledge there is no information on the interaction between alachlor and the soil minerals and on the fine structure of the complex which may be formed between these components. The results presented herein demonstrate our efforts to study the adsorption of alachlor by Na- and Al-polyhydroxy cross-linked montmorillonite. Since montmorillonite is the principal clay mineral in most Israeli soils and in many other places, this can be used as a model for the interactions of this herbicide in Israeli soils.

As well this study may lead to prepare a controlled release formulation for agricultural uses from a pillared clay. Controlled release enables efficient and economical application of the active ingredient while at the same time reducing the danger of undesired side-effects such as environmental pollution. The controlled release of pesticides can, in many cases, permit safer, more efficient and more economical crop production.

In the present study alachlor was loaded on Na-montmorillonite and on Al-polyhydroxy treated clay. The physico-chemical characters of this complex were tested by DTA, XRD, SEM and Thermo-FTIR spectroscopy.

Experimental

Materials

Montmorillonite was obtained by Fisher. Alachlor (93% purity) was supplied by Agan Chemicals. It was used without further purification. $AlCl_3$, NaCl and NaOH were of analytical quality.

Preparation of the clay samples

Na-montmorillonite: The homoionic Na-montmorillonite was prepared by washing the commercial Fisher bentonite five times with 1N NaCl solution, followed by removal of excess salt by dialysis. The end of the washing process was determined by $AgNO_3$.

Na-montmorillonite/alachlor: 200 mg of Na-montmorillonite were treated with 200 mg of alachlor dissolved in 1 ml acetone. The acetone was evaporated at room temperature.

Al-polyhydroxy cross-linked montmorillonite (PILC): An Al-hydroxide solution with an OH/Al molar ratio of 1.85 was prepared by dropwise addition of aqueous 0.2 M NaOH to a 0.2 M $AlCl_3$ solution. The resulting solution was aged at 25°C for one week. Under these conditions the Al-polyhydroxy cation $[Al_{13}O_4(OH)_{24}H_2O]^{7+}$, known as the Keggin ion, was formed in solution. The Keggin ion solution was added dropwise with vigorous stirring to a 200 mg L^{-1} Na-montmorillonite suspension. The Al/montmorillonite ratio was 1.96 mM g^{-1}. The resulting flocs were left to settle for two hours, the supernatant was then removed, and the sediment was freeze-dried.

Al-polyhydroxy-montmorillonite/alachlor: 200 mg of alachlor were mixed with 200 mg of Na-montmorillonite, and the mixture was suspended in one liter of water. The produced suspension was treated with a Keggin ion solution as described above. Dry material from Keggin ion solution (DKI) was obtained by freeze drying of the aqueous Keggin ion solution.

Differential thermal analysis

A home-made DTA instrument was used [8]. The thermocouples were made of platinum and platinum +10% rhodium. The rate of heating was 10°C min^{-1}. Several milligrams of the temperature markers AgCl (445°C) and NH_4NO_3 (85, 125, 212°C) were added to the inert material to act as internal temperature indicators.

X-ray diffraction

X-ray diffraction patterns were measured using a Philips PW 1720 diffractometer with Ni-filtered CuK_α radiation. The scanning rate was one degree per min. Samples were measured as powder at room temperature and after overnight heating at 200 and 300°C.

Scanning electron microscopy

Scanning electron micrographs were carried out on freeze dried samples using a Jeol JSM-T330A instrument.

Thermo infrared spectroscopy

FTIR spectra were obtained with a Nicolet model Magna 550 spectrometer in KBr disks. The clay was saturated with excess amounts of alachlor. Samples were studied by IR spectroscopy: a) two days after saturation of the clay with alachlor (fresh samples); b) half a year after the the saturation (aged samples). KBr disks were prepared and the spectra were recorded immediately after the preparation of the disks. Since the disks contained excess alachlor they were thermally treated at 105°C for five days and after re-pressing the disks the spec-

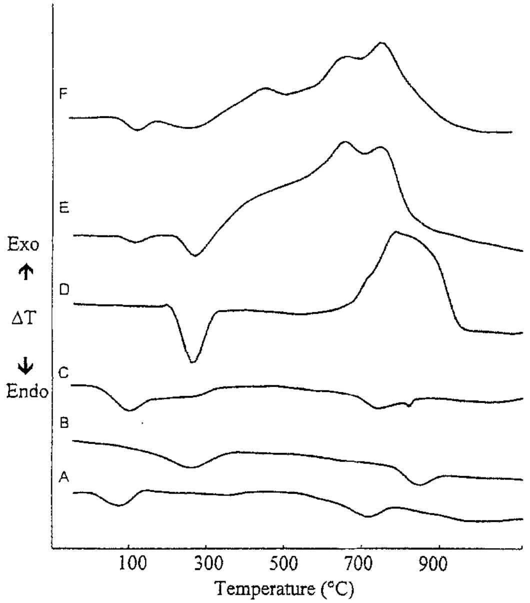


Fig. 1 DTA curves of (A) Na-montmorillonite, (B) Alumina gel (freeze dried Keggin ion), (C) Al-polyhydroxy-montmorillonite (PILC), (D) Alachlor, (E) Na-montmorillonite treated with alachlor and (F) Al-polyhydroxy-montmorillonite treated with alachlor

tra were recorded. The excess free alachlor was evolved during the thermal treatment and the recorded spectrum was that of the adsorbed alachlor.

Results and discussion

Thermal analysis

DTA curves of Na-montmorillonite, Al-polyhydroxy treated clay (PILC) and of these two clays treated with alachlor are shown in Fig. 1. For comparison, the DTA curves of DKI (obtained by drying the Keggin ion solution) and of alachlor are also shown. Na-montmorillonite (curve a) shows two endothermic peaks at 90 and 690°C which represent the dehydration and dehydroxylation of the clay respectively. Al-polyhydroxy clay (curve c) shows an additional broad endothermic effect ranging from the dehydration peak up to 280°C. This is probably due to the evolution of water initially hydrating the Keggin ion followed by the evolution of Keggin ion structural water, migrating through the channels of the cross-linked aluminum-polyhydroxy cation [9]. In addition to the dehydroxylation peak of Al-polyhydroxy clay a small endothermic peak appears at 745°C, which might be due to residual interlayer aluminum oxy-hydroxide.

The DKI DTA curve (curve B) shows an endothermic effect which starts at about 70°C and represents dehydration. This effect ends with an endothermic peak at 270°C which represents the first stage of the dehydroxylation of the alumina gel. Up to this stage the DTA curve is similar to the DTA curve of a gel which was precipitated at *pH* 5 by Mackenzie and Berggren [10]. The second endothermic peak appears in our curve at 800°C which seems to be high for the second stage of dehydroxylation of the alumina gel as reported by Mackenzie and Berggren [10].

The DTA curve of neat alachlor shows an endothermic peak at 220°C which probably represents the boiling of the compound. According to the "Pesticide Manual" alachlor boils at 100°C under a pressure of 0.02 mm Hg [11]. This compound decomposes during boiling in air atmosphere. At the boiling point most of it evaporates from the DTA cell and the residue is polymerized and later is oxidized. The DTA curve shows that the oxidation starts at about 580°C. An extraordinary shaped exothermic peak appears at 770°C.

The DTA of Na-montmorillonite treated with alachlor shows an endothermic peak at 220°C, indicating that the sample contains free alachlor. The dehydration peak at 90°C becomes very weak, compared with the DTA curves of Na-montmorillonite which were not saturated with alachlor. This is an indication that the adsorbed alachlor replaced interlayer water, and is located in the interlayer space.

The oxidation of the adsorbed alachlor starts immediately after the endothermic peak showing a bend at 390°C and two exothermic peaks at 600 and 700°C. The differences between this DTA curve and that of the neat alachlor is due to the fact that the herbicide is sorbed by the clay.

The exothermic region of the DTA curves of the Al-pillared clay/alachlor complex is similar to the Na-montmorillonite/alachlor complex, in that both show that the herbicide is adsorbed by the clay. However, in the Al-pillared clay complex, only small amounts of free alachlor are present, as is indicated by the small endothermic peak at 220°C. In contrast to Na-montmorillonite, the dehydration peak at 90°C becomes only slightly smaller than that peak in the DTA curve of Al-pillared clay, indicating that only part of the interlayer water is replaced by the organic molecule.

The exothermic region of the DTA curves in Na-montmorillonite and Al-pillared montmorillonite treated with alachlor shows three exotherms. The first exotherm at 390°C (shoulder) and 450°C in the curves of Na-montmorillonite and Al-pillared montmorillonite, respectively, represents the oxidation of hydrogens associated with polymerization of carbons to charcoal. The second exotherm at 600°C in both clays represents the oxidation of the charcoal obtained from aliphatic carbons. The third exotherm at 700°C in both clays represents the oxidation of the charcoal obtained from aromatic carbons [12]. The differences between the intensities of these peaks in the two curves can be explained as follows: The sample of the Na-montmorillonite contains more alachlor than the sample of the pillared clay. Consequently at the low temperature only hydrogens are oxidized and all carbons polymerize to charcoal. In Al-pillared montmorillonite some of the aliphatic carbons are also oxidized at this stage and consequently the intensity of the 600°C peak is weaker than that of the aromatic carbons oxidation.

X-ray diffraction

Table 1 summarizes the interlayer spacings of the Na- and Al-polyhydroxy-montmorillonite before and after treatment with alachlor. Na-montmorillonite dehydrated to 0.97 nm during the thermal treatment at 300°C whereas Na-montmorillonite treated with alachlor did not shrink to this spacing, this indicates that the organic material was present in the interlayer space. At 300°C the sample became black indicating the intercalated alachlor was graphitized.

Table 1 Interlayer spacings (nm) of montmorillonites before and after treatment with alachlor at room temperature and after thermal treatments

Sample	25°C	200°C	300°C
Na-montmorillonite	1.09	1.06	0.97
Na-montmorillonite/alachlor	1.60	1.60	1.58
Al-polyhydroxy-montmorillonite	1.43–1.53	1.74	1.77
Al-polyhydroxy-montmorillonite/alachlor	1.79	1.80	1.63–1.71

In contrast to Na-montmorillonite, Al-polyhydroxy-montmorillonite did not shrink to 0.97 nm at 300°C. This substantiates that the polyhydroxy cation is located in the interlayer space. The c-spacing of this sample after the thermal treatment increased from 1.4–1.5 nm at room temperature to 1.77 nm at 300°C, indicating structural rearangement of the Al-polyoxy cation obtained from the dehydroxylation of Keggin cation at elevated temperatures [9]. Al-polyhydroxy-montmorillonite treated with alachlor inditially shows a higher c-spacing than the non-treated clay. It shrinks slightly just after heating at 300°C, proving that alachlor was intercalated in the interlayer space of the Al-polyhydroxy treated clay, and thus disturbed the rearrangement of the skeleton of the oxyaluminum cation which was observed with the PILC.

Scanning electron microscopy

Representative scanning electron micrographs of Na- and Al-polyhydroxy-montmorillonite and these clays treated with alachlor are shown in Fig. 2. Na-montmorillonite shows platy, book-like structure. The Al-polyhydroxy-montmorillonite on the other hand, shows a spongy flocculated mass, with a book house structure. The layers in a book are held together by bridging Al-hydroxy

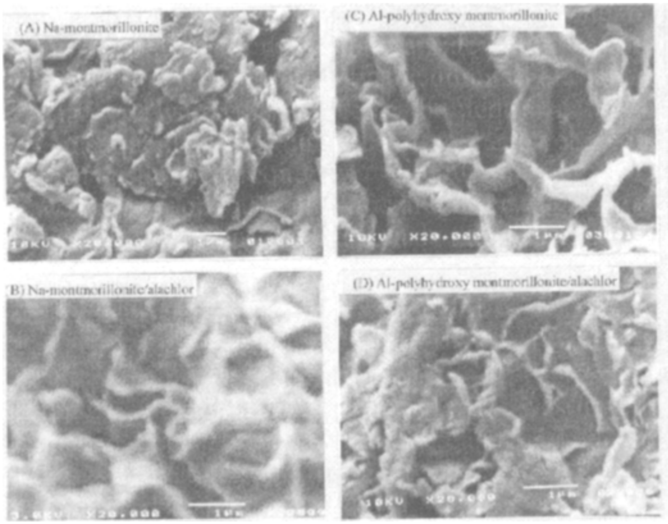


Fig. 2 Representative scanning electron micrographs of (A) Na-montmorillonite, (B) Al-polyhydroxy-montmorillonite, (C) Na-montmorillonite treated with alachlor, and (D) Al-polyhydroxy-montmorillonite treated with alachlor

cations, and the books appear swollen compared to the books in Na-montmorillonite. The books form flocs with an edge to face structure. This structure is obtained due to the polyhydroxy cations which are adsorbed at the edges of the books contributing to the broken bonds positive charges. A few edge to edge associations are also observed.

The micrograph of Al-polyhydroxy-montmorillonite saturated with alachlor is similar to the sample without alachlor but the voids are slightly smaller and some of the books are less swollen. Due to this similarity it is suggested that the floc formation in this case is controlled by the presence of Al-polyhydroxide.

The micrograph of Na-montmorillonite saturated with alachlor looks different from the other samples. The sample forms flocs with a significant edge to edge associations of the books. The voids are smaller than those which were obtained with the Al-polyhydroxy-montmorillonite in the absence or presence of alachlor. As well, the voids are elongated in contrast to the circular voids which are obtained in the Al-polyhydroxy samples. Due to the high edge to edge interaction, the book seems to be more elongated compared to the other samples.

The different floc forms seems to be due to the fact that the alachlor molecule, to some extent, is an amphipatic molecule, the N–(CO–CH_2–Cl)(CH_2–O–CH_3) is a polar head which is bound to the clay layer edge (broken bonds), the aromatic ring with the two ethyl groups is the hydrophobic part of the molecule, which, when absorbed at the clay edges, is directed to the opposite side. An edge to edge association is obtained by van der Waals interaction between the edges.

Thermo-infrared spectroscopy

Samples treated with alachlor and heated at 105°C in KBr disks were examined two days after their preparation and six months later (Fig. 3, Tables 2, 3). Fresh Na-montmorillonite did not show degradation products of alachlor, whereas Al-polyhydroxy-montmorillonite showed some signs of degradation products already two days after the preparation. In the first stage features of adsorbed alachlor will be described and this will be followed by the features of degraded alachlor.

Fresh samples:

C=O vibration: The C=O stretching vibration appears at 1687 cm^{-1} in the spectrum of solid alachlor in a KBr disk. In Na- and Al-polyhydroxy-montmorillonite saturated with alachlor and heated at 105°C as KBr disks for five days, this band is shifted to lower frequences and is splitted to several maxima. The shift indicates the involvement of the C=O groups in new hydrogen bonds. The several maxima indicate that hydrogen bonds with different strengths are obtained. Hydrogen bonds are formed with the interlayer water (Scheme 1A).
C (aromatic)-N vibration: The CN stretching vibration appears at 1319 cm^{-1} in the spectrum of alachlor in a KBr disk. In a disk of Na-montmorillonite saturated

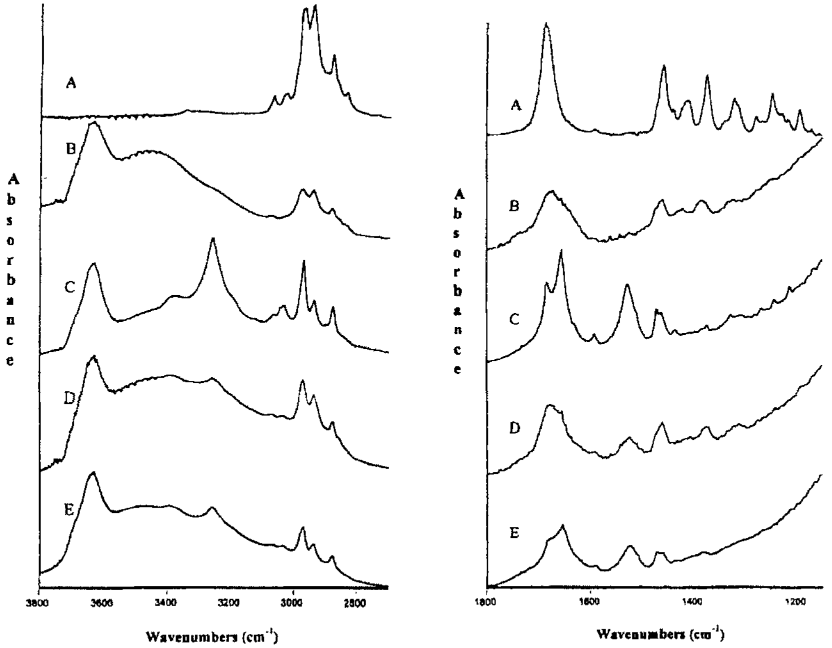


Fig. 3 Infra-red spectra of (A) alachlor, (B) Na-montmorillonite treated with alachlor (fresh sample), (C) sample B aged six months, (D) Al-polyhydroxy-montmorillonite treated with alachlor (fresh sample) and (E) sample D aged six months

with alachlor and heated at 105°C this band is splitted to 1310 (Scheme 1A) and 1323 cm^{-1} the latter indicates the involvement of the nitrogen in hydrogen bond with interlayer water (Scheme 1B).

C (aliphatic)-N vibration: In the spectrum of the neat alachlor two bands can be assigned as CN stretching vibration at 1245 and 1193 cm^{-1}. The location of the former is due to some contribution of a double bond character and is therefore attributed to carbon 1 of the 2-chloroacetamide group. The latter is attributed to carbon of the methoxymethyl group. When alachlor is adsorbed by Na- or Al-polyhydroxy-montmorillonite the 1245 cm^{-1} band splits to two bands at 1241–2 and 1251–2 cm^{-1}. This splitting could be explained by the presence of

Table 2 Assignments and wavenumbers (cm^{-1}) of characteristic absorption bands in the IR spectra of alachlor, neat and adsorbed by Na- and Al-polyhydroxy-montmorillonite

Band assignment*	Neat	Na-mont.	Al-polyhydroxy-mont.
CH(aromatic)	3067, 3026	3070br, 3026sh	3070, 3034
CH_3	2972, 2880	2972, 2880	2972, 2878
CH_2	2940, 2834	2940, 2835sh	2938, 2857sh
C=O	1688	1677, 1671	1677, 1672
		1656, 1647	1655, 1650sh
Ring	1590vw, 1438	1590vw, 1431	1590vw, 1431
	1413, 1410	1419, 1407	1407
C–CH_3	1458, 1373	1458, 1375	1459, 1375
C(aromatic)-N	1319, 1311sh	1323, 1310	1322, 1311
C(aliphatic)-N	1245	1251, 1241	1252, 1242
	1193	1193	1194

*According to Rao [13]; br – broad, sh – shoulder, vw – very weak.

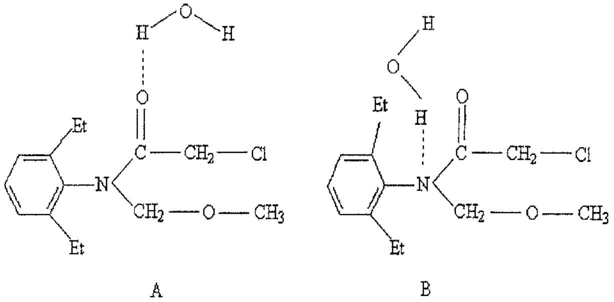
Table 3 Several characteristic new bands in the IR spectra (cm^{-1}) of aged Na- and Al-polyhydroxy-montmorillonite

Band assignment*	Na-mont.	Al-polyhydroxy-mont.
NH	3385, 3261	3398, 3260
C=O stretching (amide I)		
Primary	1684	1684, 1680
Secondary	1653	1658
Tertiary	1678sh	1676
NH deformation (amide II)		
Secondary	1526	1527, 1523

*According to Rao [13]; sh – shoulder

two sites for hydrogen bond formation with water molecules, the oxygen and the nitrogen atoms of the tertiary amide group, as shown in Scheme 1A and B respectively. The probability for double bond character between N and C-aliphatic (in which the nitrogen is the electron pair donor) is smaller in B than in A. Consequently B results in a shift to the lower frequency, wheares A results in a shift to a higher frequency.

Ring vibratioins: Slight shifts are observed in the ring vibration, which may indicate some π intractions between the aromatic ring and the oxygen plane.



Scheme 1 A model showing two different sites for proton acceptance in alachlor and hydrogen bond formation with interlayer water molecules

The C–O–C stretching bands are located at 940 and 1122 cm^{-1} in the spectrum of dimethylether. It is expected that similar bands will appear in the spectrum of alachlor. We therefore assigned bands at 929 and 1125 cm^{-1} as the symmetric and asymmetric C–O–C stretching bands, respectively. Since this region overlaps the Si–O and Al–OH absorption of the clay it was impossible to detect these bands in the spectra of adsorbed alachlor. For the same reason the C–Cl band was not observed in the spectra of adsorbed alachlor.

Aged samples:

The bands which characterise alachlor appeared in the spectra of the aged samples, however they were relatively weak compared to the bands in spectra of fresh samples. Two new bands appeared in the range 3200–3400 cm^{-1} which may be attributed to primary or secondary amide (NH groups). These groups are obtained by hydrolysis of the tertiary amide. In the spectrum of the Na-clay the high frequency band is very weak and broad whereas the second band is sharp and very intense. It is therefore assumed that most of the hydrolysis product is a secondary amide. The primary amide, if formed, is present in relatively small amounts. In the range 2800–3000 cm^{-1} the absorbance decreased significantly indicating the evolution of aliphatic chains. Mainly the CH_2 bands became weaker indicating that the 2-chloroacetamide was the evolved fraction.

In the 1800–1200 cm^{-1} new intense bands appear at 1654 and 1526 cm^{-1} which may be attributed to amide I and amide II bands of a secondary amide.

The principal contribution to bands I and II are the CO and NH group, respectively [13]. A weaker band appeared at 1684 cm^{-1} which is attributed to a primary amide. The amide II band of the primary amide was not detected probably because it was present in small amounts and because this band overlaped the H_2O deformation band.

Al-polyhydroxy-montmorillonite treated with alachlor showed similar degradation products. They were observed already after only 48 h, but their relative amounts increased tremendously after six months.

Conclusions

In the present study the possible adsorption of the herbicide alachlor by Na- and Al-polyhydroxy-montmorillonite was investigated. DTA showed that the thermal curves of alachlor were changed in the presence of both montmorillonites indicating that this herbicide was adsorbed by these clays. The thermal curves also showed that alachlor replaced most interlayer water Na-montmorillonite and to some extent also interlayer water of Al-polyhydroxy-montmorillonite.

X-ray diffraction showed that the adsorbed molecules were located in the interlayer space of Na- and Al-polyhydroxy-montmorillonite. Electron microscopy showed different micrographs between Na- and Al-polyhydroxy-montmorillonite, when Al-polyhydroxy-montmorillonite was treated with alachlor the micrographs were similar to that of the non-treated Al-polyhydroxy-montmorillonite. Floc formation edge-to-face in both cases was due to the polyhydroxy cations which were adsorbed in part at the edges of platelets. Na-montmorillonite showed a book-like structure. When the clay was saturated by alachlor edge-to-edge flocs were obtained due to van der Waals interactions between the non-polar hydrophobic part of the organic molecules which were at the platelet edges.

Thermo-FTIR spectroscopy showed that the adsorption of alachlor was obtained with hydrogen bonds between interlayer water molecules and the N or O atoms of the amide groups. As well, IR showed that aged alachlor-montmorillonite associations degraded by hydrolysis. The aliphatic chains were evolved and a secondary amide was obtained. To a small extent primary amide was also obtained. Al-polyhydroxy-montmorillonite was a better catalyst for this degradation than Na-montmorillonite.

* * *

This research was supported in part under Grand No. HRN5544 GOO2069, US-Israel Cooperative Development Research Program, Human Capacity Development, Bureau for Global Programs, Field Support and Research, USAID, and in part under Grant No. I 195128 12/91, German-Israeli Foundation (GIF) for Scientific Research and Development.

References

1 N. Lahav, U. Shani and J. Shabtai, Clays and Clay Minerals, 26 (1978) 107.
2 R. Burch, Ed., Pillared Clays, Catalysis Today, Vol. 2, Elsevier, Amsterdam 1988.
3 L. G. Morrill, B. C. Mahilum and S. H. Mohiuddin, Organic Compounds in Soils: Sorption, Degradation and Persistence. Ann Arbor Sci. Pub. Inc., Ann Arbor, MI., 1982.
4 S. S. Harper, T. B. Moorman and M. A. Locke, Dev. Ind. Microbiol., 31 (1990) 65.
5 B. N. Stople and P. J. Shea, Soil Sci., 160 (1995) 359.
6 J. M. Tiedje and M. L. Hagedorn, J. Agr. Food Chem., 23 (1975) 77.
7 G. Almendros, European Journal of Soil Science, 46 (1995) 287.
8 M. Gal, J. Thermal Anal., 37 (1991) 1621.
9 S. Aceman, N. Lahav and S. Yariv, J. Thermal Anal., This issue.
10 R. C. Mackenzie and G. Berggren, Differential Thermal Anal., Ed. R. C. Mackenzie, Academic Press, London, 1970 Vol. 1, p. 273.
11 C. R. Worthing and R. J. Hance, Eds., The Pesticides Manual, 9th Ed. British Crop Protection Council, 1991, p. 13.
12 S. Yariv, in "Thermal Analysis in Geosciences - Lecturers Notes in Earth Sciences", W. Smykatz Kloss and S. St. J. Warne, eds., Springer-Verlag, Berlin 1991, p. 328.
13 C. N. R. Rao, Chemical Application of Infrared Spectroscopy. Academic Press, New York 1963, p. 259.