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Adsorption of carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl carbamate) and fenamiphos (ethyl 4-methylthio-m-tolyl-isopropyl phosphoramidate) by homoionic montmorillonite - humic acid complex

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تفاعل الكاربوفران والفيناميفوس مع المونتمريونايت والمواد الحمضية المركبة

لقد بينت هذه الدراسة تأثير الكاتيون المحشو في المركب المعدني(Argilo-humique) على شدة الالتصاق لمبيدين للحشرات الكاربوفران والفيناميفوس. تحصيل المعطيات بينت بأن الالتصاق شديد بالنسبة للفيناميفوس مقارنة مع الكاربوفرانولقد بين طيف الأشعة ما تحت الحمراء تحول منطقة الإمتصاص الطاقي بالنسبة للروابط C=O وC-N للكاربوفيران وP=O للفيناميفوس. ومن جهة أخرى بينت معطيات الإنتشار السيني أن المسافة الفاصلة بين طبقات المركب قد زادت مما يدل على احتوائها المحتمل للكاتيون.

الكلمات المفتاحية : المونتمريونايت الأيونية- المركبات العضوية - التفاعل- الكاربوفران- الفيناميفوس

Adsorption du carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl carbamate) et du phénamiphos (ethyl 4-methylthio-m-tolyl-isopropyl phosphoramidate) par les complexes de montmorillonite homoionique-acide humique

L'étude de l'adsorption a montré l'influence du cation de saturation des complexes argilo-humiques sur le phénomène d'adsorption des deux pesticides carbofuran et phénamiphos. L'analyse des résultats des différents complexes argilo-humiques (Me-M-HA) a montré que l'adsorption du phénamiphos est plus importante que celle du carbofuran. L'analyse des spectres d'absorption infra-rouge a montré des modifications importantes dans les fréquences de vibration des groupements fonctionnels des deux molécules pesticides au cours de leur adsorption par les complexes argilo-humique. L'analyse par diffraction aux rayons-X des complexes argilo-humiques traité par le carbofuran ou le phénamiphos a montré une augmentation significative de la distance réticulaire d_{001}, indiquant la possibilité de pénétration de ces molécules dans l'espace interlamellaire des complexes saturés par des cations polyvalents.

Mots clés : Montmorillonite homoionique - Acide humique - Spectroscopie I.R. - Diffraction aux R.X - Adsorption-Carbofuran - Phénamiphos

Adsorption of carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl carbamate) and fenamiphos (ethyl 4-methylthio-m-tolyl-isopropyl phosphoramidate) by homoionic montmorillonite - humic acid complex

This study was conducted to examine the influence of the interlayer cation in clay-humic acid binary associations on adsorption of the two insecticides carbofuran and fenamiphos. The results obtained indicated that the adsorption capacity of fenamiphos by all samples Me-M-HA tested is higher than that for carbofuran. Infra-red spectra showed that the stretching bands undergo modifications in the spectra for both pesticides molecule. The XRD d_{001} values of clay-humic acid complex before and after treatment with carbofuran or fenamiphos showed that these pesticide were able to penetrate the interlayer space of the complex saturated with polyvalent cations.

Key words : Montmorillonite homoionic complex - Humic acid - I.R. spectroscopy - X-ray diffraction - Adsorption-Carbofuran - Fenamiphos

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INTRODUCTION

Humic substances are important natural products that occur in soil, sediment and water. They have been shown to interact with many pollutants including heavy metals, pesticides and other hydrophobic organic compounds. The presence of humic substances in soil and water have shown to increase adsorption, photo-degradation of contaminants and the apparent water solubility of highly insoluble compounds and decrease biological uptake and toxicity of pollutants (Cox *et al.*, 1994).

Studies on sorption of pesticides by clay minerals and humic substances have been very helpful in evaluating the role of the different soil constituents in sorption, and in assessing interaction mechanisms (Laird *et al.*, 1998; Hermosin & Cornejo, 1993). In soils, however, the intimate association between the individual constituents may cause some modification of their sorptive properties (Cox *et al.*, 1995).

Recently, there has been increasing interest in the behavior of model colloïdal soil components on their inter-association in sorptive of organic contaminants (Onken & Traina, 1997). Association processes between components frequently lead to changes in properties such as pH, specific surface area, and functional group availability, which can make the sorption behavior of the association different from that expected for the sum of the individual constituents (Onken & Traina, 1997).

The purpose of this paper was to investigate the adsorption processes of two insecticides, carbofuran (2,3-dihydro-2,2-dimethyl benzofuran-7-yl carbamate) and fenamiphos (ethyl 4-methylthio-m-tolyl-isopropyl phosphoramidate) on synthetic model systems, which are structurally close to those present in soil. Carbofuran and fenamiphos are respectively an insecticide and a nematicide substances currently used in Moroccan agricultural practices (tomatoes, banana and sugar beets) (El M'Rabet *et al.*, 2000; Dahchour *et al.*, 1998). Approximately 11% of farmers use these insecticides for the protection of tomatoes, sugar beet and banana plantation at 40 kg/ha for Nemacur 10G (fenamiphos) and from 70 to 100 kg/ha for Furadan 5G (carbofuran) (Ammati & Boufardi, 1996).

Focus will be made on adsorption on clay-humic acid complex using adsorption isotherms and confirmation of interaction mechanism by X-ray diffraction (XRD) and infra-red (I.R) spectroscopy techniques.

MATERIAL & METHODS

The Montmorillonite (<2 µm) used in the study was from fluka, Chemie, AG, Switzerland. Homoionic suspensions of Na^+, K^+, Ca^{2+}, Cu^{2+}, Ba^{2+}, Mg^{2+}, and Al^{3+} cations were obtained from the K-montmorillonite form according to the method described by Gonzalez Garcia *et al.* (1953). The homoionic montmorillonite–humic acid complexes were obtained by interaction of commercial humic substance (from Fluka chemical corporation) and montmorillonite saturated with cations species and used as adsorbent matrices. A total of eight different organo-mineral complexes were prepared by adding 5 g of homoionic–montmorillonite (Me-M) to 500 ml of water solution (pH=6.5) of 500 mg/l humic acid. After shaking for 24 h, clay mineral–humic acid associations were washed twice with distilled water, dried at 60°C for 12 hours and stored at room temperature until use.

A suspension of humic acid (1000 ppm) or clay-humic acid complexes (1000 ppm) and carbofuran or fenamiphos (10 ml) was incubated for 24 h at 20°C, under shaking conditions. The mixture contained 10 mg of humic acid or 100 mg of organo-mineral complex and pesticides at concentrations ranging from 10 to 100 µg/ml. Incubation tests were performed in 0.01M $CaCl_2$ solution for humic acid and in distilled water for organo-mineral samples. The suspensions were then centrifuged at 5000 g for 10 min. The supernatants of all preparation were analyzed for the residual pesticide concentration with a Varian Cary UV 100 spectrophotometer apparatus (the absorption maxima were 279 nm and 249 nm for carbofuran and fenamiphos, respectively).The linear range for the absorbency of the two pesticides was 10 – 100 µg/ml ($r \geq 99$, $p<0.001$). The amount of pesticide adsorbed on various matrices was calculated by the difference between the initial (C_0) and the equilibrium concentration (C_e) of the pesticide in solution. All tests of adsorption studies were duplicated.

Adsorption data were plotted according to the Freundlich model : $Ç= K_f C_e^{nf}$ where C_s (µg/g) is the amount of pesticide sorbed at the equilibrium concentration C_e (µg/ml), and K_f and n_f are empirical constants, which are characteristic of the sorbent-sorbate system. The constant n_f is a measure of the non linearity of the isotherm and indicates concentration dependence of adsorption.

The value of K_f coincides with the adsorbed concentration (C_s) value when C_e=1; and hence, can be used to compare the relative adsorption on different adsorbents.

To obtain a sufficiently large concentration of the two pesticides on clay-humic acid complexes for determination of the pesticide-clay humic acid by X-ray and infra-red techniques, 1,2-dichloroethane (1,2-DCE) was used as the solvent. The clay-humic acid complexes were immersed in 2% carbofuran or fenamiphos solutions in 1,2-DCE for one week. The XRD diagrams for the samples thus treated were recorded on a Philips PW 1010 unit with 114.7 mm diameter cameras and CuK_α radiation. For the infra-red studies, KBr pellets of the samples were prepared by mixing 300 mg of the KBr and 1 mg of sample. Spectra were recorded on a Bomen MB-100 FTIR spectrophotometer.

RESULTS & DISCUSSION

The adsorption isotherms of carbofuran by homoionic montmorillonite saturated by humic acid are shown in figure1. For HA, Na-M-HA, Ba-M-HA, Cu-M-HA and Mg-M-HA samples, isotherms were of the S-type (n_f>1) according to the classification of Giles *et al.* (1960), indicating low adsorbate-adsorbent affinity, which increases with the rise in the concentration of adsorbate in solution. Adsorption isotherms of K-M-HA, Ca-M-HA and Al-M-HA complex were special case of L-type (n_f<1) curves, in which the solute has such high affinity that in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in solution.

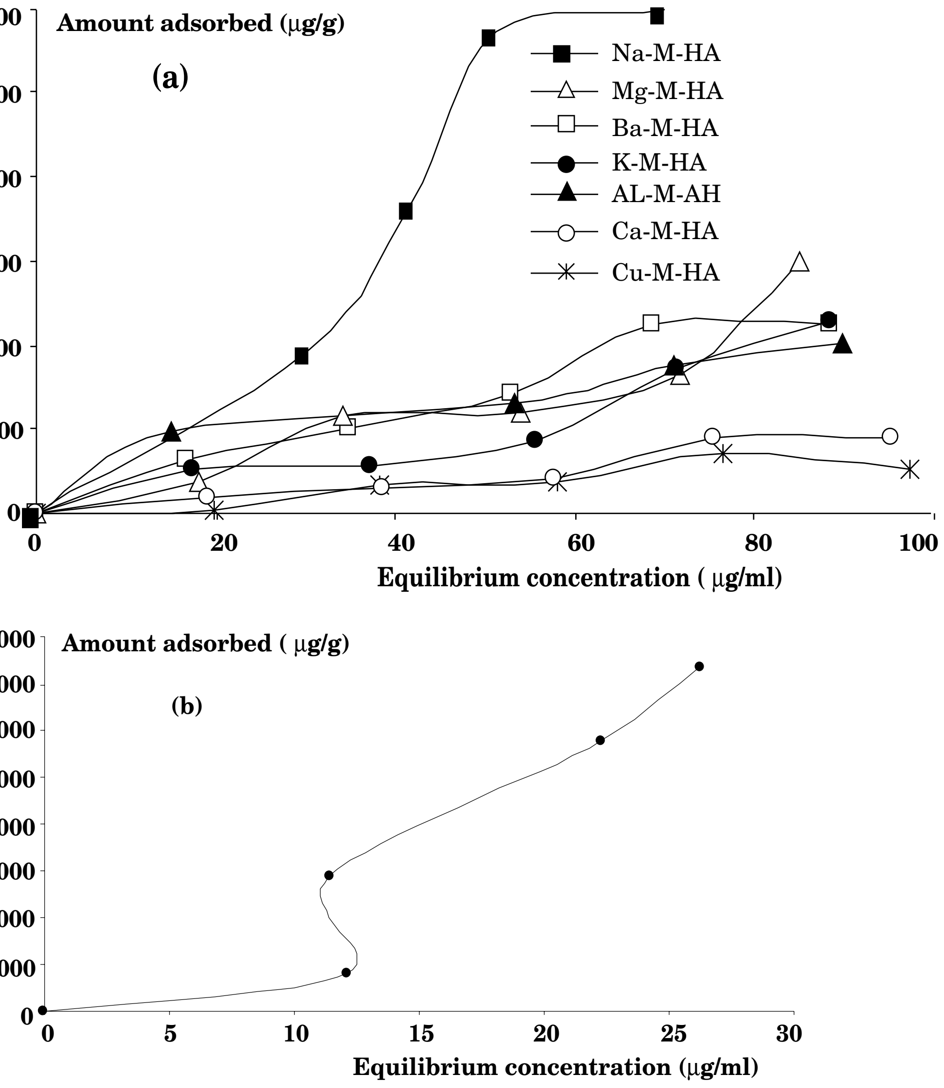

Figure 1. Carbofuran adsorption isotherms on homoionic montmorillonite-humic acid complex (a) and humic acid (b)

For fenamiphos, the adsorption isotherms were L-type ($n_f<1$) for all complexes (Figure 2), indicating a relatively high affinity between the solid and solute in the initial stages of the isotherm. As more sites in the substrate are filled, it becomes increasingly difficult for the solute molecules to find a vacant site available. The adsorption isotherm for HA was S-type ($n_f>1$) indicate that new sites become available to the solute as the adsorption. In all cases, the adsorption of carbofuran and fenamiphos is influenced by the nature of the interlayer exchange cation present on clay mineral–humic acid complex.

The K_f constant for the adsorption of carbofuran by the homoionic montmorillonite-humic acid complex ranged between 0.30 and 157.6 (Table 1). The highest values corresponded to Al-M-HA (157.6) and K-M-HA (15.3) samples, whereas the lowest ones corresponded to Ba-M-HA (2.92) and Cu-M-HA (0.30). The K_f values for the adsorption of fenamiphos (Table 1) ranged between 44.14 (Na-M-HA) and 430.54 (Al-M-HA).

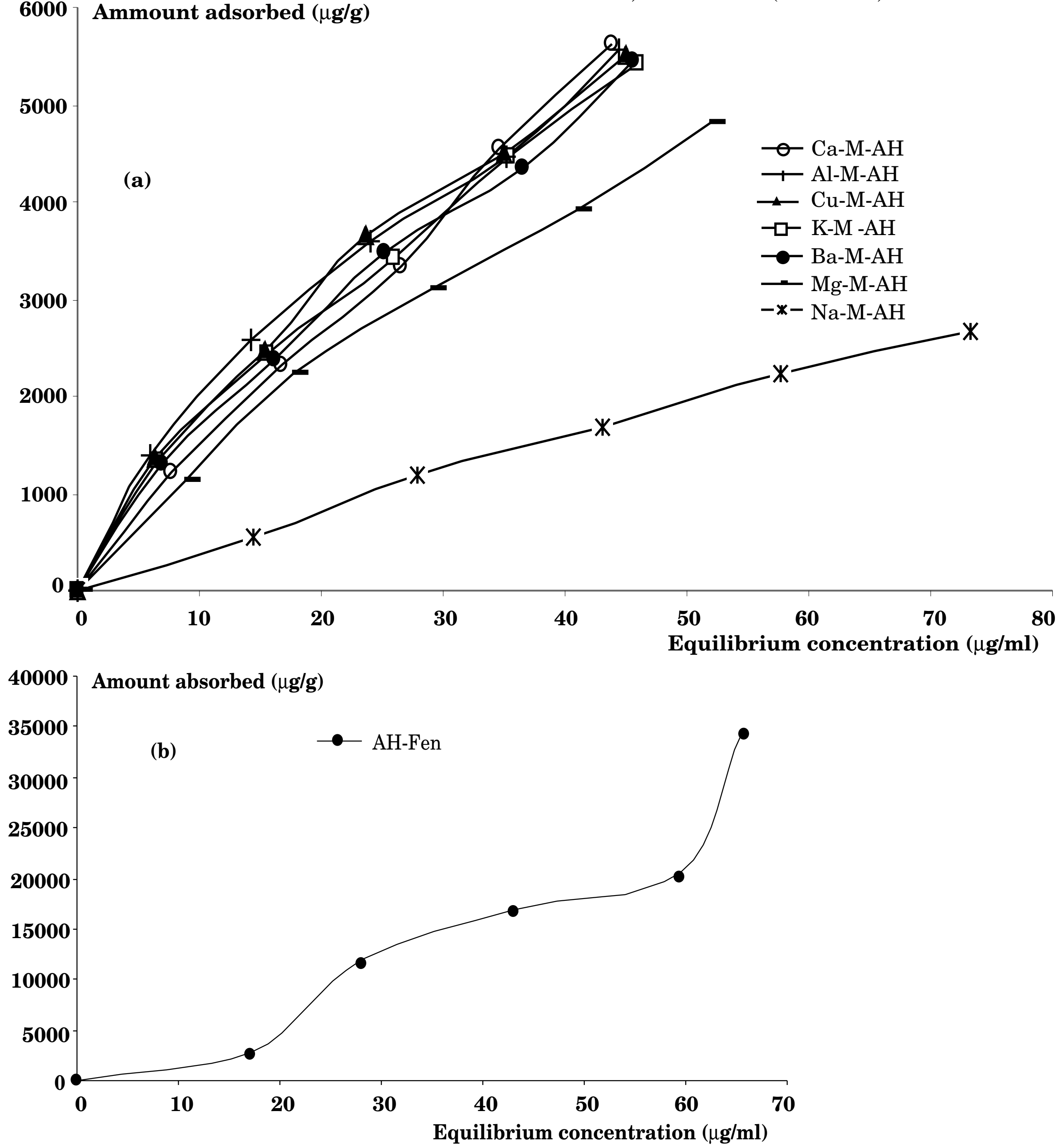

Figure 2. Adsorption isotherms of fenamiphos (Fen) on homoionic montmorillonite-humic acid complex (a) and humic acid (b)

Table 1. Freundlich adsorption constants (K_f and n_f) and correlation coefficient (r) for the adsorption of carbofuran and fenamiphos by homoionic montmorillonite (Me-M) saturated by humic acid (HA)

	......................Carbofuran..................			...........................Fenamiphos..................		
Samples	K_f	n_f	r^2	K_f	n_f	r^2
Na-M-HA	8.84±0.94*	1.41±0.01*	0.94	44.14±19.19*	0.97±0.10*	1.00
K-M-HA	15.27±0.20	0.91±0.07	0.88	349.05±58.41	0.71±0.05	1.00
Ba-M-HA	2.92±0.09	1.37±0.01	0.99	299.51±54.37	0.75±0.05	1.00
HA	125.46±17.10	1.95±0.08	0.82	85.34±6.35	1.35±0.04	0.93
Ca-M-HA	5.38±050	0.96±0.03	0.95	201.85±4.70	0.87±0.01	1.00
Cu-M-HA	0.30±0.04	1.58±0.02	0.93	370.24±91.77	0.71±0.07	1.00
Mg-M-HA	4.97±0.10	1.23±0.01	0.98	203.60±2.64	0.80±0.01	1.00
Al-M-HA	157.59±20.35	0.38±0.08	0.82	430.54±63.74	0.67±0.05	1.00

* Numbers are means ± standard deviation.

For carbofuran and fenamiphos, the same complex had the highest values of constants K_f, Al-M-HA and K-M-HA. The results obtained indicate that the adsorption capacity of fenamiphos by all Me-M-HA complex tested is higher than for carbofuran (Table 1).

Table 2 shows the stretching frequencies of the C=O and C-N groups of carbofuran at free and adsorbed forms by different homoionic montmorillonite-humic acid complexes. Frequencies for all the organo-clay-humic acid complexes showed that the C=O (1724.0 cm^{-1}) and C-N (1531.0 cm^{-1}) stretching bands undergo modifications in the spectra of adsorbed carbofuran in relation to those of the free pesticide. The following changes were observed in the spectra of the Me-M-HA systems as compared with pure components:

- decrease in the frequency of the absorption band from 1724.0 to 1632.0 cm^{-1} (C=O stretching in the carbonyl group of carbofuran),
- increase in the frequency of the adsorption band from 1531.0 cm^{-1} to 1544.0 cm^{-1} (C-N stretching in the amide group of carbofuran).

Table 2. C=O and C-N stretching frequencies (cm^{-1}) of carbofuran in the unadsorbed phase and when adsorbed on homoionic montmorillonite (Me-M)-humic acid (HA) complexes

Band	*CF	K-M-HA	Ca-M-HA	Ba-M-HA	HA
C=O	1724.0	1641.0	1636.0	1632.0	1632.8
C–N	1531.0	1536.0	1535.0	1535.0	1544.0

*CF : Carbofuran

The significant shift of the C=O stretching band to lower frequencies suggested the establishment of a coordination band, through a water bridge, between the C=O group and exchangeable cation of the clay-humic acid complex (Sanchez-Camazano & Sanchez-Martin, 1983).

Table 3 includes the stretching frequencies of the P=O group of the fenamiphos at free (1231.0 cm^{-1}) and adsorbed form by homoionic montmorillonite-humic acid complexes. These frequencies shift to lower values (1218.8-1212.0 cm^{-1}) when the fenamiphos is adsorbed by these complexes. Furthermore, the magnitude of this decrease is a function of the polarizing power of the exchangeable cation. This latter fact shows that the interactions took place between the exchangeable cation and the P=O group. These results suggest that interlayer exchange cations interacted with the P=O group of the insecticide. Similar modifications have been observed in other studies on the interaction of the other compounds with organophosphorus pesticides with montmorillonite (Sanchez-Camazano & Sanchez-Martin, 1983), and have been attributed to the decrease in the character of the double band of the P=O group.

Table 3. P=O stretching frequencies (cm^{-1}) of fenamiphos in the unadsorbed phase and when adsorbed on homoionic montmorillonite - humic acid complexes

Band	Fenamiphos	K-M-HA	Ca-M-HA	Ba-M-HA
P=O	1231,0	1218,8	1212,0	1215,0

Table 4 shows the d_{001} spacing from the XRD diffractograms for the untreated and pesticide-treated homoionic montmorillonite-humic acid samples as well as the increase in the spacing relative to the value of the dehydrated montmorillonite (d_{001}=9.6 A). As can be seen, the d_{001} spacing of the montmorillonite increases in all cases, suggesting that the pesticide molecules penetrate into the interlayer spacing of the silicate and expanded its layer. The expansion gives rise to the formation of well defined-interlayer complexes (Table 4).

Table 4. Basal d_{001}(A) spacing of homoionic montmorillonite and homoionic montmorillonite–humic acid complexes treated with carbofuran and fenamiphos solution

Complex	Untreated complex d_{001}(Å)	Carbofuran d_{001}(Å)	Carbofuran Δ(Å)	Fenamiphos d_{001}(Å)	Fenamiphos Δ(Å)
M–Ba–HA	13.60	17.67	8.07	19.20	9.60
M–K–HA	14.26	17.67	8.07	17.67	8.07
M–Ca–HA	15.78	17.68	8.08	18.03	8.70

The Ba-M-HA and Ca-M-HA complex treated with carbofuran gave basal d_{001} spacing of 17.67 A and when treated with fenamiphos the d_{001} spacing, respectively 19.20 A and 18.03 A. These spacing represented expansions of 9.60 A and 8.70 A, respectively. The same d_{001} spacing was obtained for M-K-HA complex for carbofuran or for fenamiphos (17,67 A). Thus with this expansion, the K^+, Ca^{++} and Ba^{++} samples form complexes with one or two molecular layers.

Similar spacing have been reported for complex formed by montmorillonite with other carbamates (Sanchez-Martin & Sanchez-Camazano, 1987 ; Sanchez-Martin & Sanchez-Camazano, 1984) and other organophosphorus pesticides.

According to the spacing increase produced by the intercalation of carbofuran in the complex, the molecular dimensions of the insecticide and the functional groups involved in the interaction, the complex with a spacing of 17.68 A must be monolayer. The increase of 8.08 A is too higher for a planar arrangement of molecules in the interlayer and too low for bilayer complex. However, it is close to the dimension of the molecule with its benzene ring normal to the plane formed by the oxygen atoms of the silicate and interacting with exchange cation through the C=O group.

The spacing increased for the fenamiphos complexes, 9.60 A, must correspond to a monolayer complex. According to Sanchez-Camazano and Sanchez-Martin (1983), the molecular arrangement compatible with this increase would have the ethyl and 4-methylthio-m-tolyl radicals on the negative surface of the oxygen atoms, and the isopropyl phosphoramidate towards the interlayer space, the P=O group interacting with the exchange cation.

CONCLUSION

The observed changes in the physicochemical properties of the individual model soil colloids (Me-M-HA) resulting from their synthetic associations affected insecticides sorption behavior compared with that of the individual constituents.

The results of this study indicated that the adsorption capacity of fenamiphos by all Me-M-HA complexes tested, is higher than for carbofuran. Study of the I.R spectra for all the organo-clay-humic acid complexes show the C=O (1724.0 cm^{-1}), C-N (1531.0 cm^{-1}) and the P=O group (1231.0 cm^{-1}) stretching bands undergo modifications in the spectra of adsorbed carbofuran and fenamiphos in relation to those of the free pesticide. The fact that adsorption is promoted by the protonation of carboxyl groups of montmorillonite-humic acid complexes and carbofuran or fenamiphos suggests that H-bonding between the C=O, C-N or the P=O groups could take place.

The XRD d_{001} values of clay-humic acid before and after treatment with carbofuran or fenamiphos in dichloroethane solution indicated changes in interlamellar space. In particular, the magnitude of d_{001} increased in all samples as an effect of adsorption.

The mechanism by which both compounds are adsorbed involves the interaction of C=O or P=O group of carbofuran and fenamiphos, respectively, is by the metal ions through direct bonds or, more probably, via hydrogen bonding involving water molecules surrounding exchange cation.

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