

# ORGANO-CLAYS AS ADSORBENTS FOR AZINPHOSMETHYL AND DICHLORVOS IN AQUEOUS MEDIUM

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**Abstract.** Using adsorption isotherms, a study was performed of the adsorption of two organophosphorus pesticides, azinphosmethyl (sparingly soluble in water) and dichlorvos (moderately soluble in water), by montmorillonites saturated with the cations hexadecyltrimethylammonium (HDTMA<sup>+</sup>), dodecyltrimethylammonium (DDTMA<sup>+</sup>) and tetramethylammonium (TMA<sup>+</sup>) in aqueous media. The results were compared with those obtained for the adsorption of these pesticides by natural montmorillonite, humic acid and by the soil organic matter and with the octanol-water partition coefficient (K<sub>ow</sub>) of the compounds. Results indicated that regarding the capacity to remove azinphosmethyl from water the organic matter derived from the organic cations HDTMA<sup>+</sup> and DDTMA<sup>+</sup> is 5–10 times more effective than humic acid; 10–20 times more effective than the organic matter from the soil and 20–50 times more efficient than octanol. However, both organic phases, that derived from the organic matter of the soil and that of the organic cations, have similar effectiveness for removing dichlorvos from water, in turn, their efficiency is 50 times higher than that of octanol. These findings may find application in the removal of azinphosmethyl or other sparingly water soluble organophosphorus pesticides from aquifers.

## 1. Introduction

The adsorption of organic, non-ionic and sparingly soluble contaminants by soils in aqueous media is essentially governed by the organic matter present in the soil. The positive correlation between the organic matter content and the adsorption of nonionic organic contaminants, such as pesticides, is well documented (Reddy and Gambrell, 1987; Blumhorst *et al.*, 1990; Sánchez-Martín and Sánchez-Camazano, 1991a, 1991b). By contrast the inorganic fraction of the soil is of little importance in the adsorption of these compounds in the soil-water system.

Among colloidal inorganic fractions, the clay mineral components have a high negative charge that is compensated by inorganic cations situated on their surface. In the soil, these cations are generally Na<sup>+</sup> and/or Ca<sup>2+</sup>. The water molecules present in the hydration sphere of these solvated cations confer a hydrophilic nature upon such surfaces. Accordingly, this kind of mineral is not good adsorbent for sparingly hydrosoluble organic compounds that are unable to compete with the highly polar water molecules.

In an attempt to design new adsorbents to remove non-ionic contaminants from water several researchers have replaced the inorganic cations of smectite by large alkylammonium cations in order to change the hydrophilic surface of this mineral into a hydrophobic one (Srinivasan *et al.*, 1985; Mortland *et al.*, 1986; Boyd *et al.*, 1988). These organo-clays have generally been considered as adsorbents of non-



TABLE I

Characteristics of natural and organic montmorillonites used as sorbents in this study

Sorbent <sup>a</sup>	CEC <sup>b</sup> saturation %	OC <sup>c</sup> %	OM <sup>d</sup> (%)	<i>d</i> (001) (Å)
Natural-M	–	0.5	0.8	12.6
HDTMA-M	99	18.0	22.5	21.5
HDTMA-M	50	9.6	12.0	16.9
HDTMA-M	25	4.8	6.0	13.8
DDTMA-M	74	10.8	13.6	17.7
DDTMA-M	49	7.2	9.1	14.2
DDTMA-M	25	3.8	4.8	13.8
TMA-M	74	3.0	4.6	13.8

<sup>a</sup> HDTMA-M, hexadecyltrimethylammonium montmorillonite; DDTMA-M, dodecyltrimethylammonium montmorillonite; TMA-M, trimethylammonium montmorillonite.

<sup>b</sup> CEC, cation exchange capacity.

<sup>c</sup> OC, organic carbon.

<sup>d</sup> OM, organic matter.

TABLE II

Characteristics of soils used in this study

Soil	Natural soils					HDTMA <sup>a</sup> -soils		
	OC <sup>c</sup> (%)	OM <sup>d</sup> (%)	Clay (%)	Smectite (%)	CEC <sup>b</sup> (cmol kg <sup>-1</sup> )	HDTMA+ adsorbed (%)	CEC <sup>b</sup> saturation (%)	OM <sup>d</sup> (%)
A	0.27	0.50	33	11	23.5	4.91	74	5.41
B	2.90	4.93	10	–	10.9	0.13	4	5.06

<sup>a</sup>, <sup>b</sup>, <sup>c</sup>, <sup>d</sup> are described in Table I.

To saturate the montmorillonite with the organic compounds, 100 mg of the clay were treated with 50 mL of aqueous solutions of HDTMA and DDTMA bromides containing amounts of the organic cation equivalent to 1.25, 0.65 and 0.30 times the CEC of the clay. In the case of the TMA<sup>+</sup> cation, the amount employed was 3.75 times the CEC. The samples were washed with water, freeze-dried and kept in an atmosphere with a relative humidity of 35% for later use. The carbon content of the clays was determined using an automatic carbon analyzer. Table I shows the names, abbreviations, carbon and organic matter contents and the *d*(001) basal spacing (determined by X-ray diffraction) of the organo-clays. The increase of *d*(001) basal spacing of montmorillonite when saturated with organic cations indicates the intercalation of these cations in the interlayer space.

Two soils (A and B) corresponding to the surface horizons of two profiles were also used. These soils were saturated with HDTMA<sup>+</sup> following the same procedure as that used for the saturation of montmorillonite, using 1g of soil and an amount

of organic cation equivalent to the CEC of the soils. The characteristics of the natural soils and the carbon contents of the treated soils are shown in Table II.

Isotherms were obtained by treating duplicate 10 mg of the organo-clay or 100 mg of soil with 10 mL of solutions containing 8, 12, 16 and 20  $\mu\text{g mL}^{-1}$  of azinphosmethyl or dichlorvos. The solutions were kept on a chamber thermostated at 30 °C with intermittent shaking. Previous kinetic research showed that equilibrium is reached in less than 24 hr. The suspensions were centrifuged at 6000 g over 30 min.

Quantitative determination of the pesticides in aqueous solutions was done with UV spectrophotometry (maximum of absorption of azinphosmethyl 228 nm and of dichlorvos 206 nm). The linear range of concentrations in the azinphosmethyl and dichlorvos measurement by UV spectroscopy was 2 to 20  $\mu\text{g mL}^{-1}$  ( $r = 0.999$ ;  $p < 0.001$ ). The precision of the method was determined by carrying out the adsorption experiments 10 times for a organo-clay sample (SD = 0.05; C.V. = 0.99% for azinphosmethyl and SD = 0.162; CV = 3.69% for dichlorvos) and for a organo-soil sample (SD = 0.007; CV = 1.30% for azinphosmethyl and SD = 0.019; CV = 5.09% for dichlorvos).

### 3. Results and Discussion

Figure 1 shows the adsorption isotherms of azinphosmethyl by HDTMA-M with different contents of organic carbon; these correspond to saturations at 99, 50, and 25% of the CEC of montmorillonite with the organic cation. The shape of the isotherms related with the adsorption capacity of the adsorbent, varies with the carbon content of the organo-clay. According to the classification of Giles *et al.* (Giles *et al.*, 1960), the isotherm corresponding to the sample with 18% of carbon appears to be of the L type, with a good affinity of the adsorbent for the adsorbate. That corresponding to the organo-clay with 9.6% carbon is linear, type C, indicating a constant partition of the pesticide between the adsorbent and the solution. That corresponding to the sample with 4.8% of carbon is of the S type with low adsorbent-adsorbate affinity, which increases with the rise in the concentration of adsorbent in solution. In principle, it may be inferred from the isotherms that adsorption increases with the rise in the content of organic carbon of the organo-clay.

Figure 2 shows the adsorption isotherms of azinphosmethyl by DDTMA-M at 74, 49, and 25% saturation of the CEC of montmorillonite. The isotherms of the samples at 74 and 49% saturation are of the L type, while that of the sample at 25% is linear, type C. As in the case of HDTMA-M, the isotherms indicate an increase in adsorption as a function of organic cation content of the samples.

Figure 3 shows the adsorption isotherm of azinphosmethyl by TMA-M with 3% carbon, corresponding to 74% saturation of the CEC of montmorillonite. The Figure also shows the adsorption isotherm of the pesticide by natural montmorillonite. Both isotherms are of the S type, that corresponding to the TMA-M sample showing greater convexity. These findings show that the surface of TMA-M, even though

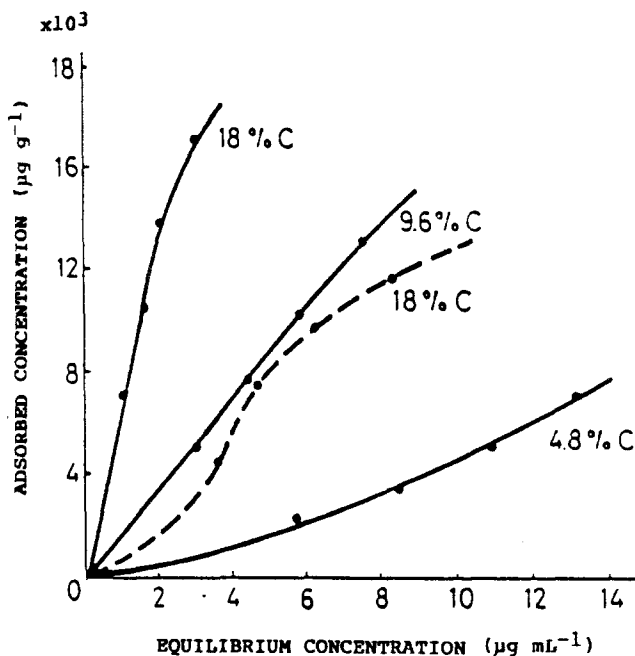


Fig. 1. Equilibrium isotherms for adsorption of azinphosmethyl (—) and dichlorvos (---) by HDTMA-M.

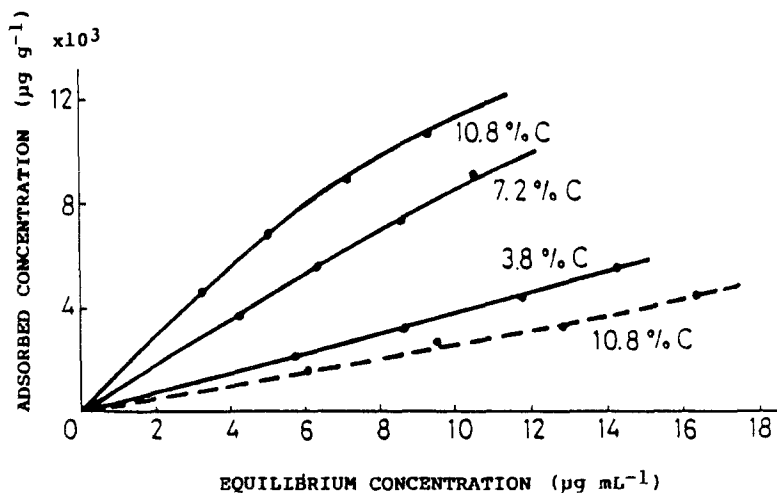


Fig. 2. Equilibrium isotherms for adsorption of azinphosmethyl (—) and dichlorvos (---) by DDTMA-M.

74% of its CEC is saturated with  $TMA^+$ , continues to be hydrophilic owing to the small size of the cation.

Together with the adsorption isotherms of azinphosmethyl by the organo-clays Figures 1-3 show the adsorption isotherms of dichlorvos by HDTMA-M, DDTMA-M and TMA-M with the highest degree of saturation in the corresponding organic cation. Figure 3 also shows the adsorption isotherm of this pesticide by natural

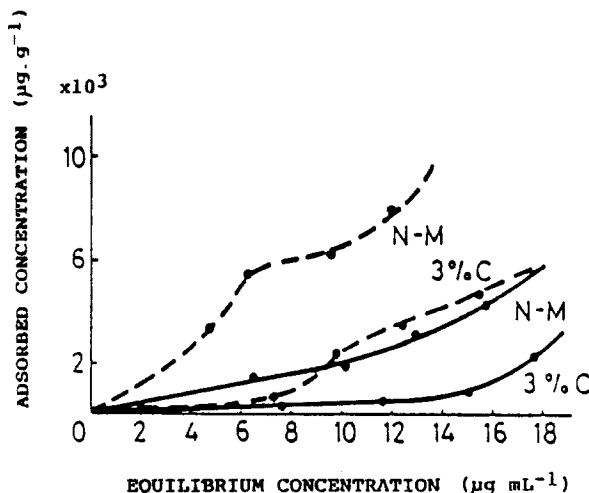


Fig. 3. Equilibrium isotherms for adsorption of azinphosmethyl (—) and dichlorvos (---) by natural montmorillonite (N-M) and by TMA-M (3%C).

montmorillonite. The adsorption isotherms of dichlorvos are of the S type for the HDTMA-M (Figure 1) and TMA-M samples and for the natural sample (Figure 3), and is linear, type C, for the DDTMA-M sample (Figure 2).

Comparative study of the adsorption isotherms shows that the organic matter adsorbed into the interlayer space of the HDTMA-M and DDTMA-M samples has a higher affinity for azinphosmethyl, sparingly soluble in water, than for dichlorvos, which is moderately water soluble. The opposite is the case for both pesticides, with respect to the affinity of the hydrophilic surfaces of natural montmorillonite and of the TMA-M sample.

In general, the isotherms fulfil the Freundlich adsorption equation with correlation coefficients equal to or greater than 0.97 ( $p < 0.05$ ) the highest values corresponding to type L or S, subtype 1 isotherms (Giles *et al.*, 1960). By contrast, the lowest coefficients correspond to isotherms of type L or S, subtype 3; in this latter kind, the curvature changes from concave to convex, or viceversa. The linear form of this equation is:  $\log X = \log K + 1/n \log C$ , where  $X$  is the amount of pesticide adsorbed ( $\mu\text{g g}^{-1}$ )  $C$  is the amount of pesticide in solution ( $\mu\text{g mL}^{-1}$ ),  $n$  and  $K$  are constants that are characteristic of adsorption;  $n$  indicates the extent to which the adsorption is a function of concentration and  $K$  is the amount of pesticide adsorbed for an equilibrium concentration equal to unity. The constant  $K$  is considered to be a measurement of the adsorption capacity.

Table III offers the values of  $1/n$  and  $\log K$  determined from the Freundlich equations. It also shows the values of this constant normalized for the organic matter content. ( $K_{om} = K \cdot 100/\%om$ ).

The values of  $\log K$  for the adsorption of azinphosmethyl by the organo-clays at different degrees of saturation are always higher than that of the  $\log K$  of natural montmorillonite, except in the case of the TMA-M sample (Table III). The values

TABLE III

Adsorption coefficient ( $K$  and  $K_{om}$ ) for azinphosmethyl and dichlorvos as a function of nature and content of organic matter of the different sorbents. The  $K$  values are given in  $\mu\text{g}^{1-1/n} \text{mL}^{-1} \text{g}^{-1}$

Sorbent <sup>a</sup>	CEC <sup>b</sup> saturation (%)	OM <sup>d</sup> (%)	Azinphosmethyl			Dichlorvos		
			1/n	log $K$	log $K_{om}$	1/n	log $K$	log $K_{om}$
HDTMA-M	98	22.5	0.88	3.80	4.45	1.08	3.10	3.75
HDTMA-M	50	12.0	0.99	3.23	4.15			
HDTMA-M	25	6.0	1.33	2.33	3.65			
DDTMA-M	74	13.6	0.76	3.30	4.16	0.87	2.58	3.44
DDTMA-M	49	9.1	0.91	3.03	4.07			
DDTMA-M	25	4.8	1.34	2.22	3.54			
TMA-M	74	4.6	1.30	0.34	1.68	1.39	0.88	2.21
Natural-M	-	0.8	1.18	2.17	-	0.88	2.95	-
Humic acid*	-	100.0	0.78	3.46	3.46			
Soil 1**	-	5.3	0.72	1.63	2.91			
Soil 2**	-	5.7	.065	1.69	2.93			
Soil 3**	-	13.1	0.64	1.84	2.71			
Soil 4**	-	5.8	0.46	1.79	3.02			
Soil 5**	-	11.0	0.57	1.87	2.82			

a, b, d are described in Table I. \* Sanchez-Martín *et al.*, 1986 \*\* Sánchez-Camazano and Sánchez-Martín, 1984.

of log  $K_{om}$  corresponding to HDTMA-M and the DDTMA-M samples are very close (4.07–4.45) to each other when the degree of saturation of the clay by the organic cation is equal to or greater than 50% of the CEC of the montmorillonite. This suggests that the surface of the clay must be completely covered by the organic cation and becomes hydrophobic, behaving as an organic compound. This does not occur for lower percentages of saturation, nor in the case of the TMA-M sample. Although 74% of its exchange capacity is saturated by the TMA<sup>+</sup> cation, the TMA-M sample, due to its small size, cannot be hydrophobic and does not behave as such in the adsorption of azinphosmethyl. Additionally, the adsorption capacity of this sample for the insecticide through cation-dipole interaction is lower than that of the natural sample, because 74% of its inorganic cations are substituted by TMA<sup>+</sup>.

The values of log  $K$  for the adsorption of dichlorvos by the HDTMA-M and DDTMA-M samples are very close to those of natural montmorillonite (2.58–3.10). The values of log  $K_{om}$  for the HDTMA-M and the DDTMA-M samples are close to each other and indicate that the adsorption of dichlorvos by the organic matter derived from the organic cations is approximately 3 to 10 times lower than the adsorption of azinphosmethyl. However, the adsorption of dichlorvos by the natural and TMA-M samples is greater than the adsorption of azinphosmethyl by the same samples. All these findings are probably due to the higher water solubility of dichlorvos. However, the different chemical structure of both compounds should be taken into account since the  $P=O$  group of dichlorvos confers the molecule

of this pesticide greater polarity than the P=S group affords the azinphosmethyl molecule.

For comparative purposes, Table III also includes the values of  $\log K$  and  $\log K_{om}$  corresponding to the adsorption of azinphosmethyl by a humic acid and by five soils, taken from previous works by the authors (Sánchez-Camazano and Sánchez-Martín, 1984; Sánchez-Martín *et al.*, 1984). These soils have different contents in organic matter, a low content in clay and no smectite. It may be seen that the organic phase derived from the C16 and C12 hydrocarbon chains of low polarity is 5–10 times more efficient than humic acid and 10–50 times more efficient than the organic matter of the soil for removing azinphosmethyl from water. Furthermore, the  $K_{om}$  adsorption coefficients of azinphosmethyl by organic matter derived from HDTMA<sup>+</sup> or DDTMA<sup>+</sup> are 20–50 times greater than the octanol-water partition coefficient of azinphosmethyl ( $\log K_{ow} = 2.70$  (Bowman and Sans, 1983)). The  $\log K_{om}$  values of the soils are close to the  $\log K_{ow}$  for azinphosmethyl. This is consistent with the results obtained on the adsorption by soils of other thiophosphates and other sparingly soluble pesticides (Briggs, 1981; Karickhoff *et al.*, 1979).

The adsorption capacity of the different forms of organic matter used seems to be related to the polarity of these adsorbents, which according to their chemical composition should decrease in the following order: organic matter of the soil > humic acid > organic phase derived from the HDTMA<sup>+</sup> and DDTMA<sup>+</sup> cations.

In order to make a direct comparison in this work between the adsorption of azinphosmethyl and dichlorvos by the organic matter of the soil and by that derived from the organic cations, two soils, differing with respect to their organic matter and clay contents were saturated with HDTMA<sup>+</sup>. Soil A, with smectite, adsorbed 4.91% of the HDTMA<sup>+</sup> and soil B, without smectite adsorbed 0.13% of the HDTMA<sup>+</sup>. After saturation with HDTMA<sup>+</sup> both soils had the same amount of organic matter, but from different origins (Table II).

Figure 4 shows the adsorption isotherms corresponding to the adsorption of the pesticides by the two HDTMA-soils. The adsorption isotherms of azinphosmethyl by both soils are almost linear whereas those of dichlorvos are of type S for soil A and type L for soil B.

In soil B, azinphosmethyl, as a hydrophobic compound (sparingly soluble), must be adsorbed by the organic matter of the natural soil. In fact, in a previous work by the authors (Sánchez-Camazano and Sánchez-Martín, 1984) addressing the adsorption of the insecticide by a series of natural soils with different organic matter contents, it was observed that the organic matter was the main parameter in the adsorption of the compound by soils. In soil A, the insecticide will be adsorbed by the organic phase arising from saturation of the soil with the organic cation.

The  $\log K$  values of the isotherms fitted to the Freundlich equation and those of  $\log K_{om}$  are shown in Table IV. Again it is seen that the organic matter from the HDTMA<sup>+</sup> cation is 10 times more effective for the adsorption of azinphosmethyl than the organic matter from soil. However, both organic phases seem to have



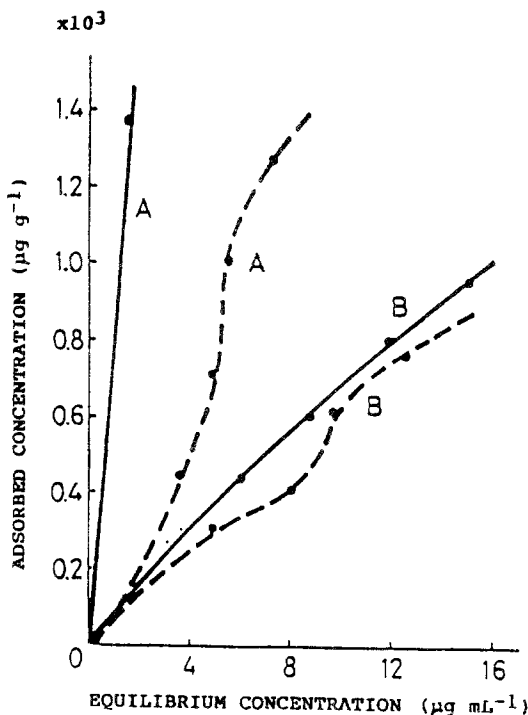


Fig. 4. Equilibrium isotherms for adsorption of azinphosmethyl (—) and dichlorvos (---) by HDTMA-soils (A = Soil A; B = soil B)

TABLE IV

Adsorption coefficients ( $K$  and  $K_{om}$ ) for azinphosmethyl and dichlorvos as a function of nature and content of organic matter of soils. The  $K$  values are given in  $\mu\text{g}^{1-1/n} \text{mL}^{-1} \text{g}^{-1}$

Soil	Azinphosmethyl			Dichlorvos		
	$1/n$	$\log K$	$\log K_{om}$	$1/n$	$\log K$	$\log K_{om}$
HDTMA <sup>a</sup> -A	1.19	2.97	4.24	1.26	1.88	3.16
HDTMA <sup>a</sup> -B	0.94	1.88	3.18	1.08	1.68	2.98

<sup>a</sup> HDTMA: hexadecyltrimethylammonium.

similar effectiveness for the adsorption of dichlorvos from water but are 50 times more effective than octanol in removing this pesticide from water ( $\log K_{ow}$  of dichlorvos = 1.45 (Suntio *et al.*, 1988)).

#### 4. Conclusions

In the light of the results obtained, the clays and soils modified by the adsorption

of HDTMA<sup>+</sup> or DDTMA<sup>+</sup> can be used: (a) as adsorbents of azinphosmethyl and possibly other sparingly hydrosoluble thiophosphate pesticides present in surface and underground water; (b) to increase the capacity of adsorption of these compounds by the particulate inorganic matter present in aquifers; (c) to increase the adsorption capacity of subsurface materials overlain by zones destined for the burial of agricultural chemical residues such as containers or chemicals that have not been used. In the latter case, this would be achieved by underground injection of the organic cation.

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